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REVISED SSGN AND VIRGINIA CLASS SUBMARINE PROCEDURES FOR SCREENING DIVER QUALITY AIR

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14. ABSTRACT: The Dry Deck Shelter (DDS) is a hyperbaric system used on submarines to transport SEAL delivery vehicles into an operating area. The system uses diver quality air (DQA) air from submarine banks to ventilate the DDS and provide breathing air to the divers, as well as for other diving operations. Currently approved procedures employ three instruments to check the quality of air prior to diver use on SSGN and VIRGINIA class submarines: (1) the TVA-1000B toxic vapor analyzer (Thermo Fisher Scientific, Franklin, MA) with both a photoionization detector (PID) and flame ionization detector (FID) to screen for volatile inorganic and organic contaminants, (2) the current Geotech HB 1.2A hyperbaric CO_2/O_2 analyzer (Geotechnical Instruments, Leamington Spa, UK) to measure CO_2, and (3) the ship's CAMS to measure O_2, CO, and two refrigerants. The recent replacement of the TVA-1000B with the TVA2020 by the manufacturer now requires that the current procedures for screening DQA be revised. This report describes NEDU's evaluation of the TVA2020 for its acceptability as a replacement to the TVA-1000B, and NEDU's recommendations about incorporating the TVA2020 into any revised DQA procedures. Additional NEDU recommendations address the need for changes in the DQA procedures (1) due to the diver's new breathing air standards in revision 7a of the U.S. Navy Diving Manual, (2) for use of the new Geotech hyperbaric monitor that is replacing the current Geotech HB 1.2A, and (3) to correct errors in the current procedures and improve the effectiveness of the screening process. NEDU's task of revising the DQA procedures was assisted by its review of past Air Purity Reports that have been completed by shipboard personnel using the current DQA screening procedures on SSGN and VIRGINIA class submarines.

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INTRODUCTION

Note that throughout this report, the terms “analyzer”, “monitor”, and “TVA” (toxic vapor analyzer; the latter term referring to the TVA-1000B and/or TVA2020, both described fully in this report) are often used interchangeably, as the first two of these terms have been used interchangeably in NEDU past reports and discussions. Also, VIRGINIA class and VA class are used interchangeably to refer to that class submarine. Lastly, some of the text in this section was directly taken from reference 1 without significant changes, as reference 1 contains much of the original rationale behind diver quality air (DQA) screening procedures.

The original intent of the special DQA screening procedures done in the field on submarines was to address air purity questions that fall outside the scope of the U.S. Navy Diving Manual and the Nuclear Powered Submarine Atmosphere Control Manual. These screening procedures provide additional testing of the gas in submarine air banks (beyond the required semiannual testing defined by the Diver’s Air Sampling Program) prior to its use for Dry Deck Shelter (DDS) and other diving missions to help ensure safe breathing gas. The justification for such DQA procedures arises from the fact that these diving operations use compressed air taken from the submarine atmosphere, an atmosphere that contains low levels of gaseous contaminants that number in the thousands of compounds. However, submarine air compressors and air banks used for supplying diver’s breathing air are still expected to comply with the semiannual testing as defined by the Diver’s Air Sampling Program.

The original methods developed in 1986 for screening submarine DQA for chemical safety relied on the shipboard Central Atmosphere Monitoring System-I (CAMS-I), portable photoionization detector (PID, model PI 101; HNU Inc., Newton Highlands, MA), and chemical detector tubes.[2] In the early 2000s, a simpler and more reliable set of procedures for air testing (referred to as “Revised Air Purity Guidelines for DDS Operations”) were produced for the new SSN 688 class of DDS host submarines with emphasis toward improving analysis of CO_2 and replacing detector tubes with their marginal performance.[1] The current DQA screening procedures for SSGN and VIRGINIA class submarines were adapted by the Navy from the SSN 688 “Revised Guidelines”.

The current procedures employ three instruments to check the quality of air: (1) the TVA-1000B toxic vapor analyzer (Thermo Fisher Scientific, Franklin, MA; noted hereafter in this report simply as “Thermo”) with both a PID and flame ionization detector (FID) to screen for volatile inorganic and volatile organic contaminants (VOCs), (2) the current Geotech HB 1.2A hyperbaric CO_2/O_2 analyzer (Geotechnical Instruments, Leamington Spa, UK) to measure CO_2, and (3) the ship's CAMS-I (VIRGINIA class) or updated CAMS-II (SSGN class) to measure O_2, CO, and two refrigerants. Unfortunately, the current DQA screening procedures are complicated and require a H_2 gas source to supply H_2 to the FID of TVA-1000B.

The recent replacement of the TVA-1000B (Figure 1) with the TVA2020 (Figure 2) by the manufacturer now requires that the current procedures be revised. However, although the TVA-1000B was believed to be a good choice for this application at the time the current procedures were produced, NEDU believes that newer alternatives to the TVAs (both to the current TVA-1000B, and to the new version TVA2020) exist that may simplify, improve the reliability, and reduce the cost of the DQA screening process.

SETTING OF LIMITS

Estimation of potential health hazards associated with chemical contamination is always difficult. For hyperbaric exposures, the problem is more complex due to little information regarding contaminant effects on humans (or animals) at pressure. Unfortunately, existing guidelines for dealing with chemical hazards in a variety of environments are inadequate to evaluate the safety of diving atmospheres and gases. Indeed, the rationale is unclear for many of the current limits for gas contaminants contained in various U.S. Navy documents (e.g., references 3,4,5).

For the current DQA screening methods, the DDS limits for O_2, CO_2 and CO for submarine compressed air used for diving were set to the respective diving air limits from the U.S. Navy Diving Manual revision current at the time the methods were finalized. In the absence of suitable guidance for hyperbaric exposures to most other gaseous contaminants, DDS limits for other contaminants were derived from recommendations from the American Conference of Governmental Industrial Hygienists (ACGIH) — after correction for maximum exposure depth of 7 ATA (atmospheres absolute, or 200 fswg). TVA unsafe limits were based on assumptions about the likely types of contaminants in the air banks being screened and the response factors of the PID and FID to these contaminants. In the **RECOMMENDATIONS** section of this report, NEDU provides recommendations regarding changes needed in the screening limits of DQA.

PROJECT GOALS

Work was tasked, funded, and completed in two phases. This report deals primarily with phase 1, although some discussion of work planned for phase 2 (expected to be funded following completion of phase 1) is included. Phase 2 of the project will be designed to take advantage of the opportunity to address some of the weaknesses inherent in the current screening procedures, while acknowledging that simply replacing the TVA-1000B with the TVA2020 may not address all the shortcomings of the current DQA procedures. At the time this report was completed, phase 2 had not been funded, nor any phase 2 work started.

GOALS

Phase 1.

1. Goal #1. Evaluate the TVA2020 for its acceptability as a replacement to the TVA-1000B and, if found acceptable, provide recommendations about revising current DQA screening procedures incorporating the TVA2020 and other necessary changes as discussed directly below.

a. Initial NEDU review of available TVA2020 information, prior to start of this project, suggests no major change in capabilities from the TVA-1000B. However, NEDU will need to carefully examine and test the instrument to confirm this conclusion. NEDU's experience with a variety of gas monitors suggests that apparent minor alterations in software or hardware often produce unexpected changes in performance of such monitors. One such example is that a preliminary list of TVA2020 FID response factors provided by the manufacturer states that these response factors may be considerably lower than those of the TVA-1000B.[6] At the least, this information concerning the response factors suggests the need to carefully evaluate the overall performance of the new TVA2020.

b. Revised DQA procedures will reflect, where needed, changes in the diver's breathing air standards in the new revision 7a of the U.S. Navy Diving Manual — e.g., revision 7a now consolidates Tables 4-1 and 4-2.[3] Past and current DQA screening procedures on submarines have never been directly linked to the diving air standards in the U.S. Navy Diving Manual. However, the DQA limits for CO_2 and CO in the current procedures were set, during development of these procedures, equivalent to the CO_2 and CO limits in revision 3 of the U.S. Navy Diving Manual.[7] Although both these two limits have remained the same through revision 6 of the Diving Manual, the limit for CO has recently been lowered from 20 to 10 ppm in revision 7a, thus potentially impacting any revision of the DQA procedures.

c. Revised DQA procedures will also include all changes needed for use of the new Geotech hyperbaric monitor that is replacing the current Geotech HB 1.2A used to measure CO_2 during screening of DQA.[8]

d. Revised DQA procedures will also include changes to correct errors in the current procedures and changes recommended by NEDU to improve the effectiveness of the screening process.

2. Goal #2. Review past "Air Purity Reports" that have been completed by shipboard personnel using the current DQA screening procedures on SSGN and VIRGINIA class submarines and incorporate any conclusions from such review into NEDU recommendations regarding revising the DQA procedures.

a. Review of these reports will reveal DQA screening history on these two class submarines, information that may be useful during the revision process in setting of contaminant limits, defining what contaminants are the main problems, and revealing other details, including TVA-1000B readings, to judge the usefulness of screening with both a PID and a FID (as is currently done). Also, NEDU expects that these reports may provide information about problems encountered using current screening procedures that may be corrected during the current revision process.

3. Goal #3. Work with PMS 399-designated personnel to update the Navy's document Appendix L (Air Purity Guidelines for DDS Operations)[9,10] to reflect TVA2020 and Geotech HYPB2.0 requirements, as well as any other recommendations in this report.

Phase 2.

1. Goal #1. Identify alternative air screening instruments, and review and test in the laboratory, where necessary, these instruments and their procedures for potential usefulness in simplifying, improving the reliability, and reducing the cost of the current DQA screening procedures. Where alternative instruments are found acceptable by NEDU, provide recommendations about revising current DQA screening procedures incorporating the alternative instruments.

a. NEDU has discussed with various Navy codes over the last several years the potential usefulness of the portable air monitor (PAM), the Geotech Diveair2, to replace part or all of the current submarine DQA screening procedures. NEDU was also contacted by Electric Boat (EB) personnel in 2013 to address a number of questions related to an EB task to review replacing the TVA-1000B with the Diveair2. The Diveair2 — that NEDU helped to develop and is currently on the Authorized for Navy Use (ANU) list — simultaneously measures O_2, CO_2, CO, and VOCs, the latter component measured using a PID, and thus potentially could perform the required DQA screening without additional instruments. Although little, or no, additional laboratory testing of the Diveair2 may be needed due to its current listing on the ANU, NEDU would need to review the suitability of the Diveair2 for the specific application of submarine DQA screening prior to making any decision.

2. Goal #2. Complete limited sampling of DQA air banks on SSGN and VIRGINIA class submarines to characterize their contaminant profiles, which may affect the reliability of any DQA screening procedures.

a. Current screening procedures are based on assumptions about the likely types of contaminants in the air banks being screened. To produce the original procedures for SSN 688 class submarines in 2001, NEDU relied on data from limited sampling of SSN 688 (and earlier) class air banks that NEDU was tasked to do. These samples were subsequently analyzed in NEDU's laboratory using gas chromatography (GC) and GC/mass spectrometry (GC/MS) to identify specific contaminants (e.g., ethanol, toluene, methyl isobutyl ketone). This type of sampling and analysis goes well beyond the routine 6-month air sampling that is normally done per the Diver's Air Sampling Program.

b. NEDU believes it desirable to begin a new effort to characterize the contaminant profiles of the air banks on the current platforms, with which the new procedures will be used, as NEDU is unaware of any such recent or ongoing DQA sampling and analysis. Although such an effort could be costly and time consuming, NEDU expects that a limited sampling exercise (with reduced cost) may provide valuable information that would assist with revision of the DAQ screening procedures.

c. NEDU recommendations regarding revising DQA screening procedures will reflect results and conclusions from the air bank samples.

3. Goal #3. Work with PMS 399-designated personnel to update the Navy's document Appendix L (Air Purity Guidelines for DDS Operations) to incorporate the alternative instruments.

SUMMARY OF METHODS (PHASE 1 ONLY)

TVA2020 EVALUATION

Three TVA2020 toxic vapor analyzers ("demonstration instruments") with both FID and PID were obtained from loan from the manufacturer after the manufacturer had serviced and calibrated these analyzers. These instruments were evaluated in the laboratory for the following:

a. General performance, including ease of use

b. Calibration and operating procedures as discussed in the manufacturer's manual

c. Instrument stabilization following startup

d. Precision of gas readings (in terms of repeatability of test results over a time period up to 10 min)

e. Short-term accuracy of gas readings up to approximately five hours after calibration, and long-term accuracy up to ~one week after calibration

f. Effects of ambient temperature on gas readings at 5, 25, and 42 °C (41, 77, and 108 °F)

g. Relative response factors

h. Effectiveness of the charcoal filter adapter

i. Effects of relative humidity from ~0 to ~95% on gas readings

j. Battery duration and charging time

k. Monitor menu functions including alarms and data logging

l. Other performance measures that may be added as the evaluation proceeds, based on NEDU recommendations and PMS 399 approval. This item allowed the flexibility in testing that NEDU has always required during past evaluation of gas screening instruments. Unfortunately, without having one or more TVA2020 analyzers in hand, and without any experience with the TVA2020, NEDU would have had difficulty predicting in advance all the required testing. Also, as testing with any instrument proceeds, results commonly suggest questions or problems that may need specific additional testing to resolve.

If the TVA2020 is found acceptable for replacing the TVA-1000B, operating procedures for the TVA2020 would first be developed based on the manufacturer's recommendations, and these TVA2020 procedures incorporated into revised DQA screening procedures.

REVIEW PAST "AIR PURITY REPORTS"

PMS 399 provided to NEDU copies of completed reports from SSGN and VIRGINIA class submarines, reports that were representative of past use of current DQA screening procedures. NEDU reviewed these reports for potential problems, concerns, or issues related to the screening procedures and/or results — with the goal of improving the revised procedures.

SIGNIFICANT DIFFERENCES BETWEEN TVA-1000B AND TVA2020[11,12]

1. Weight (PID/FID version).

TVA-1000B: 11.9 lb. analyzer, 1.75 lb. enhanced probe.

TVA2020: 9.4 lb. analyzer, 1.5 lb. enhanced probe.

2. Size (analyzer).

TVA-1000B: 13.5" x 10.3" x 3.2".

TVA2020: 11.5 x 9.0 " x 4.0".

3. Battery.

TVA-1000B: NiCad. Per manufacturer specifications, minimum 8 hours continuous use, ~16 hours to recharge fully discharged battery. Use of the backlight on the enhanced probe shortens battery life.

TVA2020: Lithium ion. Per manufacturer specifications, minimum of 10 hours continuous use, maximum 10 hours to recharge a completely discharged battery. Use of the backlight on the enhanced probe shortens battery life.

4. H_2 supply.

TVA-1000B: on/off valve.

TVA2020: no on/off valve.

5. PC software (for downloading and other functions); data transfer mode.

TVA-1000B: Windows 8 compatible; RS-232.

TVA2020: No software required (TVA2020 functions as an external drive); USB-2.

Summary of differences. Compared to the TVA-1000B, the new TVA2020 is lighter, smaller, has a longer lasting battery that charges more quickly, and does not require special software for downloading and other functions. However, the TVA2020 does not have a valve to turn on and off the H_2 supply so care must be taken to remove or unscrew partially the H_2 tank after the monitor is turned off to avoid bleeding down the H_2 tank when the TVA2020 is not in use.

LABORATORY METHODS: TVA2020 EVALUATION

Testing was facilitated by using the TVA functions accessed by the push buttons on the front panel, while moving through a series of menu screens on the LCD. Functions used for testing included: checking battery, setting date and time, calibration, logging ("auto", 10 sec for the current work), and downloading. Downloading of logged data files did not require any special software to be installed on the computer. Rather, after putting the TVA2020 into the "USB mode" with several keystrokes, followed by using two standard USB cables to connect a USB barrier device in line between the computer and the TVA, a set of TVA files (including a log.txt file with the logged data) was transferred into a TVA 2020 window that automatically opened on the computer.

TVAs were tested at one of two locations: (1) on the laboratory bench at ambient pressure in the laboratory (~1 ATA), at temperatures between 19 and 25 °C; and (2) inside a temperature-controlled hyperbaric chamber — although unpressurized and therefore also at ambient laboratory pressure — at 5 and 42 °C. As the monitors were not designed to be used at pressure, the hyperbaric chamber was simply used to allow testing at specific controlled temperatures. During periods when instruments were not being tested, the monitors were turned off and plugged into their battery chargers, and stored on the laboratory bench, again at ambient temperatures between 19 and 25 °C. All TVA testing, including calibration, was limited by the need for greater than 16% O_2 in the gas, to support the FID flame.[12]

Up to three monitors were simultaneously tested on the bench, depending on the specific test being conducted. However, chamber testing could only be done with one monitor at a time due to space limitations within the chamber. Testing was done while each monitor was disconnected from its battery charger and powered by its internal battery — although the TVA can be operated while connected to the charger and simultaneously charging its battery.

The following gases were obtained commercially in pressure cylinders and used during testing:

1. High purity Air: CO_2-free, hydrocarbon-free; that will be referred to in this report also as "zero Air".

2. Individual gravimetric standards of benzene, n-butane, Freon 113, Freon 114, hexane, HFC-134A, isobutylene, methane, n-octane, toluene, and m-xylene, all at nominal concentrations up to 20 ppm. All standards were in balance hydrocarbon-free air and certified to +/-1% or +/- 5% relative.

Testing results reflected the error associated with the reported concentrations of the gas standards.

During most testing, including calibration that was always done on the bench, high-purity cylinder regulators were used to deliver test gas to one monitor at a time via Teflon and/or stainless steel tubing using a precision gas divider (STEC model SGD-710, Horiba/Stec Inc.; Austin, TX). The final leg of the gas delivery circuit consisted of an in-series rotameter flowmeter — (confirmed in lab to read correctly based on water displacement testing) and ended in an open 5 mL syringe barrel into which the TVA probe was inserted halfway for sampling. This configuration allowed flow to the monitor to be adjusted in most cases to ~1.2 L/min (slightly greater than the nominal sample flow rate of 1 L/min per manufacturer specifications), although higher and lower flows were used to evaluate the effect of flowrate.

For chamber testing with the STEC, the outlet of the STEC was attached using Teflon tubing to a stainless steel penetrator on the exterior of the chamber wall. Gas flowed from the penetrator into the chamber and was delivered in a similar manner as on the bench through a rotameter, ending with the syringe barrel for sampling. STEC tests done in the test chamber allowed testing under both cold and hot conditions, but again with only one monitor at a time due to space limitations.

The STEC device allowed any of the gas standards to be blended with a diluent gas (for NEDU testing, zero air) in ten equal steps of 10% each, from 0 to 100% of the gas standard concentration. Thus, with the STEC, an entire response curve could be generated from the 10 concentrations produced from a single gas standard — although for TVA testing, the actual gas dilution steps varied depending on the specific test. For TVA calibration, the STEC was also used as a convenient way to deliver zero and span gas to the monitor.

At each STEC setting, one monitor was allowed to sample the gas for at least 2 min that allowed readings to stabilize before moving the gas delivery line with its open syringe barrel to the next monitor and inserting the monitor's probe into the syringe barrel. When all three monitors had sampled the gas, the STEC was adjusted to the next concentration and the TVA sampling repeated, until all planned gas dilution steps had been completed. As just described, each complete test procedure with a single gas standard is hereafter referred to as a "STEC test" in this report. Commonly, a STEC test first stepped down from 100% of the test gas (e.g., 10 ppm of span gas) to 0 ppm, then back to 10 ppm in pre-selected dilution steps to evaluate the effect of decreasing and increasing concentrations of the test gas. Testing has previously shown that the STEC, using low ppm levels of VOCs is linear within the manufacturer's specification of +/- 0.5% of full scale as reported in reference 13.

During testing inside the hyperbaric chamber, the temperature of the chamber was maintained within 1 °C of that set for 5 °C testing, and within 2.5 °C of that set for 42 °C, by a temperature controller (model 89000-10, Cole-Parmer Instrument Co.; Barrington, IL). Although the lower and upper test temperatures for chamber testing do not fully span the range in operating temperature (-10 to 45 °C) given by the manufacturer,[12] this range of test temperatures represents the extremes in those temperatures at which the NEDU chamber could be reliably maintained.

Prior to start of chamber testing, monitors were allowed ~60 min for temperature equilibration inside the already equilibrated chamber, with the realization that the monitor probably did not equilibrate fully with a cold or hot chamber until at least several hours or more had passed. Thus, only one cold or one hot chamber test was performed each day to avoid the potential unknown effects of changing from one chamber temperature to another temperature during a single day, with little knowledge about the cooling and warming characteristics of the monitor.

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, and within five feet of the chamber when testing with a monitor inside the chamber. Barometric pressures in the laboratory were also recorded with a digital barometer (model AG400, Honeywell Sensotec Sensors; Columbus, OH) that the manufacturer had calibrated within the year. These ambient temperature and pressure data, as well as other test data including some monitor readings and chamber temperature readings, were recorded by hand on data sheets. However, to collect most gas and other readings from the monitors during testing, data logging was used with the TVA fixed logging interval of every 10 sec that collected the displayed gas readings at the end of every 10 sec. The logged data were downloaded at the end of each test day, or at the beginning of the next test day, using procedures described earlier in this section of the report.

Startup and calibration

At the beginning of most test days, one or more fully charged monitors (depending on how many monitors would be tested that day) were disconnected from their chargers, H_2 tanks (previously refilled to at least 1500 psig using the H_2 refilling assembly) inserted, and monitor(s) turned on. If not already done the previous test day, data was downloaded prior to clearing the TVA memory (previously logged data), and battery status checked. The monitor date and time were then checked and monitor clock time synchronized to within 1 sec of the laboratory clock time — thus allowing linking of the logged data times with all laboratory test procedures. Then data logging settings were checked to ensure that data would be logged automatically every 10 sec. Finally, "Run" on the TVA menu was pressed to put the TVA into the Run mode, thereby initiating ignition of the FID and display of both the PID and FID readings, and logging of the gas readings — as the TVA had to be in the Run mode for logging to occur.

To eliminate instrument alarms from being triggered during testing, both PID and FID alarms for STEL (short-term exposure limit), low ceiling, and high ceiling were all set to 0.0 ppm (which disables the alarms) for most of the project testing —except to confirm that the alarms were functional. Also, during all NEDU testing, measurement units were set at 0.1 ppm, the smallest units available; these measurement units applied both to the displayed and logged gas readings.

The next step usually was calibration of both the PID and FID on the bench — except for some testing that required that no calibration be done before testing began. However, before starting the calibration process, at least 30 min was allowed to pass following the time the TVA had been put into the Run mode, a period of time recommended by the TVA manual for best performance.[12]

Monitors were calibrated by first zeroing both the PID and FID together with high-purity air, followed by spanning both detectors with a gravimetric standard nominally of 10 ppm isobutylene/balance air — after allowing each monitor to sample the zero or span gas for at least 2 min. Besides the function of calibrating the monitors, the calibration procedures were designed to provide information on the calibration status of the monitors prior to calibration. Thus, zero and span gas readings were taken before and after both the zeroing and spanning function. This approach provided data on instrument stability since the last calibration and on the effect of recalibration prior to the day's testing, which required that after each of the zeroing and spanning steps, instruments be returned to the main gas display screen to allow viewing the gas readings and logging of the data.

Instrument stabilization following startup

Following the 30-min warmup period and calibration (taking approximately 20 min), data were then logged for approximately 5 hours (while the TVA was sampling the span gas) to determine stability of gas readings, stability that was necessary so that the rest of testing described directly below could be effectively done.

Precision and accuracy

Precision (i.e., short-term repeatability) of gas readings was determined on the bench at ambient temperature, after monitors had been allowed to warm up for at least 30 min, and span gas had been sampled for at least 5 min, allowing stable readings. Precision was then measured by reviewing the range in values of data logged at 10-sec intervals over time periods up to 10 min. Since the data logged at these intervals were presumably recorded directly from the displayed values (with the displayed data updated every second), these precision values should have reliably estimated the precision for the displayed data.

Short-term accuracy (i.e., up to approximately 3 hours after calibration) was assessed on the bench at room temperature (between 19 and 25 °C) by performing STEC tests using span gas. Such testing commonly followed calibration at the start of the test day and involved one STEC test with three monitors together, a test that began no more than 2 hours after completion of calibration. Short-term accuracy STEC tests were also done in the test chamber under cold or hot conditions (5 °C and 42 °C), tests that began no more than 2 hours after calibration with only one monitor at a time.

Calibration stability (i.e., Long-term accuracy up to 8 days after calibration)

Stability of calibration between one test day and the next test day was assessed by comparing pre-calibration and post-calibration gas readings when sampling zero air and span gas following the normal 30-min warmup period at the beginning of each test day.

Stability of calibration and the effect of any drift in calibration over multiple days on accuracy was evaluated by conducting STEC tests on the bench over a multiday period without recalibration. Two sets of STEC tests were completed: one set of tests over a 5-day period and a second set over another 8 days, all tests begun no more than 3 hours following the warmup period. The relatively large amount of testing time devoted to calibration stability was designed to provide sufficient data to allow NEDU to make a recommendation on the required frequency of calibration of the TVA2020, about which NEDU had no experience.

Relative response factors

During separate testing, gravimetric standards of a number of VOCs discussed earlier were tested alongside the span gas to define response factors relative to isobutylene following normal calibration of monitors. Relative response factors were calculated by dividing the TVA response (both FID and PID) in terms of equivalent isobutylene units (the calibration gas) by the actual concentration of the species tested (X).

Of particular interest were the response factors for Freon 114 and HFC-134A to determine the need to change the current adjustment of FID measurements for refrigerants on SSGN and VIRGINIA class submarines.

$$\text{Relative Response Factor} = \frac{\text{Measured TVA Response (of test gas)}}{\text{Actual Concentration (of test gas)}}$$

The relative response factor can be used to correct a TVA reading while sampling a specific gas to the estimated concentration of that gas by dividing the TVA reading by the factor.

Limited testing by NEDU in the past indicated very low FID sensitivity to H_2 by the TVA-1000B (e.g., 2% H_2 in air is equivalent to only several ppm of hydrocarbons).[1] No such testing was done with the TVA2020, and any effect on the TVA2020 by low amounts of H_2 sometimes found in submarine atmospheres was ignored.

Charcoal filter adaptor

A charcoal adaptor is used in the current screening procedures to remove trace organic vapors heavier than methane, ethane, and some related compounds from both (1) the span gas used to calibrate the TVA-1000B and (2) from DQA sample gas. Filtering allows use of the span gas (containing ~10 ppm isobutylene) (1) for zeroing both the PID and FID, as well as (2) for the determination in samples of the relatively high level of methane that is often found in submarine atmospheres. Subtraction of the filtered from the unfiltered measurement produces a total volatile organic reading that omits the non-hazardous methane contribution.

Although the charcoal filter was used for both these functions with the TVA-1000B, charcoal testing with the new TVA2020 was done due to questions about the effectiveness of the charcoal filter for the revised DQA procedures. Following calibration, span gas, zero gas, and a methane standard were individually sampled with and without the charcoal filter. Three separate charcoal filters were used (one for each of the three monitors) after the adaptors were loaded with fresh charcoal up to 2 weeks before testing was completed.

Relative humidity

The effect of water vapor (i.e., relative humidity [RH]) on monitor readings on the bench was examined by sampling span gas before and after the dry span gas had been humidified to ~95% RH. Water vapor was added to the span gas by using two water bubblers connected in series situated in a ~35 °C water bath, with the gas delivered to the analyzers using the STEC with the same delivery tubing and open syringe barrel used for most other testing. Gas temperature, RH, and dew point were first measured by inserting into the syringe barrel the probe of a hand-held humidity and temperature meter (model HM70; Vaisala Oyj, Finland) — with calibration traceable to the National Institute of Standards and Technology. When RH readings were stable, the probe of the monitor was inserted into the syringe barrel, and monitor readings were recorded after allowing at least 2 min for the monitor to equilibrate with the dry or wet gas.

Although there is potential for water in the bubbler to remove some of the isobutylene from the span gas, previous testing has shown that humidifying a similar test gas (95% RH) with this system reduces only up to 3% of the isobutylene in dry test gas.[14] The magnitude of reduction in this gas can be explained entirely by the estimated water vapor pressure in the sample gas — as the water vapor pressure displaces an equivalent pressure of the dry test gas. Although some isobutylene would be expected to dissolve in water, previous testing suggested that isobutylene saturation of the water in the bubbler of the humidifying system had occurred before testing started, so no additional reduction in isobutylene was evident due to gas going into solution in the bubbler.

Battery duration and charging time

Battery duration was tested by following normal startup procedures already described, then allowing monitors to operate on the bench sampling ambient air until they shut off due to low battery voltage. Battery duration was then determined from the logged data file by observing the time of the last logged reading — after recharging the battery and downloading the data file. For this testing, the backlight on the enhanced probe display (used in all other testing in this report) was turned off, so the backlight would not draw additional current from the battery.

Following each battery duration test, the time required to recharge the battery was determined by observing the time until the charging LED went from the initial orange charging state to the green fully charged state. Charging times were approximate (estimated to be to the nearest 15 min) as laboratory personnel frequently, but not constantly, observed the charging process until complete. Although no testing was done to determine how accurate the green LED was regarding a “fully charged battery”, the assumption was that monitor batteries would be charged in the field based on this “fully charged” green LED criterion, and thus these charging results should be useful for field personnel.

Additional monitor functions

The monitor’s visual and audio alarms were briefly tested on the bench using the STEC to deliver the span gas. Other menu functions were evaluated by stepping through the menu and confirming operation of the function.

DATA ANALYSIS: TVA2020 EVALUATION

Some of the data were used to calculate absolute error:

Absolute error = Observed reading – Expected reading.

Results from this analysis will of course reflect the specific error (i.e., ±1% or ±5% relative) associated with the certified concentration of each of the commercially obtained gas standards used for testing.

Expected gas readings

Expected gas readings were based on the concentration values on the certificates of the gas standards used for testing:

1. Expected gas readings when using the STEC to deliver test gas to the monitors were calculated by multiplying the gas certificate values by the dilution factor at the specific STEC setting: e.g., for a STEC setting of 30, the expected % O_2 value = the certificate % O_2 value • 0.3.

2. Expected gas readings when using a regulator to deliver the undiluted test gas directly to the monitors were equal to the certificate values of the test gases.

Editing of logged data files

To assist with the analysis of the results, the monitor-generated logged data files were commonly edited by deleting much of the data to produce one set of stabilized readings for each test condition (e.g., readings at each STEC setting).

RESULTS AND DISCUSSION: TVA2020 EVALUATION

NEDU conducted laboratory testing of the three loaned TVA monitors from July 2018 to November 2019. However, most of the data presented in this report are from testing from January 2019 forward, a time period following the correction by Thermo of a NEDU-identified TVA regulator problem that produced substantial drift in both PID and FID readings (item #2 below). Consequently, NEDU chose to exclude these earlier data except to describe the drift problem in the section below.

During all testing, laboratory ambient temperatures ranged from 21 to 25 °C, and barometric pressures ranged from 1013 +/- 15 mbar (1 +/- 0.015 ATA).

General performance and miscellaneous problems or issues

During laboratory testing, the three monitors were tested for hundreds of hours. For the majority of testing, the monitors worked well and without incident. The menus and operating procedures were very similar to those of the TVA-1000B, although NEDU testing revealed a number of problems or issues of concern that are discussed directly below.

1. Initial testing in August 2018 showed that one of the three TVAs displayed significant signal noise in both the PID and FID readings over a short time period. The unit was returned to Thermo, and they repaired the monitor by cleaning contamination found in the FID and replacing the PID sensor that was found to perform below specifications.

2. Instrument stabilization following startup. During subsequent testing in Nov 2018, NEDU observed in all three TVAs a downward drift in both PID and FID readings that interfered with NEDU's evaluation of the TVA. As a result, NEDU conducted the following testing to better understand the significance of this drift: following the 30-min warmup period and calibration (taking ~ 20 min), data were then logged for ~5 hours while the TVA was sampling span gas. Results confirmed that over several hours, the PID drifted down $\leq$3 ppm from the initial 10 ppm span readings (Figure 3), and the FID drifted down $\leq$3.5 ppm from the span gas readings (Figure 4), with the FID drift an apparently greater problem based on limited testing. Thermo determined that the drift was due to faulty regulators inside the TVAs that were replaced with different ones, and the TVAs returned to NEDU in January 2019. Two days of similar testing with the three repaired monitors showed that the drift was considerably reduced with the downward PID drift over 5 hours now well less than 1 ppm and that in the FID only $\leq$1 ppm (Figures 5-6). Going forward, Thermo confirmed that all TVAs would have the improved regulators. However, Thermo's suggestion that Navy users delay calibration for a couple of hours (following the normal 30-min warmup period) to avoid the remaining FID drift is viewed by NEDU as impractical for the Navy's use.

3. The TVA2020, unlike the TVA-1000B, has a lithium ion battery which can raise potential safety concerns. However, PMS 399 requested and received Navy approval for use of the TVA2020 in scenarios as planned.

4. Unlike the TVA-1000B, there is no valve to turn on/off the H_2 flow from TVA's H_2 tank to the FID due to a design decision during transition to the TVA2020. NEDU concerns include (1) during periods of nonuse, the need to remember to remove (or at least back out a couple of turns) the H_2 tank to avoid bleeding down of the H_2 as a partially or fully removed tank does not leak, and (2) if the tank is removed, providing a cover or empty tank to fill the space where the tank normally sits to prevent debris and dirt from entering.

5. There is very poor viewing of all text on the main LCD of the TVA (that cannot be backlit) making it difficult to read in low and even medium light conditions. As the enhanced probe display (that may be backlit) is only active in the Run mode (where gas

concentrations are displayed), the inability to easily see all the other items on the LCD that are required for operating the TVA concerns NEDU. These items include instrument checks and settings, data logging and downloading, calibration, and TVA warning alerts; these being only a few important functions. Fortunately for NEDU testing, after repeatedly going through the operating steps to operate the TVA2020, there was less need for NEDU personnel to be able to read in detail the displayed text due to familiarity with the monitor menu; this would not be the case with less experienced users in the Fleet. However, although not the ideal solution, a flashlight can be shined on the display to help make the display more readable.

6. The battery charger consists of a charging "box" with three indicating lights (representing power on, battery temperature, and TVA charge state) and a set of input and output leads. This arrangement apparently is meant to address potential safety concerns with the lithium ion battery such as overheating leading to possible fires. Although this charger may be acceptable for Fleet use, NEDU wonders if a more compact charging system might make sense for the Navy.

7. The battery charger sometimes displayed three red lights for no apparent reason after being connected for a time to the monitor. These three indicating lights commonly changed to green after turning the charger off for various durations, and then turning it back on. If the "three-red-light" event is a common occurrence, it would useful to know more to allow relevant guidance to be developed for any Navy use of the TVA2020.

8. Logged data files did not contain the serial number of the TVA — either within the file or the file name. As logging was routinely used during NEDU testing, NEDU was very careful to insert the serial number into the renamed file to link the data with a specific TVA. Although NEDU is unsure of how much, if any, logging will be done during routine Navy use, NEDU has only rarely seen this type of serial number omission with other non-TVA monitors.

9. During calibration, following both zeroing and spanning, the user is prompted to accept or reject the calibration based on "detector counts" that are displayed, although those counts probably do not mean very much to anyone other than TVA staff at Thermo. Displaying the concentrations (ppm) to allow the user to judge acceptability of the calibration may be more useful.

10. During each day of TVA testing, one or more of the monitors frequently (e.g., often every several days) experienced a fault that consisted of the following series of warnings on the display: 'PID lamp not operating", then when NEDU exited out of this, "FID flameout" appeared, then when exited out of this, "line plugged" appeared. This fault commonly occurred an hour or more after startup in the Run mode while sampling gas, and often also produced a notation in the logging file that both detectors had failed. To restore the monitor to normal operating condition, NEDU commonly turned the monitor off and then on, although sometimes simply exiting out of one of the fault displays returned the monitor to operation.

11. Toward the end of NEDU laboratory testing of the TVA2020 in April 2019, a meeting was held at NEDU among Navy representatives (including PMS 399) and Thermo to discuss issues and problems that had arisen to date as well as how any transition by the Navy to the TVA2020 might occur.[15] Following this meeting, Thermo investigated some of the items that had been brought up and provided the following response in June 2019:

a. The fault issue (item #10 above) appeared to be caused by a communication problem between the A/D converter and the microprocessor. New TVA2020 firmware was expected to correct this problem.

b. The new firmware will include the new feature of including the TVA2020 serial number in the logged data files (addressing item #8 above).

c. A new ATEX battery charger upgrades the current chargers that NEDU had, and is expected to eliminate the three-red-light condition (item #7 above).

d. When the new TVA2020 firmware becomes available (estimated late July 2019), NEDU would return the three loaner TVA2020s to Thermo to be upgraded to the new firmware, and three new ATEX battery chargers would be sent to NEDU. Once the upgraded TVA2020s were returned to NEDU, NEDU would conduct additional testing to determine acceptability of these modifications.

12. Following the meeting at NEDU, NEDU discovered during its testing that anytime the span gas concentrations (normally entered by the user into the TVA2020 memory for calibration) are changed, the TVA needed to be immediately re-spanned. Otherwise, a “bad detector” warning came up on the LCD followed by the displayed gas readings locking up. Lockup of screen readings remained despite turning the TVA2020 off and then back on. This lockup situation raised a number of concerns of which the most important may be the inadvertent lockup when a beginner user is being trained in stepping through the menu and the resultant confusion, unless someone at the time is aware of how to reverse the lockup. This was actually the case when NEDU first encountered the lockup situation.

13. Upgraded monitors were returned to NEDU in September 2019 with the following modifications made by Thermo (firmware versions 01.00.52S and 01.00.53S):

a. Firmware to correct the intermittent fault conditions (PID not operating, FID flameout, flow line plugged).

b. The option to generate data files with the TVA2020 serial number in the filename.

c. Temperature compensation for the FID. This modification had not been discussed with NEDU prior to its implementation, and was a surprise to NEDU.

Three new ATEX battery chargers had been previously were sent to NEDU.

14. Limited testing of the three upgraded monitors and new battery chargers occurred from September to November 2019 — after most other planned testing had been completed. The focus of this testing was to observe if there were any evidence that (1) the intermittent fault and battery charger issues had not been resolved, and (2) the modifications, particularly the new temperature compensation for the FID, had any inadvertent effects on monitor performance, particularly on accuracy of gas readings. Additional testing defined the relative response factors for the two refrigerants (Freon 114 and HFC-134) used on SSGN and VIRGINIA submarines — as this previously planned testing had not been completed before the monitors had been returned to Thermo for the upgrade. The unexpected addition of temperature compensation to the FID was one important concern as this modification presumably would be adjusting the FID readings based on some model incorporating ambient temperature, and therefore potentially affecting FID readings in other ways. Results of the upgraded testing are described below near the end of this section (**Upgraded monitors**) although the results of the refrigerant response testing are given under **Relative response factors.**

Precision

Precision is important to determine first, since any accuracy testing is affected by short-term changes in measurements. Precision determined on the bench at ambient temperature for the three monitors while sampling span gas was

PID : +/-0.1 ppm isobutylene equivalents;
FID : +/-0.1 ppm isobutylene equivalents

Conclusions. Precision is at the level of resolution in both the displayed and logged gas measurements, and therefore is as good as is possible with the TVA2020.

Accuracy

Based on STEC testing on the bench at ambient temperature, and within 2 hours after completion of calibration, measurement error across the test range of 0 to 10 ppm isobutylene for the three monitors is plotted in Figures 7-8. On average, measurement errors were

For the PID: up to 0.2 ppm low for two monitors and up to 0.6 ppm low for the third monitor #7;

For the FID: up to 1 ppm low for two monitors and up to 1.2 ppm low for monitor #7.

Based on STEC testing in the chamber at temperatures of 5 °C or 42 °C, and within 2 hours after completion of calibration, measurement error across the test range of 0 to 10 ppm isobutylene for the three monitors is plotted in Figures 9-12. Based on two tests with each of the three monitors, measurement errors were

For the PID: up to 6 ppm high at 5 °C and up to 12 ppm high at 42 °C;

For the FID: up to 8 ppm high at 5 °C and up to 60 ppm high for 42 °C.

The hysteresis observed during accuracy testing on the bench, in terms of larger errors in some cases during the return phase of testing from 0 to 10 ppm, most likely reflects the continuing drift in gas readings — despite installation of improved TVA regulators reported earlier in this section of the report. Interestingly, TVAs differed in response to temperature, with some of the readings really high for both PID and FID, and some of the paired replicated tests not agreeing well. The lack of significant hysteresis during the temperature testing in the chamber suggests that the TVAs had thermally equilibrated by the start of the STEC testing.

Results from cold or hot testing should be viewed in the context that, according to Thermo[15] in the unmodified TVA2020s that were tested here, only PID readings are compensated for temperature. FID readings are not compensated for temperature due to the high operating temperatures of the FID. This is in contrast to the TVA-1000B where both the PID and FID are compensated for temperature. Subsequently, as discussed above in the subsection **General performance and miscellaneous problems or issues,** Thermo implemented thermal compensation for the FID in the upgraded monitors that were delivered to NEDU toward the end of this project; see discussion of results of the upgraded monitor testing below in the **Upgraded monitors** subsection.

Conclusions. Measurement error on the bench appears to be within the level of the downward drift remaining after the regulator repair: PID drift over 5 hours is well less than 1 ppm, and that in the FID is only up to ~1 ppm. Therefore, bench accuracy appears to meet the manufacturer's specifications of

PID: +/-20% of reading or +/-0.5 ppm, whichever is larger, determined at the temperature of calibration;

FID: +/-10% of reading or +/-1.0 ppm, whichever is larger at the temperature of calibration.

These acceptable errors that are less than the manufacturer's stated errors were for the TVA-1000B. At the time that the TVA-1000B procedures were produced, it was estimated that such error might range up to +/- 20% relative, based on limited NEDU experience. Although most portable gas analyzers do not compensate well for ambient temperature, the size of the temperature effect on the FID (that was not compensated in the TVA2020s that were tested) and the PID (that is compensated) was surprisingly large.

Calibration stability (i.e., Accuracy up to 5 or 8 days after calibration)

Comparing pre-calibration and post-calibration gas readings when sampling zero air and span gas following the normal 30 min warmup period at the beginning of each test day indicated that any shift in calibration from day to day could be due to shifts in the zero setting, span setting, or both.

PID readings for TVA #3 changed little (e.g., within several times the level of precision reported above in the **Precision** subsection) over the 5-day or 8-day test period without recalibration, as judged by comparing the STEC response curves completed on the first day (square symbols), last day (triangle symbols), and a few in-between days (small circles; Figures 13-14). However, there was considerably more instability over time for some of the tests for TVA #7 and #8, with readings often more than 1 ppm higher or lower than those on Day1. There were also differences between the 5-day and 8-day stability results for both #7 and #8 (Figures 15-18).

As with the PID, FID readings for TVA #3 changed much less than for #7 and #8 over the 5-day or 8-day test period, with the readings for TVA #3 over the 5-day test within the level of precision (Figures 19-24), and those for TVA #7 and #8 again often more than 1 ppm higher or lower than those on Day1.

Conclusions. Calibration stability under the favorable testing environment of the laboratory is a necessary prerequisite to any desired stability in the field. However, the degree of calibration stability varied among the monitors and showed that without recalibration, the PID and FID measurement errors from day to day in the laboratory could be large. Therefore, TVAs should be recalibrated prior to each day's use (as is the current policy with the TVA-1000B), and more frequently if TVA readings appear suspect or ambient temperatures change markedly (based on results from the **Accuracy** subsection).

Relative response factors

Table 1 gives the relative response factors that were calculated from the results of testing a number of VOC standards alongside the span gas. Each gas was tested once on each of two days, with the span gas tested at the start and end of each test series. For each gas, there was generally good agreement between test days as well as among the three TVAs for both the PID and FID. However, the presence of response factors for isobutylene significantly less than 1.00 — the expected value as isobutylene is being compared to itself — probably was due to the previously discussed downward drift in readings remaining after the installation of the new regulator by Thermo, a drift that was greater for the FID.

Included at the bottom of each listing (i.e., PID and FID) are PID values taken from reference 16 (the manual for the PID sensor used in the TVA2020), and FID values from reference 12 (the TVA2020 manual), although the "response factor multipliers" from both references needed to be divided into 1 to convert into the "relative response factors", allowing direct comparison. Not all response multipliers were available from the two references (12 and 16), and the PID did not respond to three of the gases that had high ionization potentials (n-butane, Freon 113, and methane) relative to that of the PID lamp (10.6 eV). However, for the comparisons possible, PID values from reference 16 agreed well with the current NEDU values, although agreement between NEDU FID values and those from reference 12 was not as close.

Table 2 gives the relative response factors for the two refrigerants used on SSGN and VIRGINIA submarines based on additional testing done with the upgraded monitors. Here, two tests with both refrigerants were done on each of two days, with the span gas tested immediately preceding each test of the refrigerants. Here, there was generally good agreement between the two tests done each day, as well as between test days and among the three TVAs for both the PID and FID. As expected, the PID was insensitive to Freon 114 and HFC-134A due to their high ionization potentials. However, FID response factors for Freon 114 and HFC-134A generally agree with those currently used for adjusting TVA-1000B readings of DQA: 1.0 for Freon 114 and 2.0 for HFC-134A. No response factors for the two refrigerants were given in reference 12 or reference 16, so no comparison with the current NEDU data was possible.

Although response factors can vary somewhat with the PID detector design and substantially with the FID design, the comparisons with the response values from references specific to the TVA2020 should have minimized the detector design variability. However, general guidance for gas monitors with PID and FID detectors recommends using response factors only for approximate readings, and calibrating with the target species for best accuracy.

Conclusions. Results confirmed that published response factors for the 3 TVA2020s tested may not be very accurate and should be used with caution, a similar conclusion previously made with the TVA-1000B. The similarity in FID response factors for Freon 114 and HFC-134A between the TVA-1000B and the TVA2020 suggests there was no need to change the multiplication factors used to adjust FID readings of DQA for these refrigerants in any revised screening procedures.

Charcoal filter adaptor

Testing the three TVAs for 2 days showed the following:

Span gas readings were reduced from ~10 ppm (without filter) to ~0 to 2 ppm (with filter) for both PID and FID.

Methane readings for the FID with the filter were from 0 to 0.8 ppm higher than those readings without the filter (~6 ppm). This test could not be made with the PID as the PID does not detect methane.

Readings of zero air with and without the filter were within 0.5 ppm of each other, for both the PID and FID.

Conclusions. The charcoal filter appeared to allow methane to pass through as expected, and not to add significant VOCs to the sample gas as shown by the agreement between unfiltered and filtered zero air readings. However, filtering the span gas may not have been an effective approach in producing zero air for zeroing the TVA (as is done with the current procedures), particularly if the charcoal was not regularly replaced as may be the case in the Fleet. More investigation is needed to resolve this issue.

Relative humidity

Comparing dry and wet span gas (~98% relative humidity) based on 2 to 4 tests (with little or no time allowed between tests) done on one day with each of the three monitors produced the following results:

TVA #3: wet PID readings ~0.5 to 1 ppm lower than dry readings
wet FID readings ~0 to 0.5 ppm lower than dry readings

TVA #7: wet PID readings ~0.5 ppm lower than dry readings
wet FID readings ~same as dry readings

TVA #8: wet PID readings ~0.5 ppm lower than dry readings
wet FID readings ~same as dry readings

Wet span gas showed up to 1 ppm decline in PID readings, and up to 0.5 ppm decline in FID readings, from the ~10 ppm readings observed with dry gas. The decline in VOC readings agrees with previous reports that PID measurements can be influenced by high humidity, although water vapor itself is not detected,[17] as well as with the expected up to 3% reduction in VOC readings simply due to humidification — as discussed earlier in the **METHODS** subsection.

Conclusions. These results suggest a small but significant reduction in VOC readings due to water vapor as expected with any PID, and little or no reduction in FID readings. Thus, there should be minimal concern over the effect of water vapor on the TVA2020.

Battery duration and charging time

Battery duration and charging time for the three monitors were tested 2 separate times. Results showed that fully charged batteries commonly last ~10 hours, and then require ~6.5 hours to recharge to full charge (again, defined by NEDU as the charger reaching the "green LED" status. All testing was done with the original chargers supplied with the loaner TVA2020s.

Conclusions. These limited data agree with the TVA2020 specification of 10 hours minimum battery operating time and 10 hours maximum charging time for a fully discharged battery. Experience in the field will help clarify battery issues, including whether battery duration is affected when batteries are used on multiple occasions without recharging, and whether the final upgraded chargers (described directly below and noted as "Nov 2019 upgraded chargers") appear to charge differently.

Upgraded monitors

Upgraded monitors were tested a number of ways. Initially, upon receipt from Thermo, monitors were operated during the day on the bench sampling ambient air to determine whether the monitors would shut off prematurely, and/or display a fault or malfunction — as directly observed and/or determined from the logged data that were downloaded at the end of each day prior to recharging the upcoming night. During this testing, the ATEX battery chargers were also observed to determine if the three-red-light condition occurred.

One week of initial testing did not reveal any fault or malfunction by the monitors, allowing other testing to begin. However, the three-red-light condition was commonly observed with one, two, or three of the chargers, although there was no apparent charging or battery problem: all three batteries following overnight charging read 7.7 to 7.8 V and ended each day's testing at ~7.1 V. As a result of our observations regarding the battery charger, and apparently those from other customers of the TVA2020, Thermo modified the firmware for the charger and provided three upgraded chargers (noted here as "Nov 2019 upgraded chargers" to distinguish from the original upgraded ATEX chargers) to NEDU for evaluation. Testing of the Nov 2019 chargers over several weeks appeared to confirm correct charging and indicating light function, with no red lights evident during the testing. However, one of the three Nov 2019 chargers toward the end of the testing period stopped charging and none of the three indicating lights lit up when plugged into line power and then connected to the monitor. This failure was assumed to be a random failure, unrelated to the three-red-light problem.

The new option to generate data files with the TVA2020 serial number in the filename produced a filename with the 12 digit serial number followed by 'LOG" (e.g., "202017092753LOG". The first 4 digits represented the TVA2020 product family, next 2 digits the year of manufacture (e.g., 17), next 2 digits the month of manufacture (e.g., 09), and the last 4 digits the sequential unit number (2753). Although this option was an improvement over the old system with no serial number included in the filename, NEDU suggests that perhaps a simpler system would have been to name the file using only the sequential unit number and that the sequential unit number also be included within the file itself to ensure against file renaming errors.

Limited additional testing was also completed to compare TVA2020 accuracy with the new FID temperature compensation turned ON to that with the temperature compensation turned OFF. Initial testing was done on one day: following calibration, span gas was sampled during at least three cycles of switching compensation from OFF to ON and back, and TVA2020 readings were observed to not change more than the level of precision reported above. Subsequent testing was done similarly to the earlier testing for short-term accuracy where up to three hours after calibration, one STEC test using span gas per day was conducted on the bench at room temperature. Here, two tests (one test per day) were done with the compensation ON, and two tests (again one test per different day) with the compensation OFF.

Temperature compensation results shown in Figures 25-30 compared the two OFF plots with the two ON plots for both PID and FID readings. For monitor #3, there is similar accuracy with OFF and ON plots overlapping within the level of precision — when tested at approximately the same ambient temperature as that for calibration. Comparison for the other two monitors was confounded due to the variability in some of the plots for both detectors — variability that for an unknown reason is greater than that reported above for bench accuracy in the original TVA2020 prior to the temperature compensation upgrade. However, despite this shortcoming, the overlap of many of the OFF data points with the ON data points suggests similar accuracy.

Review of Thermo's data used to develop the new temperature compensation for the TVA2020 FID revealed that Thermo used a gas of 500 ppm methane for testing. Results suggested that FID readings were ~5-12% higher than expected in the cold (10 °C) and ~5-12% lower than expected in the hot (40 °C) — whereas NEDU data showed much larger increases in both PID and FID readings in both the cold (5 °C) and hot (42 °C); see Figures 9-12. This observation raised the question of whether the disagreement between Thermo and NEDU is due to the large difference in test gas concentrations between Thermo (500 ppm methane) and NEDU (0 to 10 ppm isobutylene). The shift upward on the 4 NEDU temperature graphs also suggested an offset shift up with both PID and FID readings at both cold and hot — an observation that did not seem to fit Thermo's findings for the FID.

The apparent difference in the FID response to temperature with the Thermo data (compared to NEDU data) raised questions about how the Thermo compensation would affect the much lower concentration NEDU data. Also, although NEDU is unsure how the Thermo PID compensation was exactly done, the fact that NEDU data showed significant effect of temperature on PID readings (even as we have been told that the PID is already compensated in the TVA2020) suggested the new Thermo FID compensation may also not work well with our FID data.

Conclusions. None of the upgraded monitors were observed to experience the fault characterized by the display of "PID lamp not operating", "FID flameout", or "line plugged". None of the Nov 2019 upgraded chargers displayed the three-red-light phenomenon. However, it would be impossible to rule both these problems out during the very limited testing NEDU conducted. Further experience with the TVA2020 by NEDU and others may provide additional insight into these two issues. The questions about the new temperature compensation suggest the best approach is to always operate the TVA2020 with the FID compensation OFF — although NEDU testing did not show any effect of the compensation on calibration readings.

Additional monitor functions

Limited testing of upgraded monitors confirmed that the visual and audio alarms, as well as the other menu functions, appeared to work as expected. Although data logging was essential for NEDU testing, its importance for DQA screening in the field is unknown at this time.

REVIEW OF AIR PURITY REPORTS

The following 21 Air Purity Reports were received together and reviewed:

SSN-784 (VA class) USS North Dakota: 3 reports from June 2018.
SSGN-727 USS Michigan: 12 reports from Jan 2018 and March 2018.
SSGN-728 USS Florida: 6 reports from Feb 2018.

In addition, 120 Air Purity Reports were received together and reviewed from SSGN-726 USS Ohio: Feb 2011 to April 2017.

For discussion purposes in order to be able to better distinguish between the relatively small set of reports from the first 3 submarines and the much larger set of reports from the USS Ohio, these two sets are discussed separately below.

Both sets of reports had instances where two or more data sheets were used the same day, but only one calibration of the Geotech and TVA-1000B had apparently been done that day. The second set of 120 reports also had a number of sheets only minimally completed. Lastly, there appeared to be numerous mistakes made on the reports that unfortunately affect that accuracy of the discussion in the **Results** section directly below. However, NEDU believes that the overall conclusions drawn from the review of the Air Purity Reports are sound.

Results

1. First set of 21 reports: Of all 21 reports reporting PID and FID measurements, 20 reports had FID with charcoal filtered readings greater than FID readings alone.
   Second set of 120 reports: Out of 100 reports listing TVA measurements, 46 reports had FID with charcoal filtered readings greater than FID readings alone.

Conclusions. Results suggest a hardware problem and/or procedural error as charcoal filtering should remove most VOCs heavier than methane and some related compounds, and thus reduce FID readings.

2. First set of 21 reports: Out of all 21 reports reporting PID and FID calibration, 9 reports did not give pre-calibration PID and FID readings.
   Second set of 120 reports: All reports (108) reporting PID and FID calibration gave pre-calibration PID and FID readings.

Conclusions. Results suggest procedural error with first set of reports.

3. First set of 21 reports (SSN and SSGN). All 21 reports list 0 millitorr for both HFC-134A and Freon 114, although only SSGN class submarines have both refrigerants; VA class submarines have only HFC-134A.
   Second set of 120 reports (all SSGN): Forty-nine reports list 0 millitorr for both HFC-134A and Freon 114, with the exception of 1 report listing 1 millitorr for HFC-134A.

Conclusions. Results suggest procedural error and incorrect report form with first set of reports, and low levels of refrigerants for both sets of reports.

4. First set of 21 reports: With the exception of three reports with non-zero PID readings (all $\leq$0.25 ppm), all other reports list PID and adjusted FID readings as equal to 0.
   Second set of 120 reports: Out of 100 reports listing TVA measurements, there were 36 reports with non-zero PID readings (all $\leq$1.3 ppm), and 13 reports with non-zero adjusted FID readings (all $\leq$3.3 ppm) although some of the adjusted FID were suspect because of apparent errors in the calculation by the personnel filling out the sheet.

Conclusions. Results suggest very low levels of contaminants.

5. First set of 21 reports: There were three reports of CO=1 millitorr from two submarines, and 6 reports of CO=2 millitorr from another submarine; all other reports show CO=0 millitorr.
   Second set of 120 reports: Out of 49 reports listing CO measurements, there were 18 reports of CO=1 millitorr, 6 reports of CO=2 millitorr, and 3 reports of CO=3 millitorr; all other reports show CO=0 millitorr.

Conclusions. Results suggest low levels of CO.

6. First set of 21 reports: There were no failures (violating the specified limits) in any report of any of the three screening categories:
   CAMS readings (O_2, CO, HFC-134A, and Freon 114)
   TVA-1000B PID and adjusted FID
   Geotech CO_2.
   Second set of 120 reports: There were no failures (violating the specified limits) in any report of any of three screening categories:
   CAMS readings (O_2, CO, HFC-134A, and Freon 114)
   TVA-1000B PID and adjusted FID
   Geotech CO_2.

Conclusions. Again, results suggest very low levels of contaminants.

7. First set of 21 reports: Three different data sheets were used:
   Figure L-3-DDS Air Purity Report (ACN 7/B, ACN 9/B). US Michigan and USS Florida.
   Figure 11. Air Purity Report (Vol 4 Pt 1 Ch 9). USS North Dakota. Contained incorrect HFC-134A correction.

Second set of 120 reports: Two different data sheets were used.
Figure L-3-DDS Air Purity Report (ACN 2/B)
Figure 1. Air Purity Report (Vol 4 Pt 7 Ch 1). Contained incorrect HFC-134A correction.

Conclusions. NEDU is unsure why different data sheets were used. Results also suggest the need to ensure correct adjustment of the FID readings for the presence of refrigerants.

FINAL CONCLUSIONS

1. The new TVA2020 was evaluated as a replacement to the TVA-1000B, rather than as meeting a set of Navy requirements for screening DQA, as such requirements do not currently exist. However, as only limited past testing of the TVA-1000B has been done by the Navy, any recommendation that the TVA2020 is an acceptable replacement to the TVA-1000B is based primarily on NEDU's conclusion about how well the TVA2020 could perform the current DQA screening now done by the TVA-1000B.

2. Laboratory testing suggested that the TVA2020 should provide DQA screening at least as well as the TVA-1000B, and in some cases better. However, certain characteristics of the TVA2020 may be of concern, including the relatively large effect of ambient temperature on gas measurements and the less than optimal viewing of text on the LCD. Whether the TVA-1000B response to temperature or its display of text on its LCD was any better or worse than the new TVA2020 is unknown at this time.

3. Review of Air Purity Reports that were available to NEDU revealed the following significant issues:

a. FID readings using charcoal taken with the TVA-1000B were commonly greater than FID readings without charcoal.

b. Failure to often provide pre-calibration PID and FID readings as well as other required information.

c. Apparent confusion over which refrigerants were on specific class submarines.

d. Use of different Air Purity Report data sheets, that sometimes contained errors including incorrect adjustment of the FID readings for the presence of refrigerants.

4. Review of Air Purity Reports that were available to NEDU suggested low levels of contaminants in DQA and no failures in any of the three screening categories, despite the question over the use of the charcoal filter raised in item 3.a directly above and in item 5 directly below.

5. Laboratory testing of the TVA2020 suggested that charcoal filtering of the span gas may not be an effective approach in producing zero air for zeroing the TVA (as is done with the current procedures), particularly if the charcoal is not regularly replaced as may be the case in the Fleet. Review of the Air Purity Reports also suggested that charcoal filtering of the sample gas may not be a useful procedure for estimating methane levels in DQA using the TVA-1000B, and presumably also the TVA2020.

6. Laboratory testing of the upgraded TVA2020 showed the following:

a. None of the upgraded monitors were observed to experience the fault characterized by the display of "PID lamp not operating", "FID flameout", or "line plugged". Further experience with the TVA2020 by NEDU and others may provide additional insight into this issue.

b. None of the Nov 2019 upgraded battery chargers displayed the three-red-light phenomenon. Again, further experience will provide better confirmation that the problem has been resolved.

c. The usefulness of the new temperature compensation for the FID for any Navy application is unknown at this time.

RECOMMENDATIONS

1. NEDU recommends that current procedures for screening for DQA on SSGN and VIRGINIA class submarines be revised with the following changes:

a. Replacement of the TVA-1000B with the new TVA2020 that should be procured along with its Nov 2019 upgraded battery charger, enhanced probe, extra H_2 tanks and refilling assembly as required, and spare parts and tools identified by Thermo to allow users in the Fleet to make limited repairs. All procured monitors should contain firmware up to versions 01.00.52S and 01.00.53S, but no future updates unless approved by PMS 399, as any future updates have not been tested by NEDU.

b. Replacement of the Geotech HB 1.2A with the new Geotech HYPB2.0.

2. Appendix A of this report provides recommended procedures for the TVA2020 that should be used in integrating the TVA2020 into the revised DQA procedures. The TVA2020 procedures differ from those for the TVA-1000B in some of the following ways:

a. Until observations concerning use of the charcoal filter for calibration and screening DQA are better understood, TVA2020 procedures will not use the charcoal filter for either procedure and will require gas cylinders of high-purity air (CO_2-free, hydrocarbon-free) for zeroing TVA2020.

b. TVA2020 procedures include steps to avoid inadvertently bleeding down the H_2 tank due, unlike the TVA-1000B, to the absence of a valve to turn off the H_2 flow.

c. A caution is included regarding the need to immediately recalibrate the TVA2020 after changing the span gas concentration in the TVA2020 menu to avoid lockup of the displayed gas readings.

d. A caution is included that the new temperature compensation for the FID should be turned OFF due to questions about its usefulness.

3. As with the TVA-1000B, the new TVA2020 should be recalibrated prior to each day's use, and more frequently if TVA readings appear suspect or ambient temperatures change markedly.

4. NEDU Technical Report, NEDU TR 15-01,[8] and NEDU Technical Letter No. NEDU TL 18-03[18] should be used for integrating the Geotech HYPB2.0 into the revised DQA procedures.

5. NEDU also recommends that the revised DQA procedures reduce the upper limit for CO from 20 ppm to 10 ppm (8 millitorr) to agree with the new revision 7a of the Diving Manual. The low CO levels routinely reported in the Air Purity Reports that were reviewed by NEDU suggest there should be no significant increase in CO failures during the screening process due to reduction in the CO limit.

6. The current DQA screening procedures for SSGN and VIRGINIA class submarines do not include testing of water and testing of oil, mist, and particulates, and NEDU does not recommend including such testing in any revised procedures — although such testing has now been added to revision 7a of the Diving Manual. NEDU believes such an expansion of the current DQA procedures is beyond the scope of phase 1 of the current task, and should require further discussion with NAVSEA 00C and others before any radical change in current DQA procedures is made.

7. NEDU also recommends that the revised DQA procedures correct any known errors in the current procedures and make any needed changes to improve the effectiveness of the screening process. These corrections and changes include the following:

a. Delete chemical categories 2, 3, and 4 (including their tables).

Until contaminant profiles have been defined for SSGN and VA class air banks — defined by sampling of their air banks and detailed analysis of specific contaminants, these three categories are of questionable value as the species contained within are at least partly based on air samples taken from earlier class submarines from over 20 years ago.

b. Ensure correct hardware references for SSGN and VA class submarines.

c. Change Category 1 Table as follows:

Ensure that both Freon 12 and Freon 11 are deleted as neither is used on SSGN or VA class submarines.

VA class: ensure that Freon 114 (1,2 Dichlorotetrafluoroethane) is deleted as Freon 114 is not used on VA class.

SSGN class: ensure that Freon 114 is present.

SSGN and VA classes: Ensure HFC-134A (1,1,1,2 Tetrafluoroethane) has been added per previous recommendations.[19]

d. Ensure NOTES (at bottom of Category 1 Table) read as follow (or correct):

Note 1. DDS limits for carbon dioxide and carbon monoxide are limits for diving air defined by the *U.S. Navy Diving Manual, Revision 7a*, 2018.

Note 2. DDS limits for oxygen are based on the range of 20 to 22% for oxygen in diving air defined by the *U.S. Navy Diving Manual, Revision 7a*, 2018.

Note 3. No HFC-134A TLV (Threshold Limit Value) is available from the American Conference of Governmental Industrial Hygienists (ACGIH, 2018). The HFC-134A limit is taken from 2017 Maximum Concentrations at the Workplace (MAKS), German Research Foundation, Federal Republic of Germany. DDS limit is HFC-134A limit divided by 7 ATA.

Note 4. (SSGN class only). TLV limit for Freon 114 is taken from ACGIH (2018). DDS limit is Freon 114 limit divided by 7 ATA.

Note 5. Odor and taste shall also be sampled and recorded.

8. At this time, the limits for both the PID and adjusted FID readings will remain at 5 ppm isobutylene equivalents. However, the adjusted FID limit will now be calculated by subtracting the refrigerants out from the "FID reading without charcoal," as again the charcoal filter will not be used in DQA procedures. Future experience with DQA screening without using the charcoal filter, and any future sampling and detailed analysis of SSGN and VA class air banks will provide guidance regarding the need or benefit to change the 5 ppm limits.

9. The current multiplication factors used to adjust FID readings of DQA readings for refrigerants (1.0 for Freon 114 and 2.0 for HFC-134A) should remain the same for any revised screening procedures.

10. Any needed correction of contaminant limits for exposure depth should continue to be implemented by dividing by the maximum exposure depth of 7 ATA (200 fswg), unless a change in depth correction is authorized by PMS 399.

11. The Air Purity Report data sheets for both SSGN and VA class submarines will need to be revised to agree with the recommended new DQA procedures, and to ensure that the current refrigerant adjustment factors (1.0 for Freon 114 and 2.0 for HFC-134A) are correctly used with the correct class submarine.

12. The final revised DQA procedures (i.e., Appendix L [Air Purity Guidelines for Dry Deck Shelter Operations]) — reflecting all the above items #1 to #11 and produced by NEDU working with PMS 399-designated personnel) — will need to be field tested, and such field testing be completed prior to any decision about transitioning these procedures as an official replacement to the current procedures. NEDU experience with gas screening procedures has shown that field testing nearly always reveals unexpected problems, issues, and concerns that may need to be addressed before transition to the Fleet.

13. Lastly, any transition of the revised DQA procedures will only be to SSGN and VIRGINIA class submarines. NEDU expects that the revised DQA procedures will be incorporated into the appropriate documents for Fleet use and that PMS 399 will ensure that the new procedures are identical in both DDS and HOSUB documents where applicable.

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Assignment 18-02: Conduct Laboratory Testing of Upgraded Geotech Hyperbaric O2/CO2 Analyzers (Model HYPB 2.0), Technical Letter no. NEDU TL 18-03, 3963/TA 18-02, Serial 02/012 of 29 Mar 18.

19. Navy Experimental Diving Unit letter, *Recommended Changes to DDS and ASDS Air Screening Procedures Due to HFC-134A Conversion*, 3910/TA 01-19, Serial 02/219 of 12 Sep 03.

TABLE 1. Relative response factors: VOCs.

PID

		start test isobutylene	benzene	n-butane	Freon 113	hexane	methane	n-octane	toluene	m-xylene	end test isobutylene
TVA #3	Day 1	0.96	1.75	0.02	0.01	0.21	0.00		1.81		0.96
	Day 2	0.95	1.73		0.00	0.21	0.00	0.49		1.93	0.94
	Day 3	0.97		0.02				0.51	1.82	2.07	0.97
TVA #7	Day 1	0.96	1.78	0.03	0.01	0.23	0.01		1.79		0.98
	Day 2	1.02	1.83		0.01	0.23	0.00	0.54		1.76	0.99
	Day 3	0.99		0.04				0.55	1.83	1.99	0.99
TVA #8	Day 1	0.98	1.80	0.03	0.01	0.23	0.01		1.85		0.97
	Day 2	1.01	1.83		0.02	0.23	0.02	0.52		1.91	0.97
	Day 3	1.00		0.02				0.52	1.88	2.07	0.99
Reference 16			1.89					0.45	1.89		

FID

		start test isobutylene	benzene	n-butane	Freon 113	hexane	methane	n-octane	toluene	m-xylene	end test isobutylene
TVA #3	Day 1	0.92	1.89	1.00	0.99	1.35	0.61		1.83		0.91
	Day 2	0.92	2.00		0.97	1.34	0.59	1.81		1.71	0.90
	Day 3	0.92		1.01				1.83	1.85	1.82	0.91
TVA #7	Day 1	0.87	1.95	0.91	1.14	1.23	0.58		1.77		0.83
	Day 2	0.91	2.01		1.13	1.28	0.57	1.78		1.60	0.84
	Day 3	0.91		0.98				1.80	1.87	1.84	0.88
TVA #8	Day 1	0.94	1.93	1.02	1.02	1.38	0.61		1.89		0.93
	Day 2	0.96	1.99		1.01	1.36	0.60	1.85		1.74	0.91
	Day 3	0.96		1.05				1.89	1.92	1.89	0.95
Reference 12			2.27	1.23		1.75			2.34	2.71	

TABLE 2. Relative response factors: refrigerants.

PID		start test #1			start test #2		
		isobutylene	Freon 114	HFC-134A	isobutylene	Freon 114	HFC-134A
TVA #3	Day 1	0.95	0.00	0.00	0.94	0.00	0.00
	Day 2	0.93	-0.03	-0.03	0.92	-0.03	-0.03
TVA #7	Day 1	0.97	0.01	0.01	0.96	0.01	0.01
	Day 2	0.98	0.01	0.01	1.00	0.01	0.01
TVA #8	Day 1	1.09	0.00	0.00	1.07	0.00	0.00
	Day 2	1.01	0.03	0.01	1.00	0.01	0.01

FID		start test #1			start test #2		
		isobutylene	Freon 114	HFC-134A	isobutylene	Freon 114	HFC-134A
	Day 1	0.95	1.05	2.09	0.94	1.05	2.09
TVA #3	Day 2	0.93	1.05	2.09	0.93	1.05	2.10
	Day 1	0.95	1.19	2.39	0.91	1.18	2.37
TVA #7	Day 2	0.85	1.16	2.45	0.86	1.17	2.44
	Day 1	1.03	1.21	2.22	0.99	1.08	2.39
TVA #8	Day 2	0.91	1.07	2.30	0.90	1.08	2.21

FIGURE 1. TVA-1000B (being discontinued).

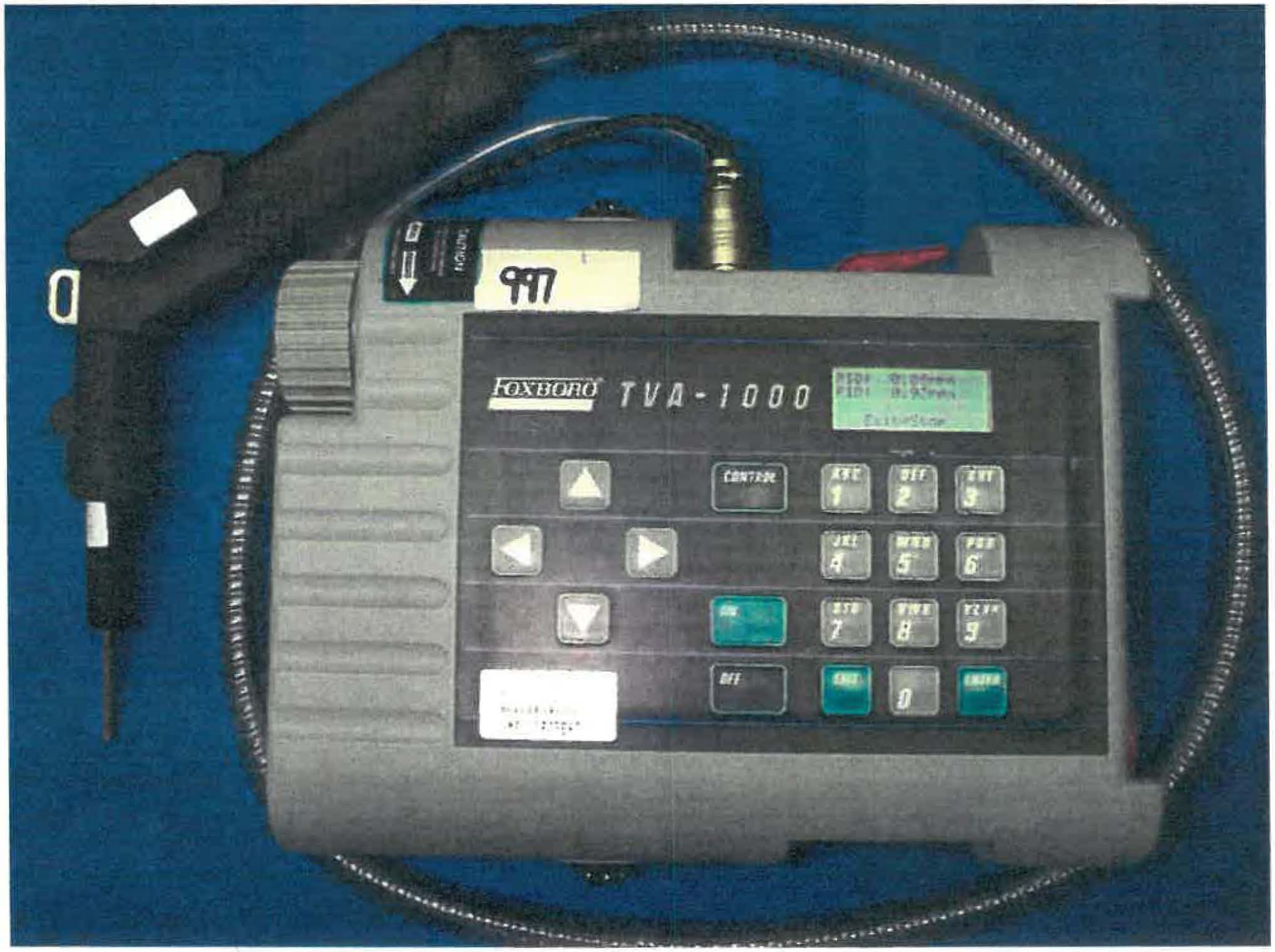


FIGURE 2. TVA2020 (new replacement).

FIGURE 3. PID drift from 3 TVAs.
N=2 tests per each TVA
PRE-Repair

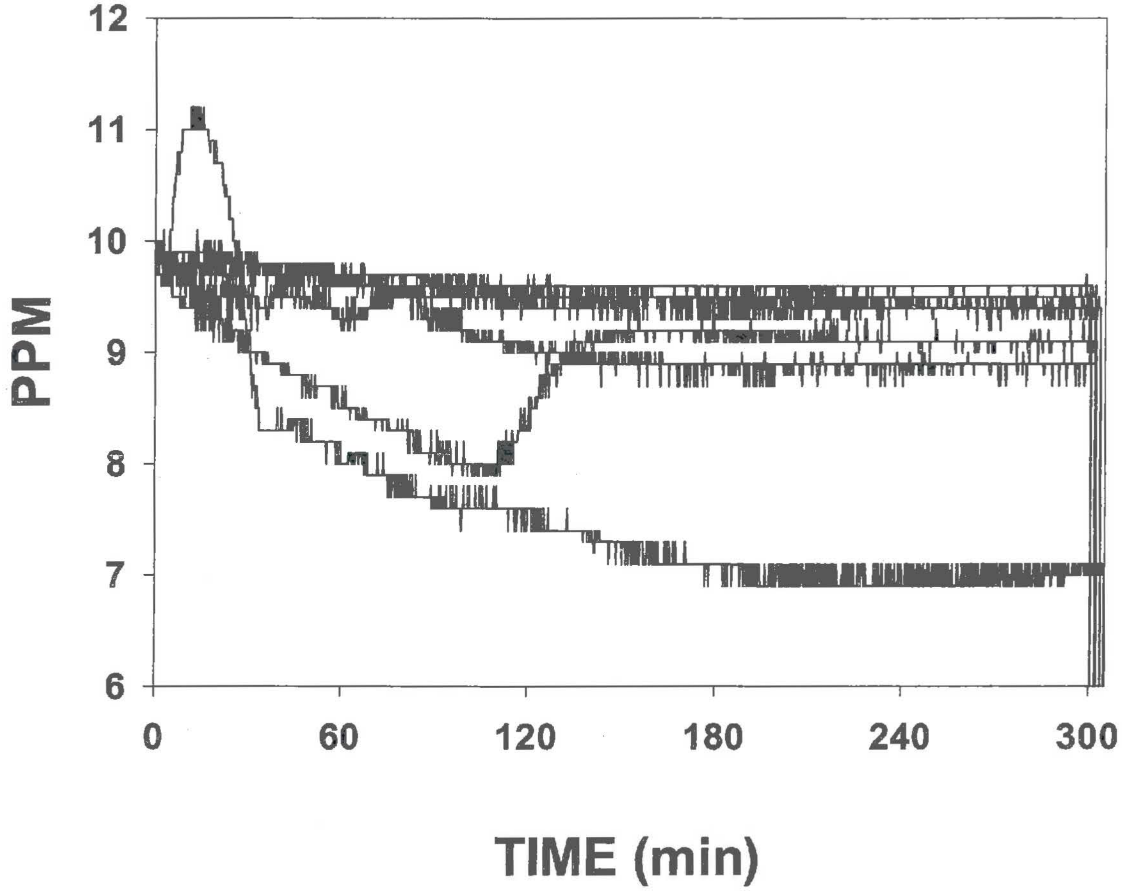


FIGURE 4. FID drift from 3 TVAs. N=2 tests per each TVA PRE-Repair

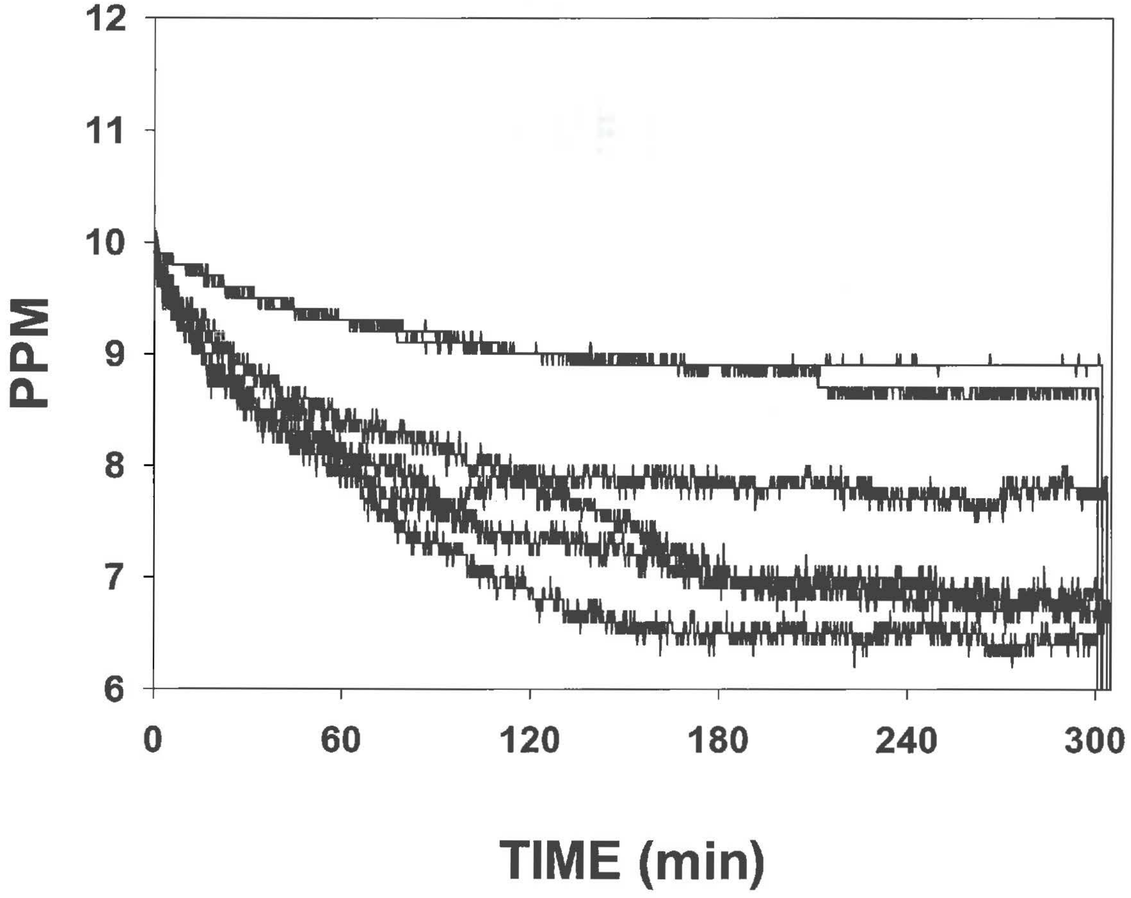


FIGURE 5. PID drift from 3 TVAs.
N=2 tests per each TVA
POST-Repair

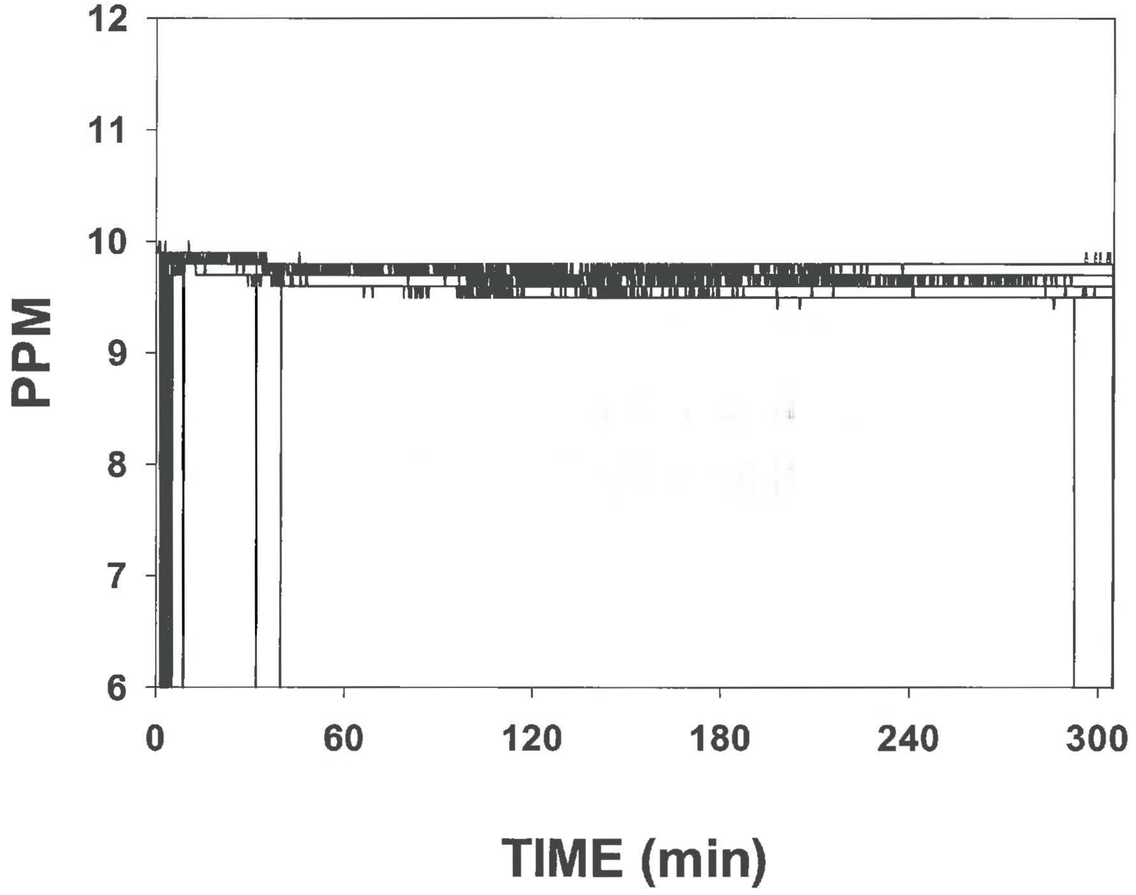


FIGURE 6. FID drift from 3 TVAs. N=2 tests per each TVA POST-Repair

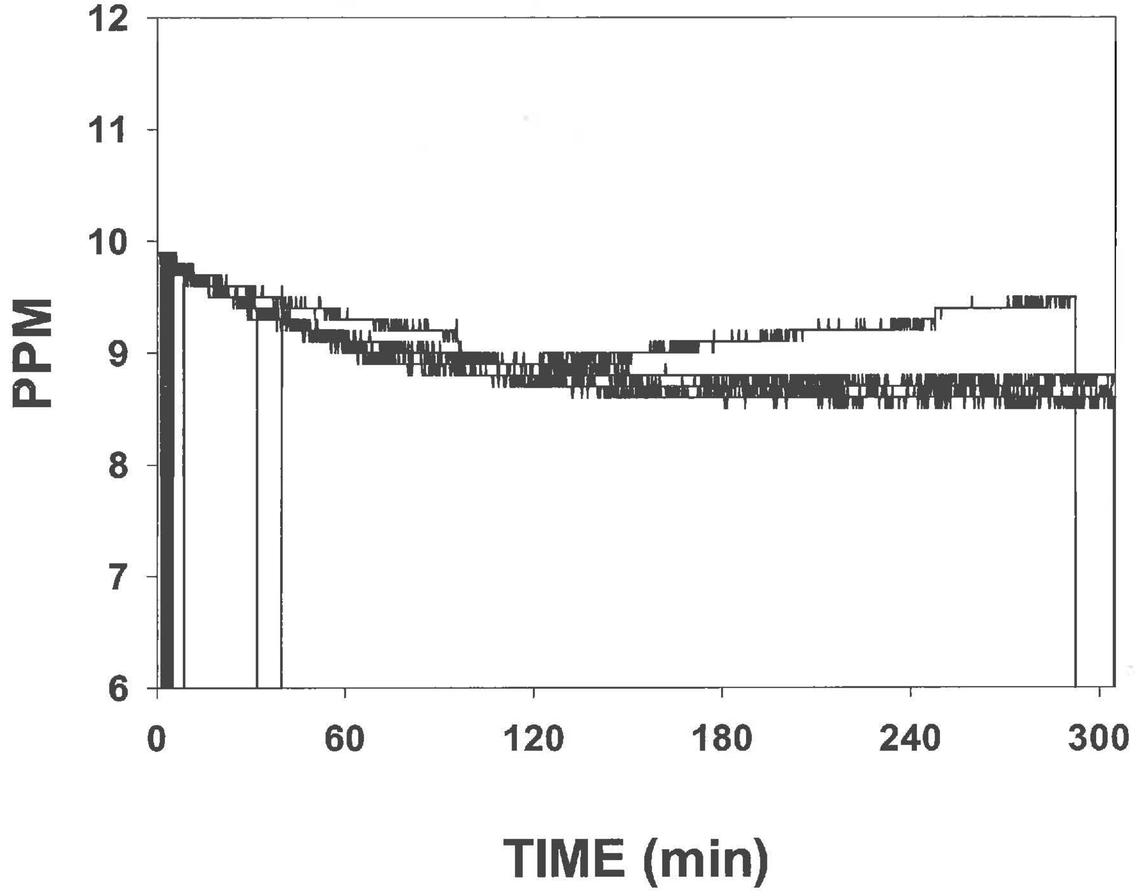


FIGURE 7. STEC accuracy on bench.
PID (ppm)
Means and SDs, N=4

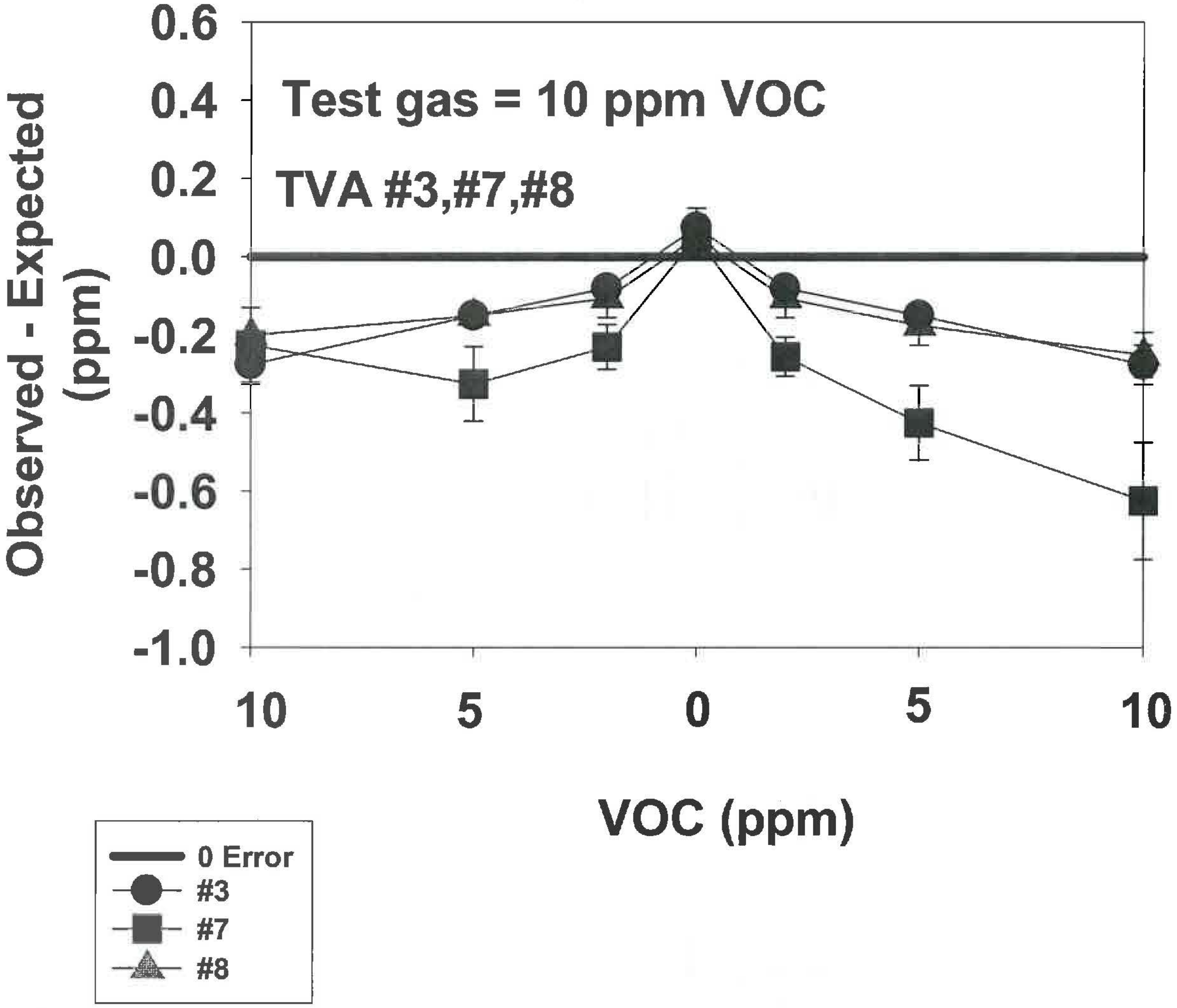


FIGURE 8. STEC accuracy on bench. FID (ppm) Means and SDs, N=4

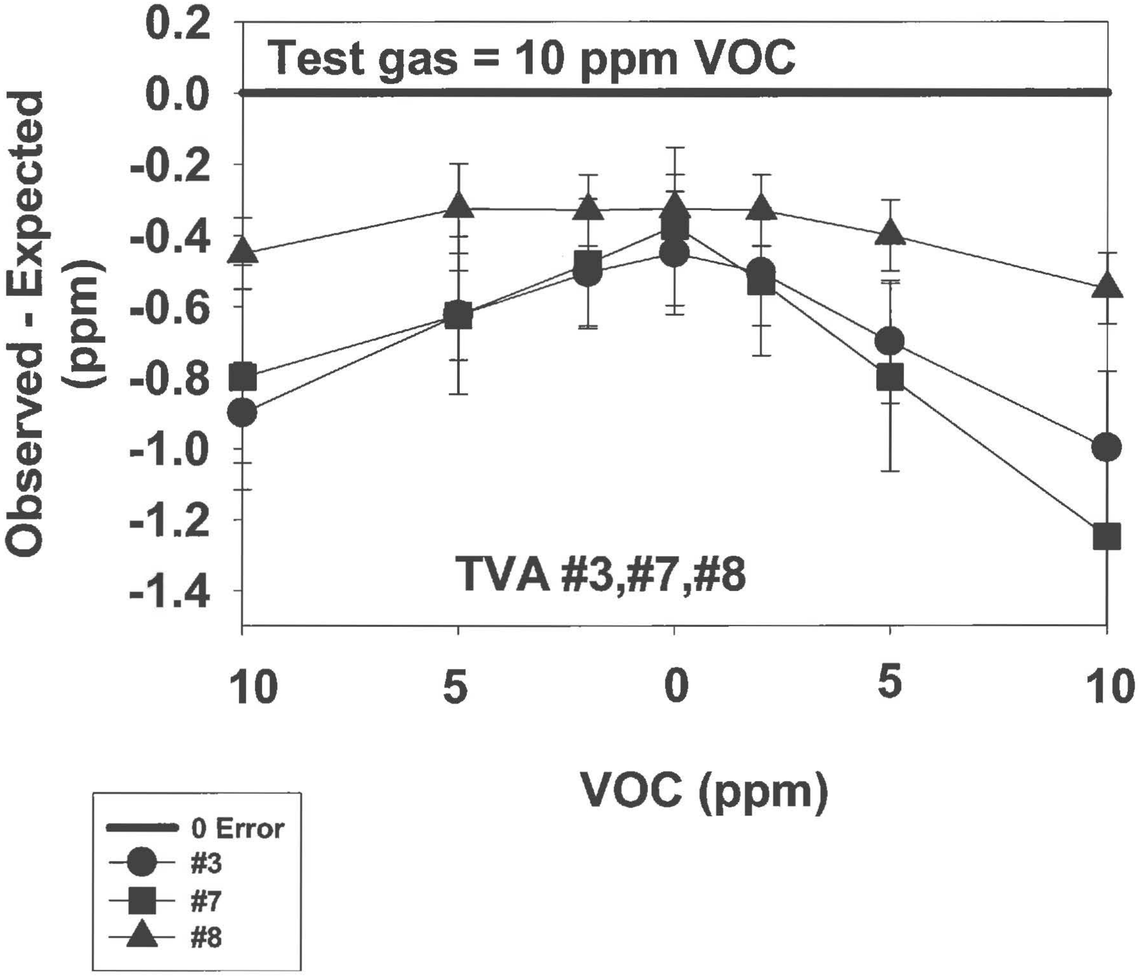


FIGURE 9. STEC 5C chamber accuracy. PID (ppm) N=2 tests for each TVA

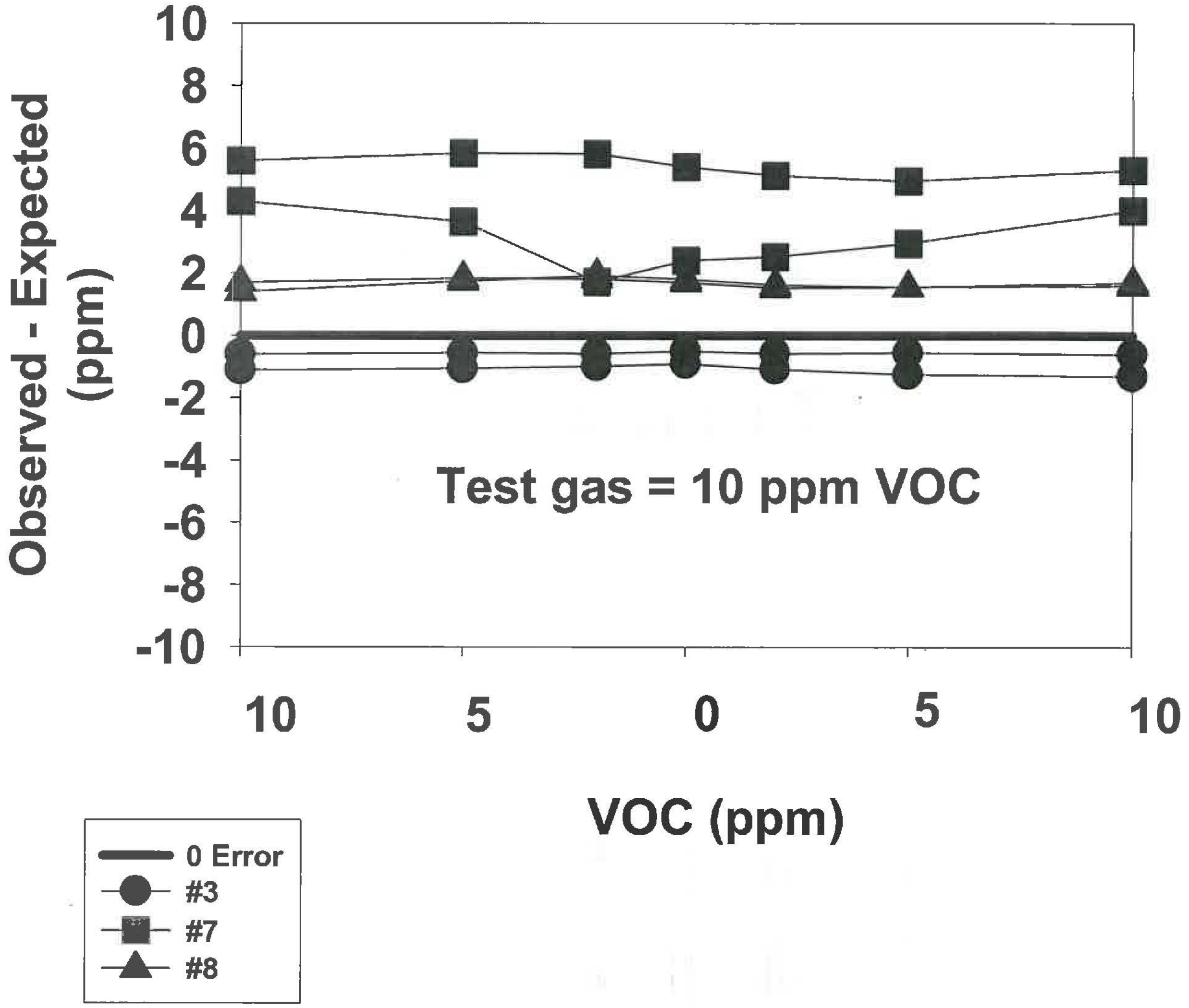


FIGURE 10. STEC 5C chamber accuracy.
FID (ppm)
N=2 tests for each TVA

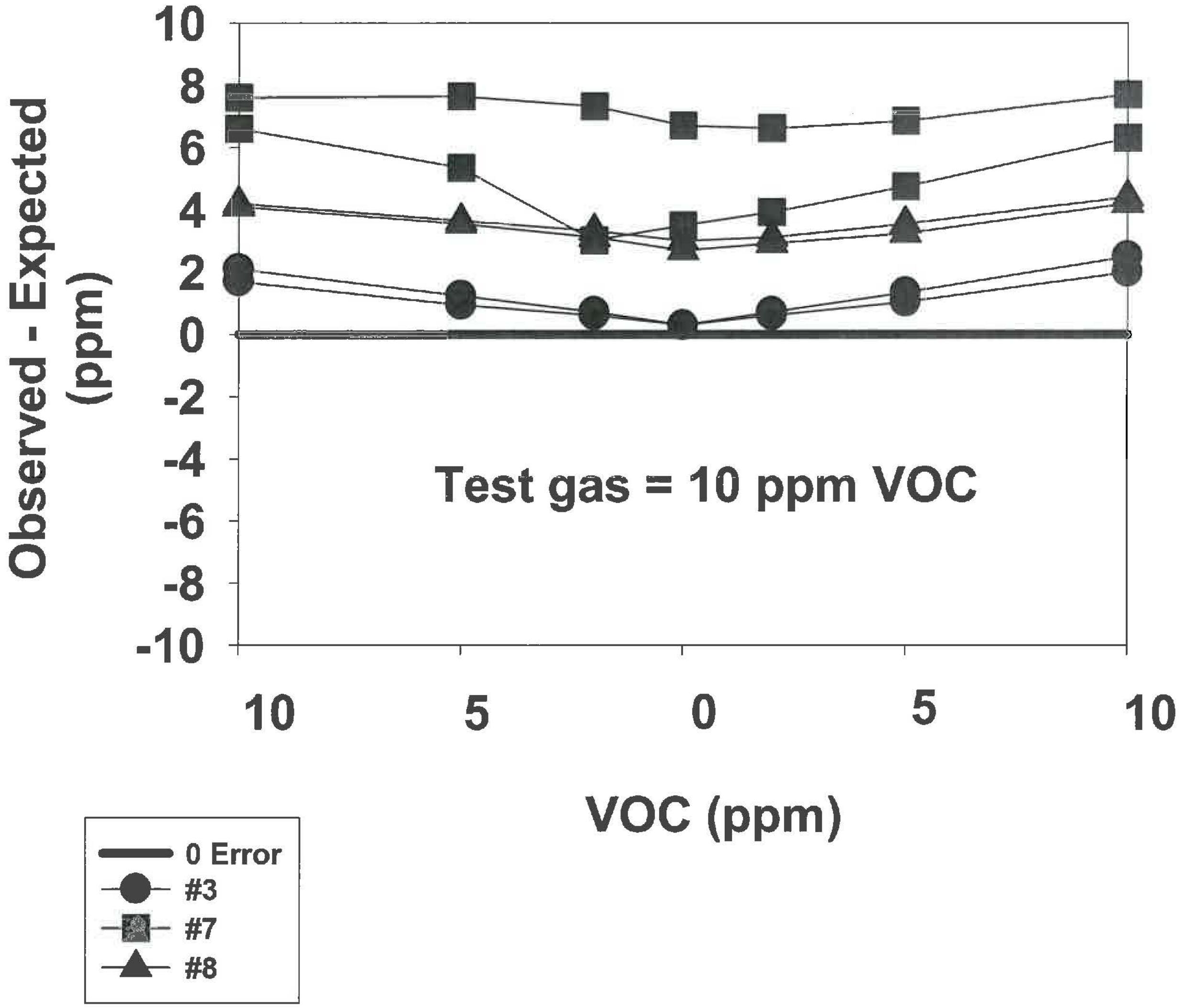


FIGURE 11. STEC 42C chamber accuracy.
PID (ppm)
N=2 tests for each TVA

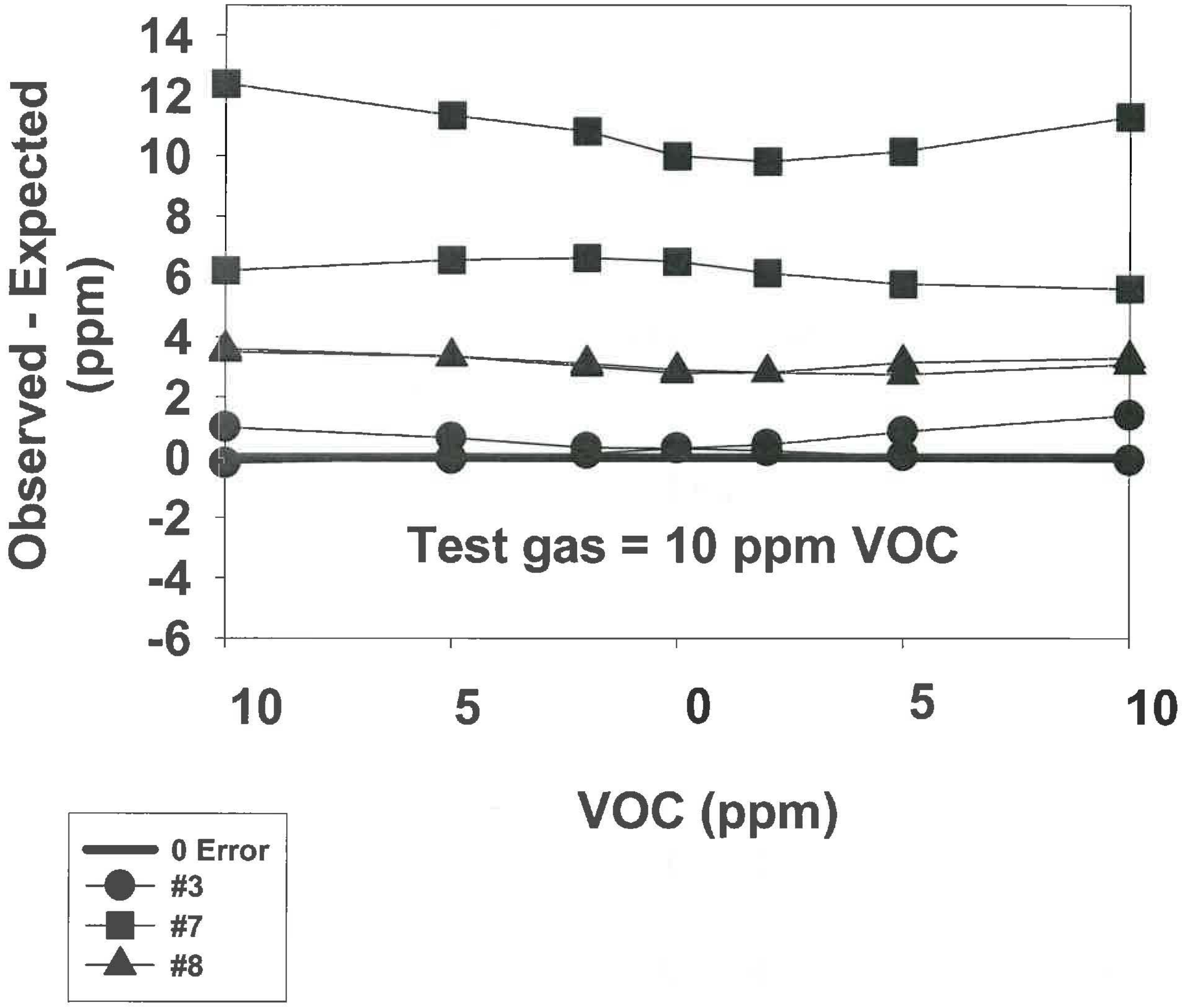


FIGURE 12. STEC 42C chamber accuracy.
FID (ppm)
N=2 tests for each TVA

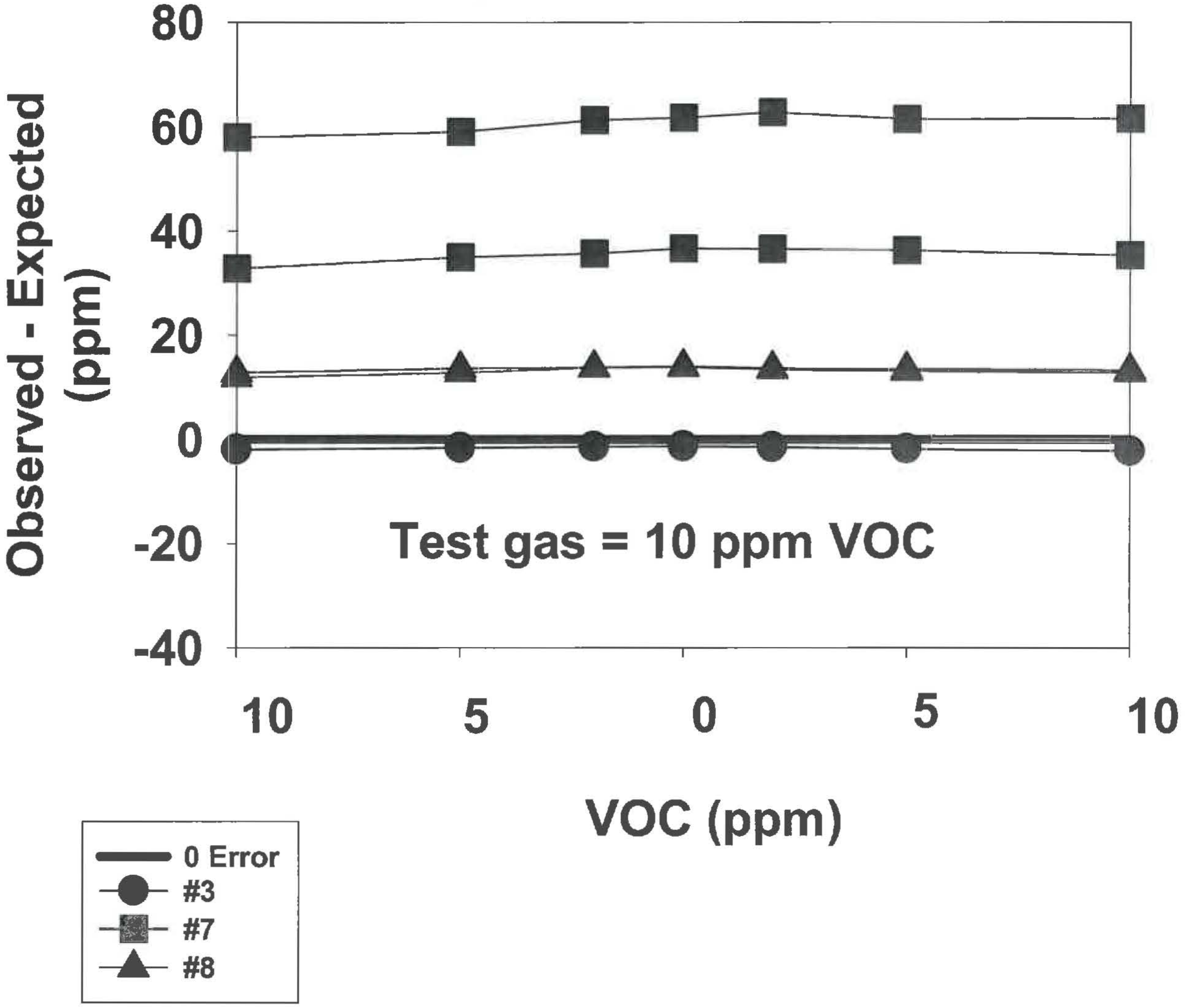


FIGURE 13. STEC stability on bench.
TVA #3, PID (ppm), No recalibration
N=3 tests over 5 days

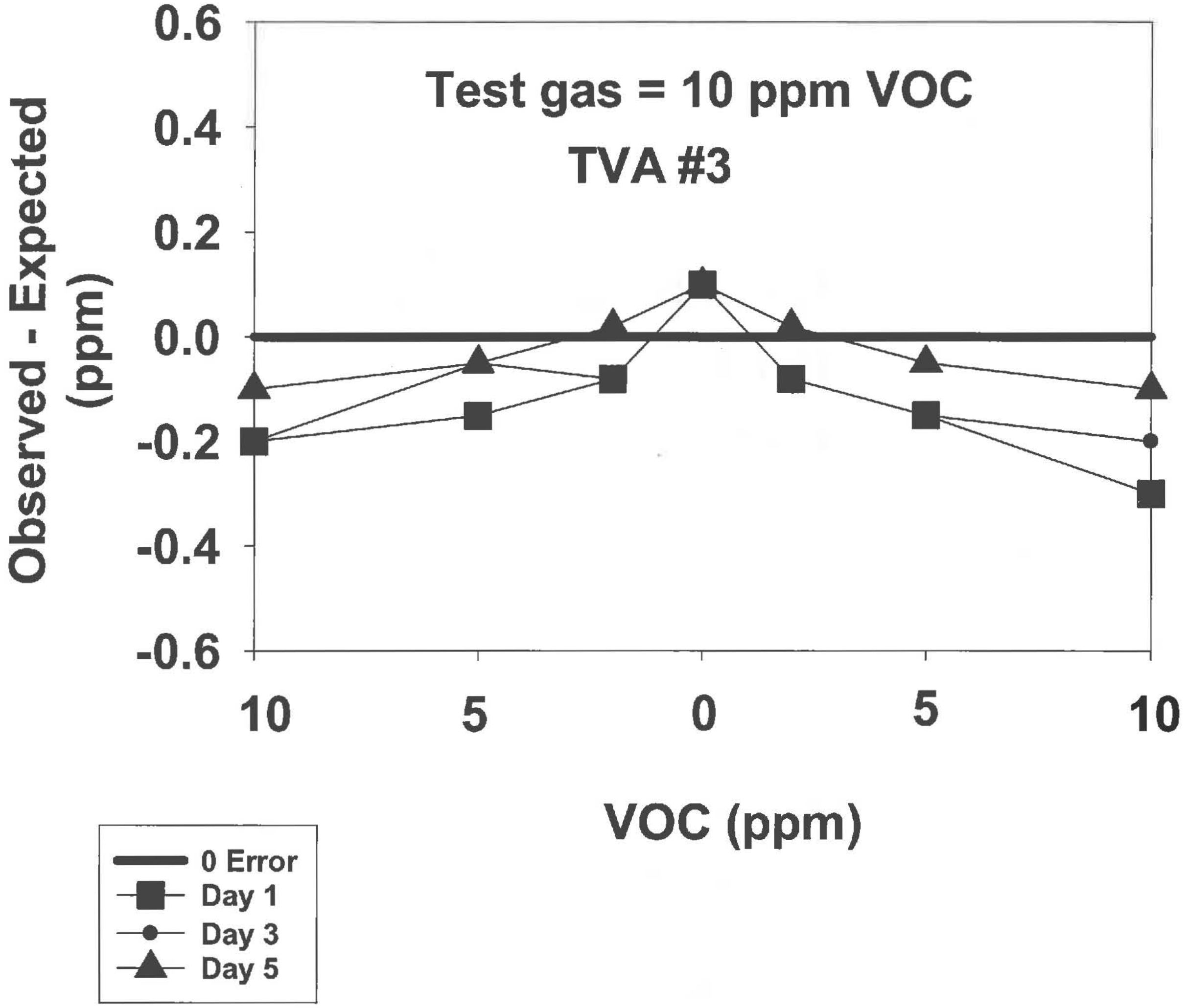


FIGURE 14. STEC stability on bench.
TVA #3, PID (ppm), No recalibration
N=4 tests over 8 days

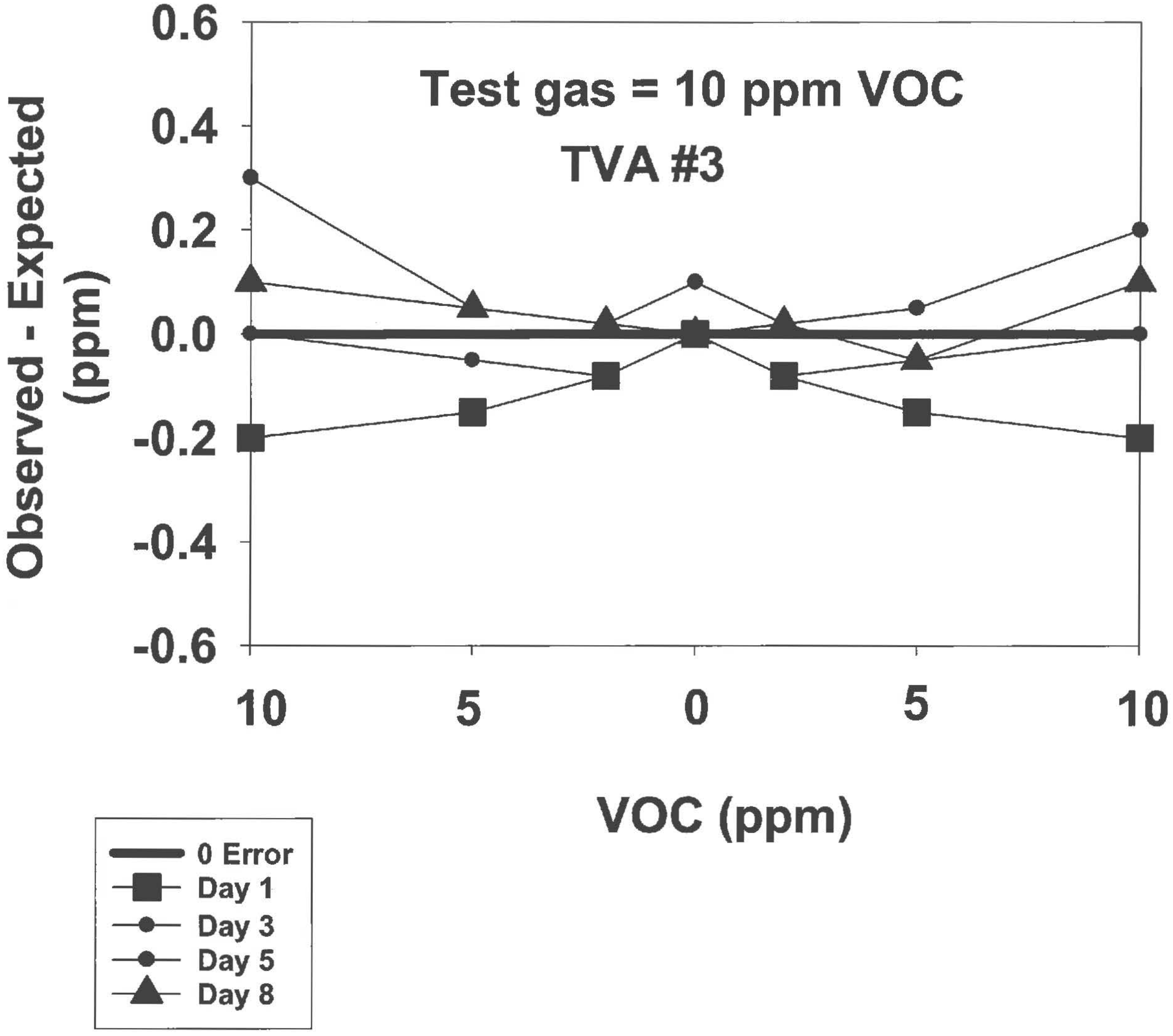


FIGURE 15. STEC stability on bench. TVA #7, PID (ppm), No recalibration N=3 tests over 5 days

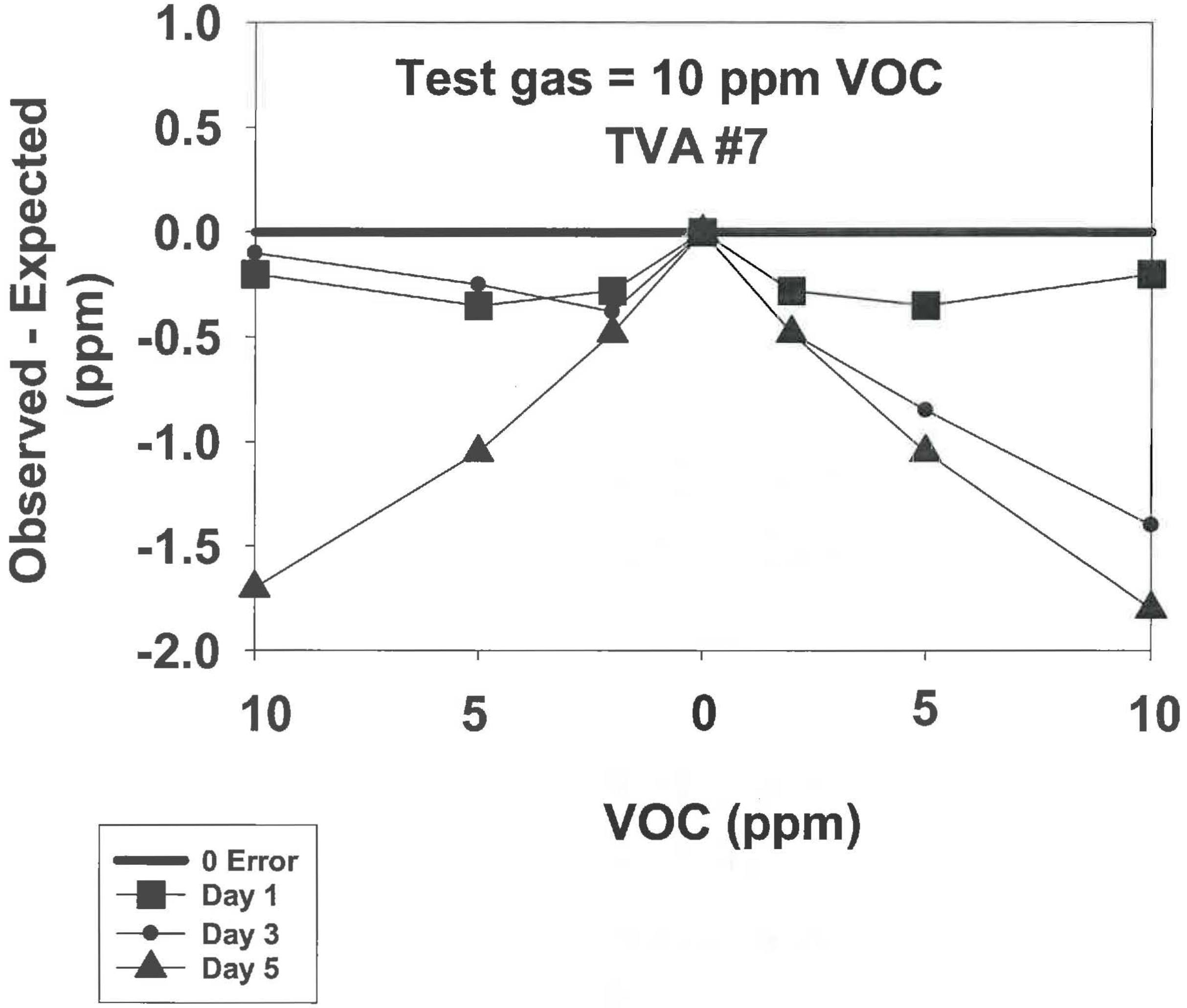


FIGURE 16. STEC stability on bench. TVA #7, PID (ppm), No recalibration N=4 tests over 8 days

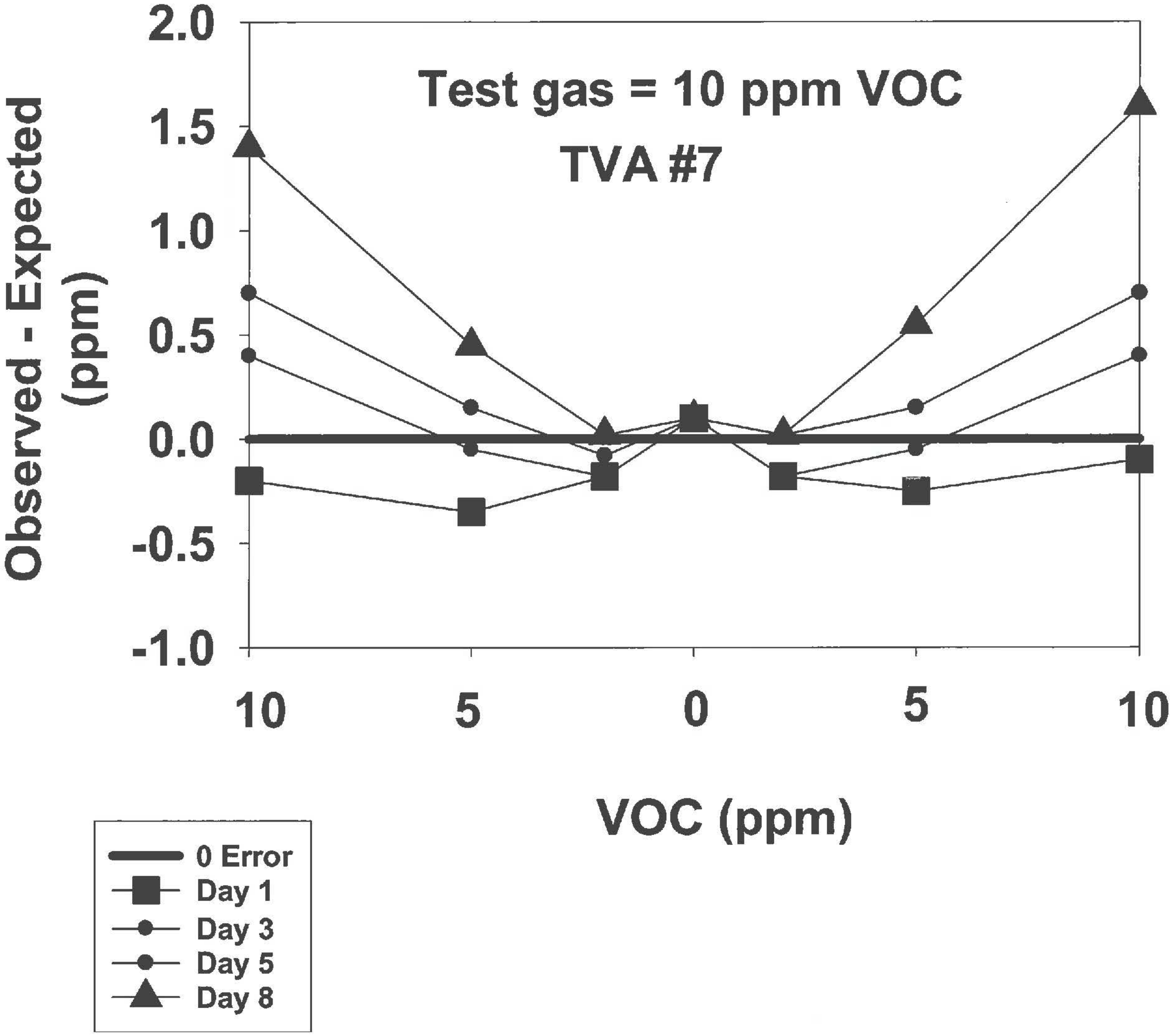


FIGURE 17. STEC stability on bench. TVA #8, PID (ppm), No recalibration N=3 tests over 5 days

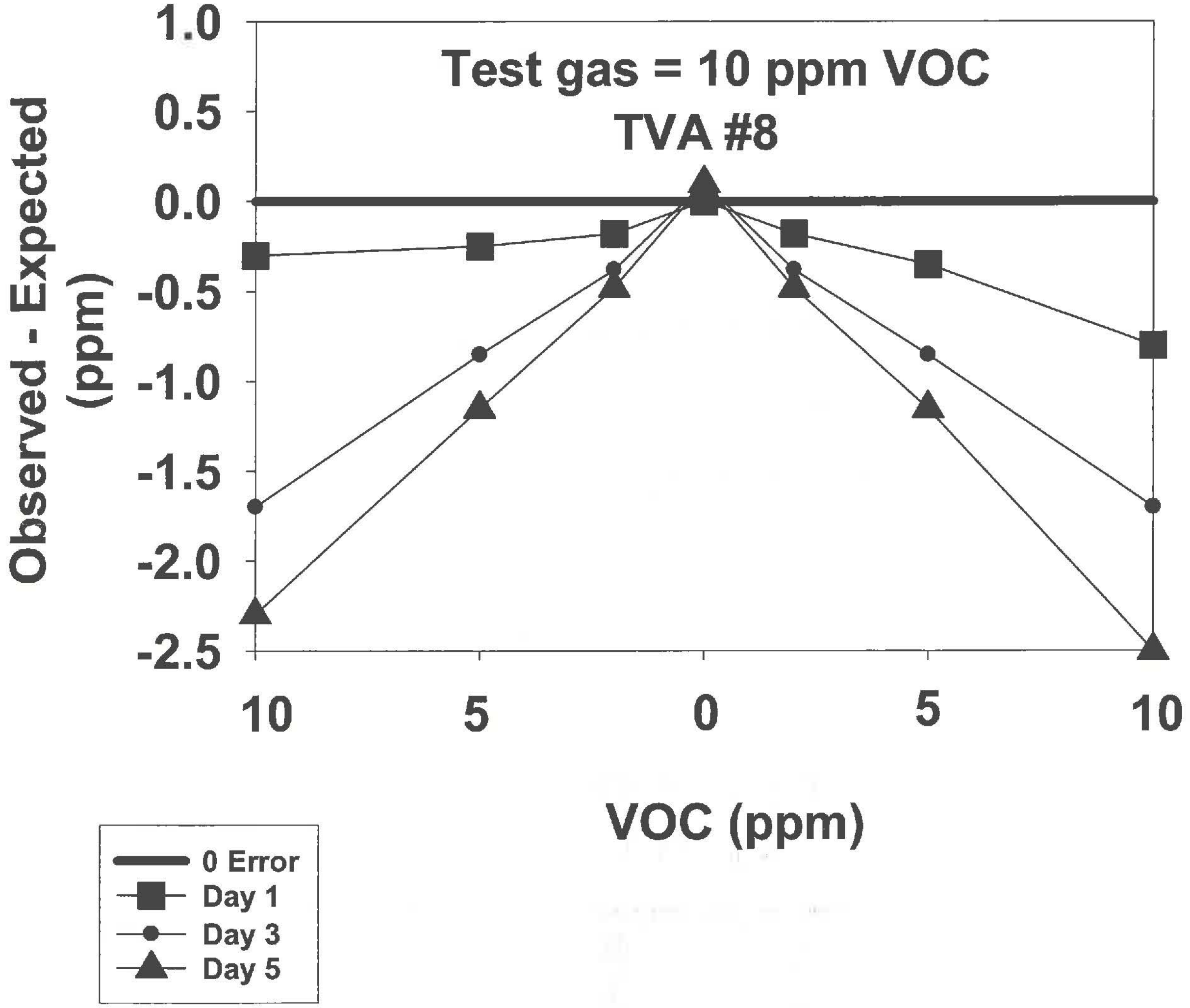


FIGURE 18. STEC stability on bench. TVA #8, PID (ppm), No recalibration N=4 tests over 8 days

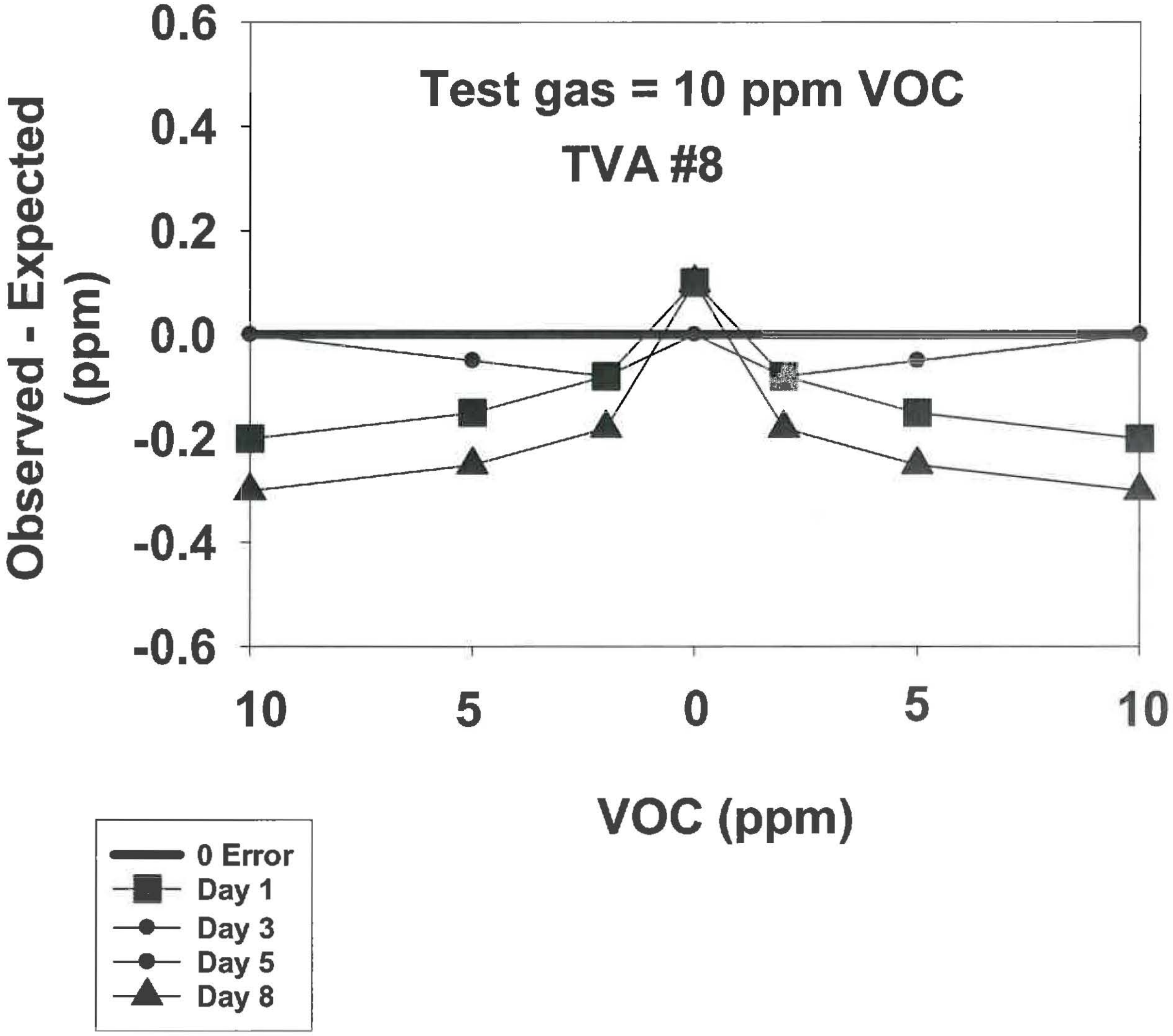


FIGURE 19. STEC stability on bench. TVA #3, FID (ppm), No recalibration N=3 tests over 5 days

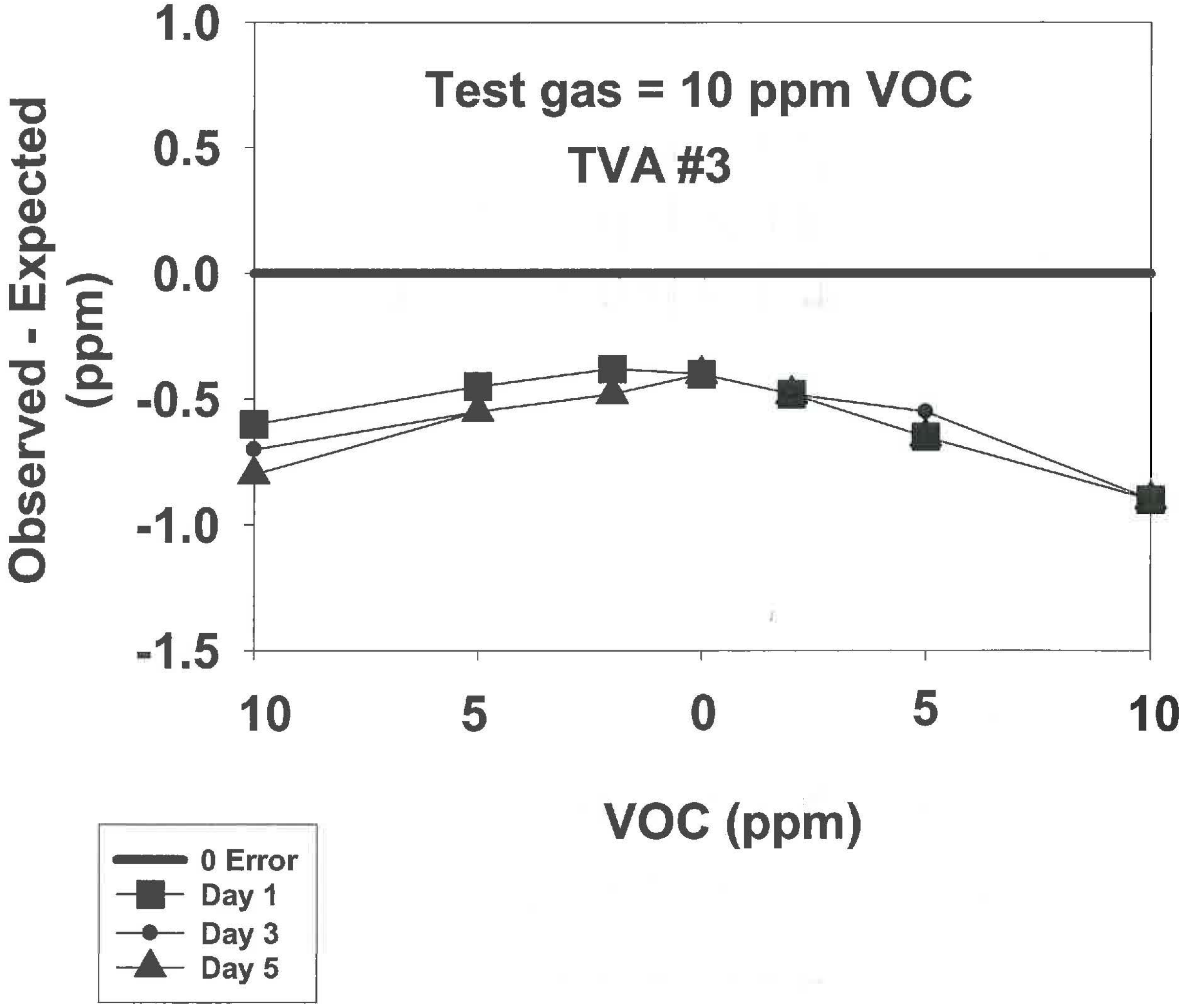


FIGURE 20. STEC stability on bench.
TVA #3, FID (ppm), No recalibration
N=4 tests over 8 days

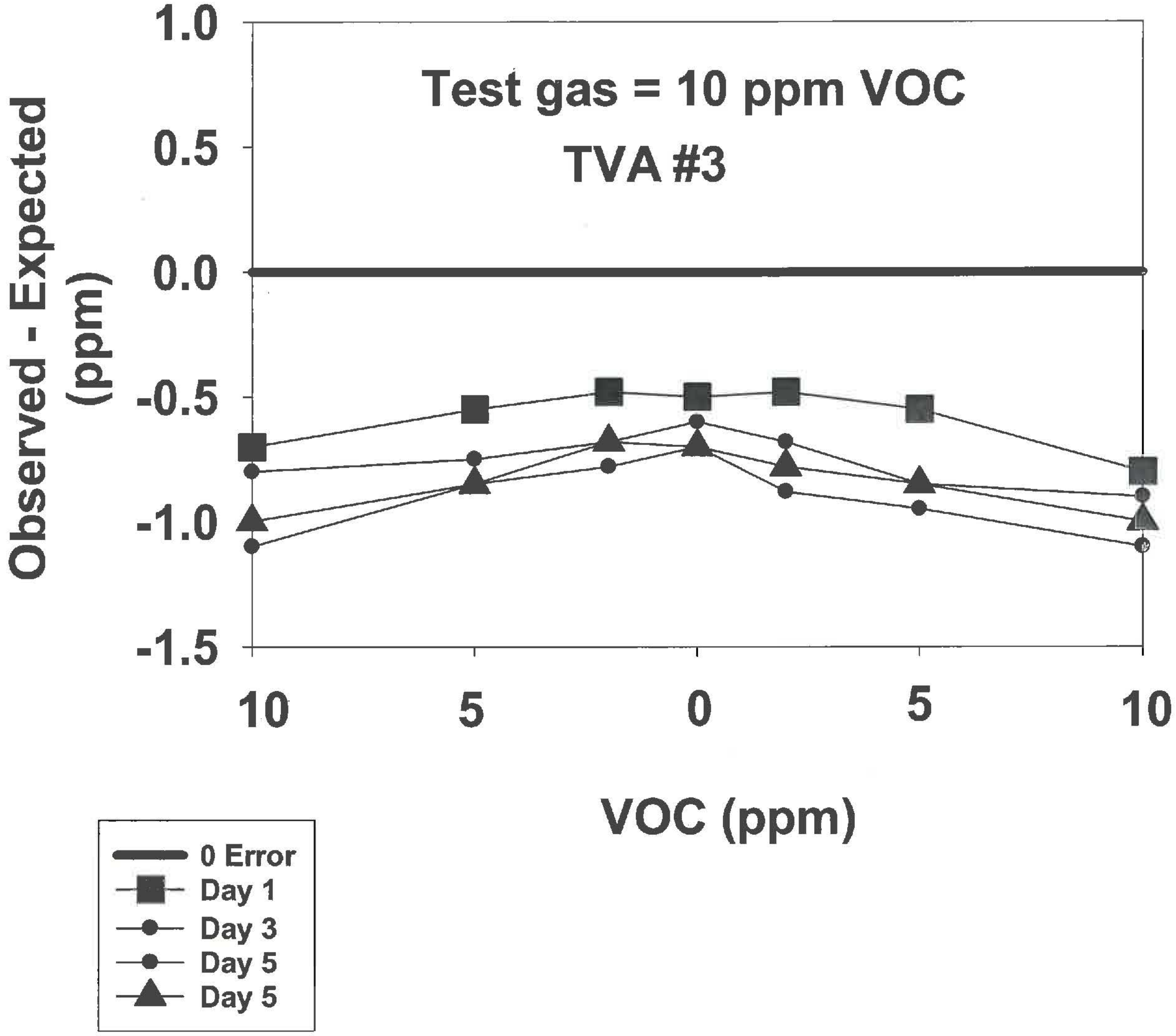


**FIGURE 21. STEC stability on bench.
TVA #7, FID (ppm), No recalibration
N=3 tests over 5 days**

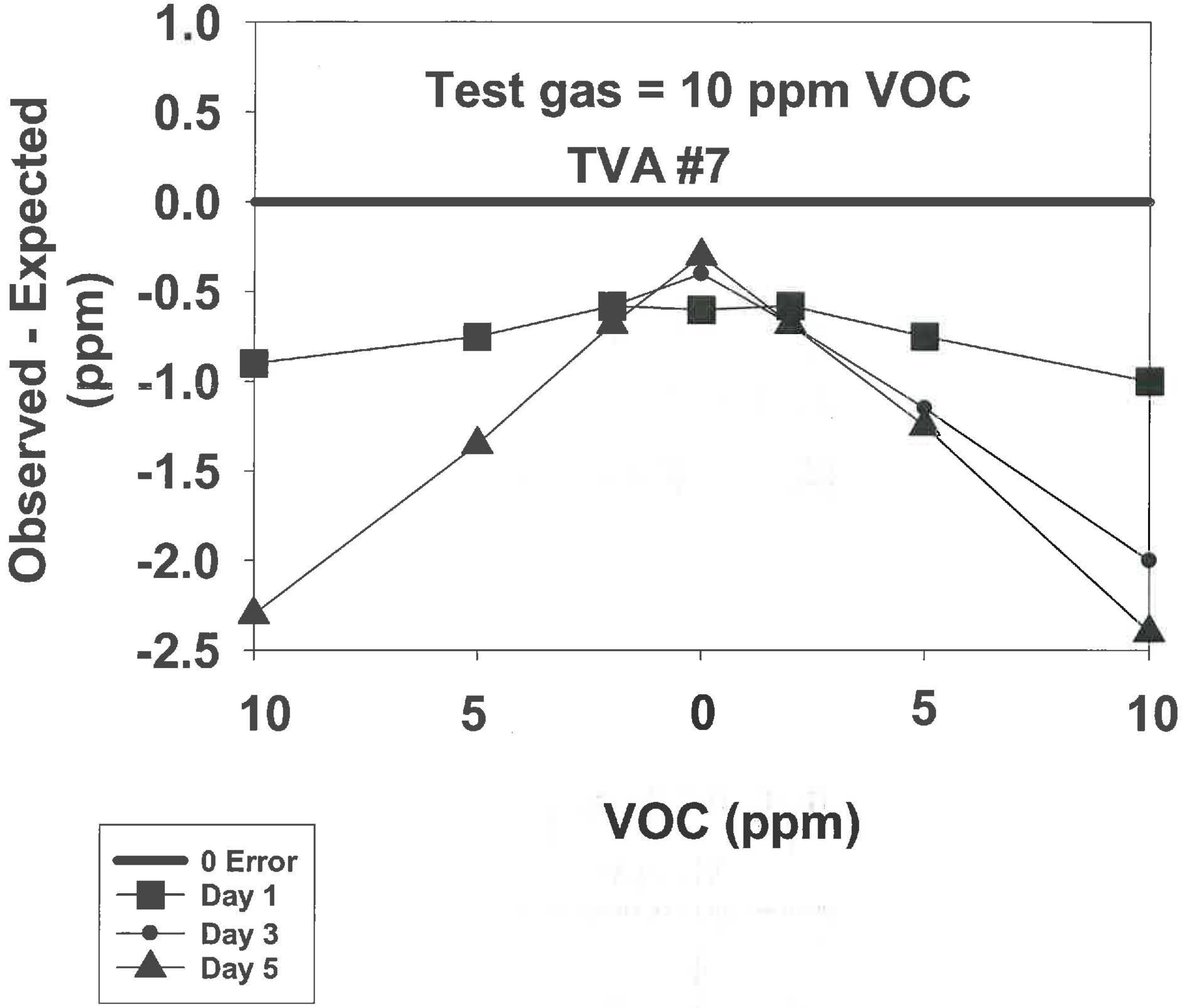


FIGURE 22. STEC stability on bench. TVA #7, FID (ppm), No recalibration N=4 tests over 8 days

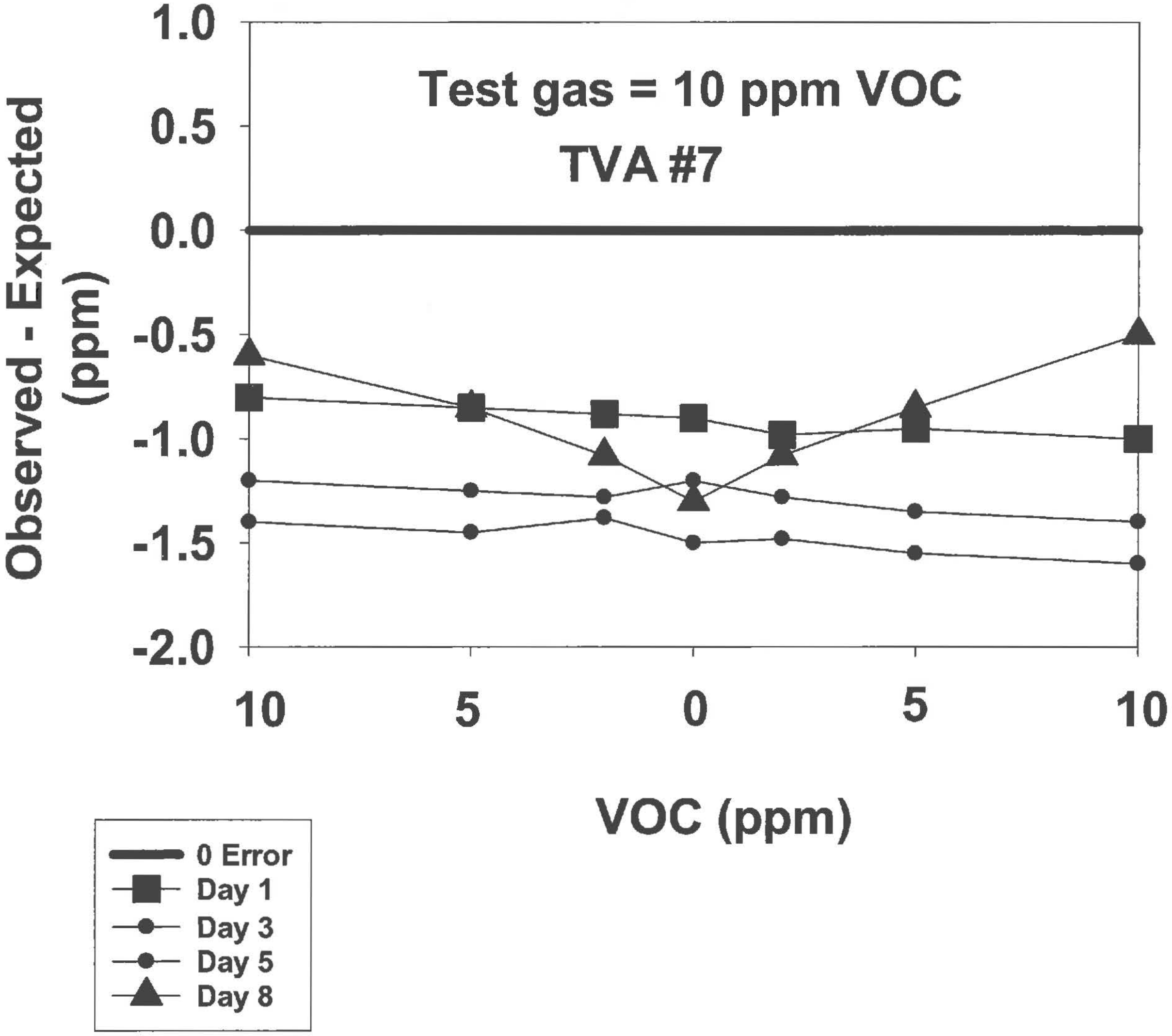


FIGURE 23. STEC stability on bench. TVA #8, FID (ppm), No recalibration N=3 tests over 5 days

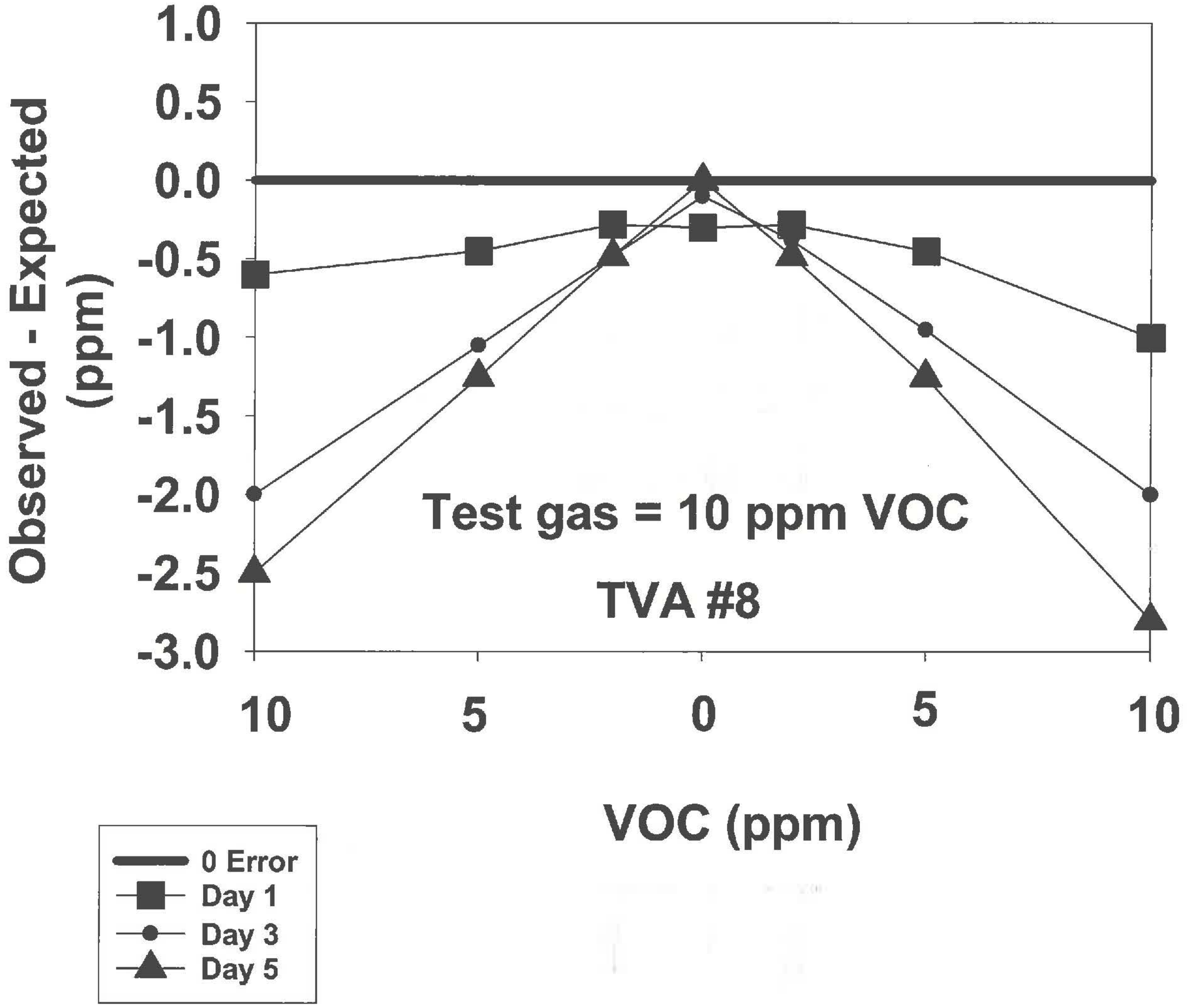


FIGURE 24. STEC stability on bench. TVA #8, FID (ppm), No recalibration N=4 tests over 8 days

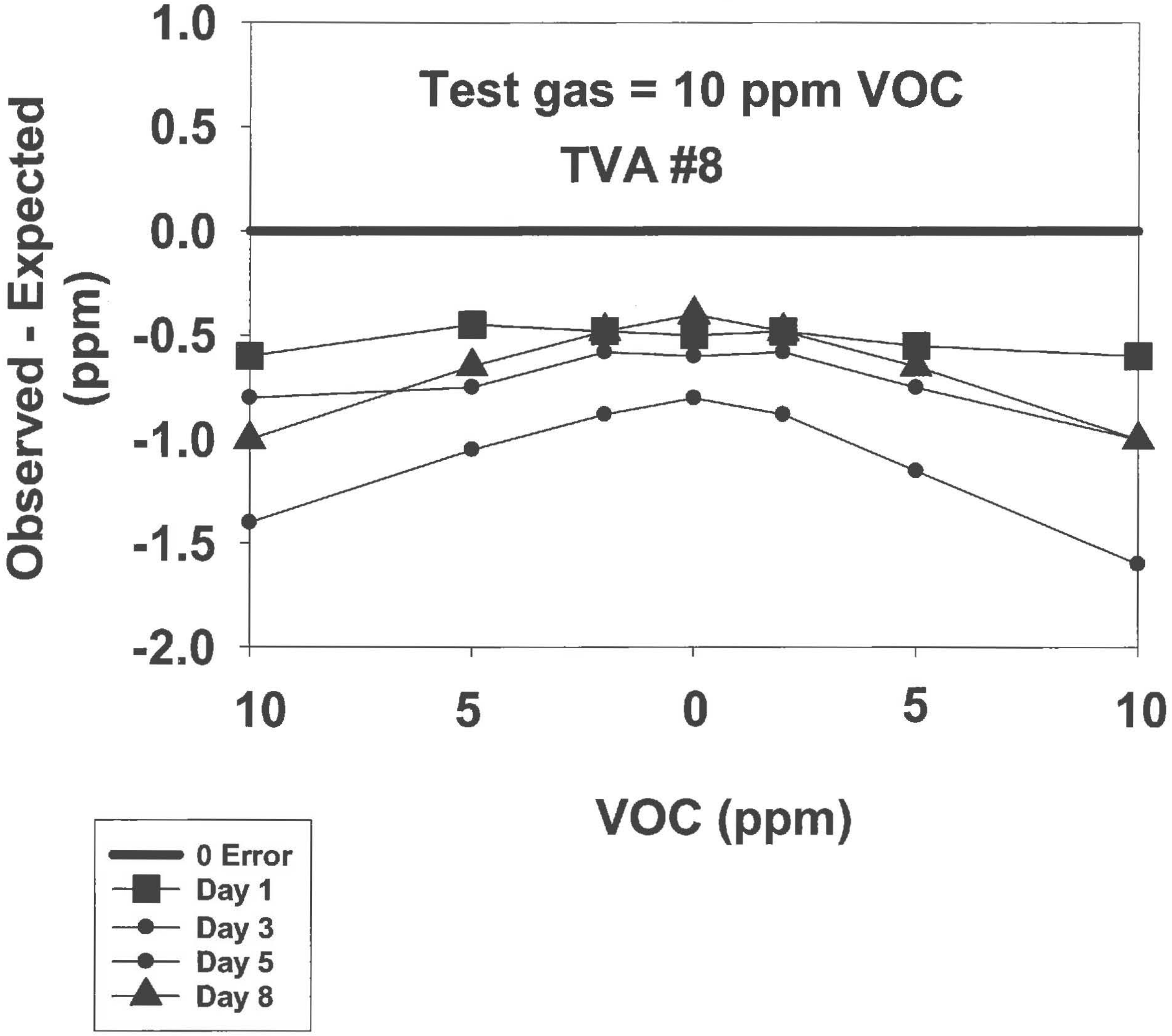


FIGURE 25. FID temp compensation testing. TVA #3, PID (ppm)

N=2 tests for compensation OFF and ON

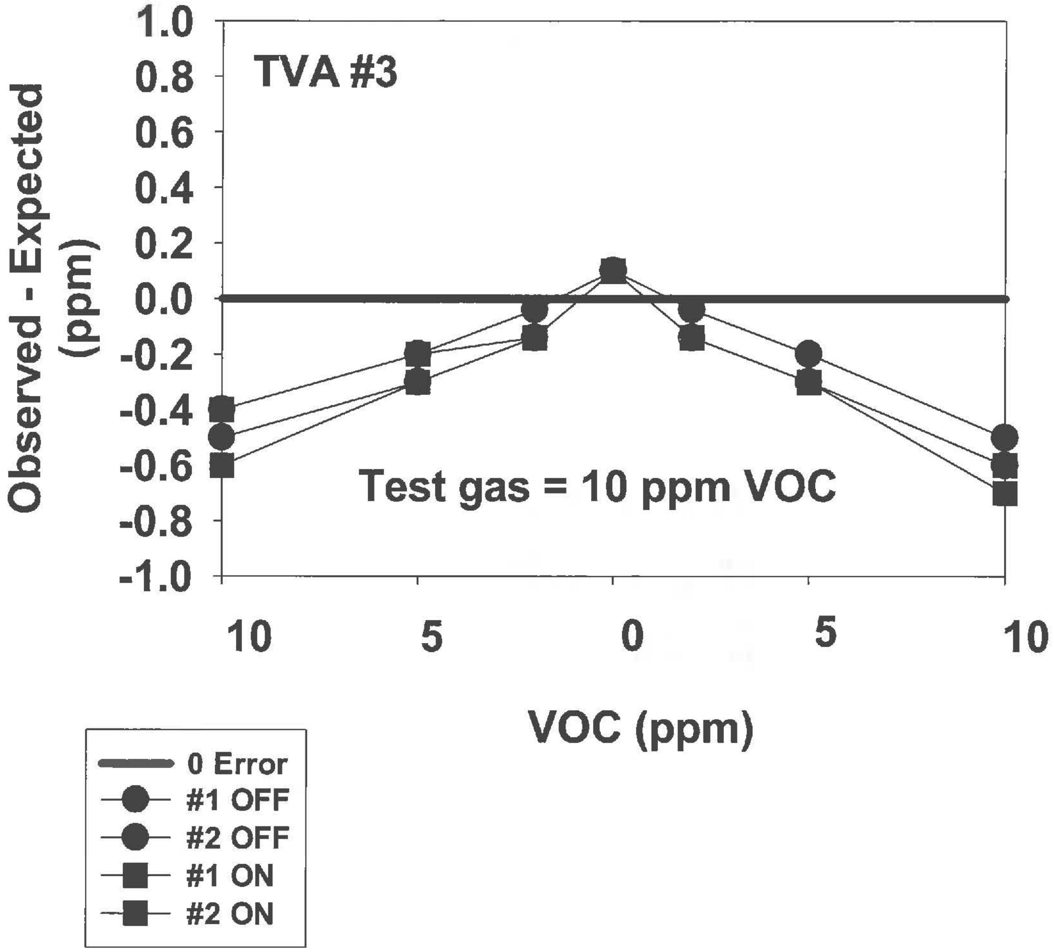


FIGURE 26. FID temp compensation testing. TVA #7, PID (ppm)

N=2 tests for compensation OFF and ON

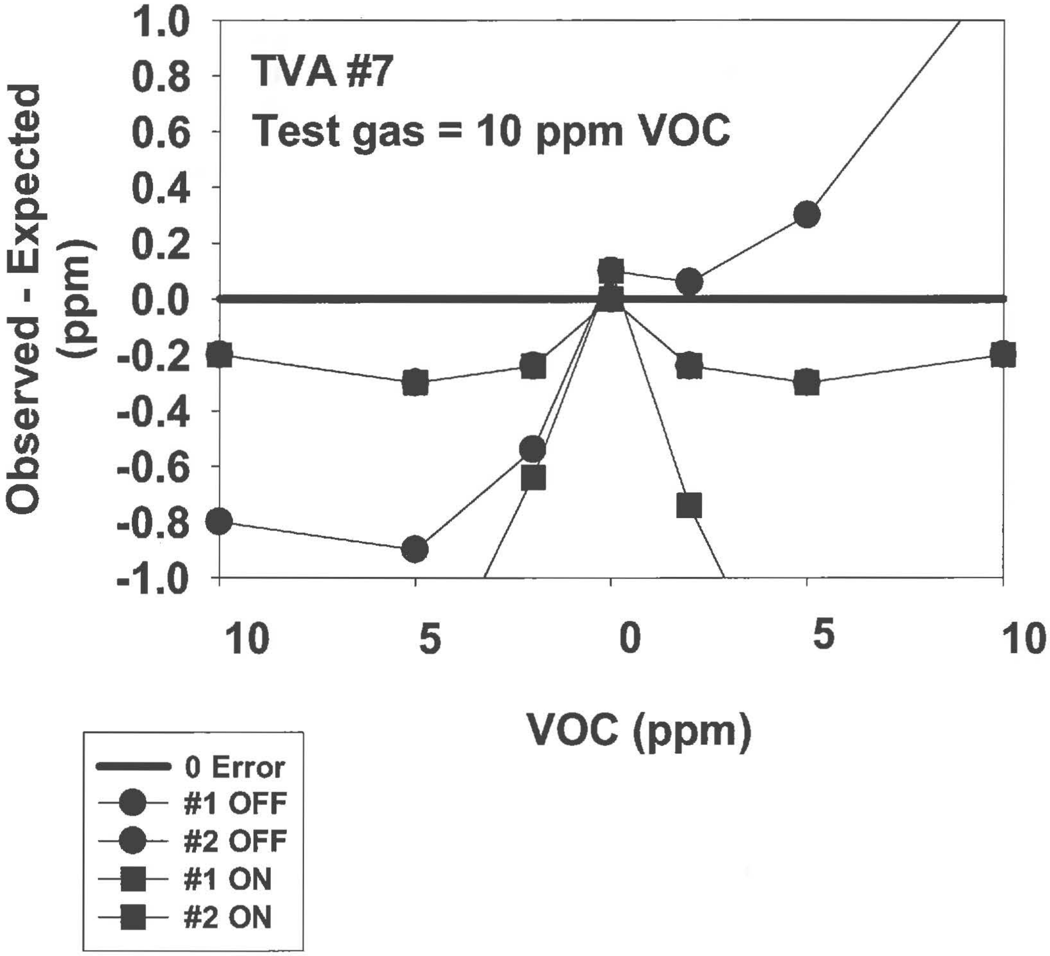


FIGURE 27. FID temp compensation testing. TVA #8, PID (ppm)

N=2 tests for compensation OFF and ON

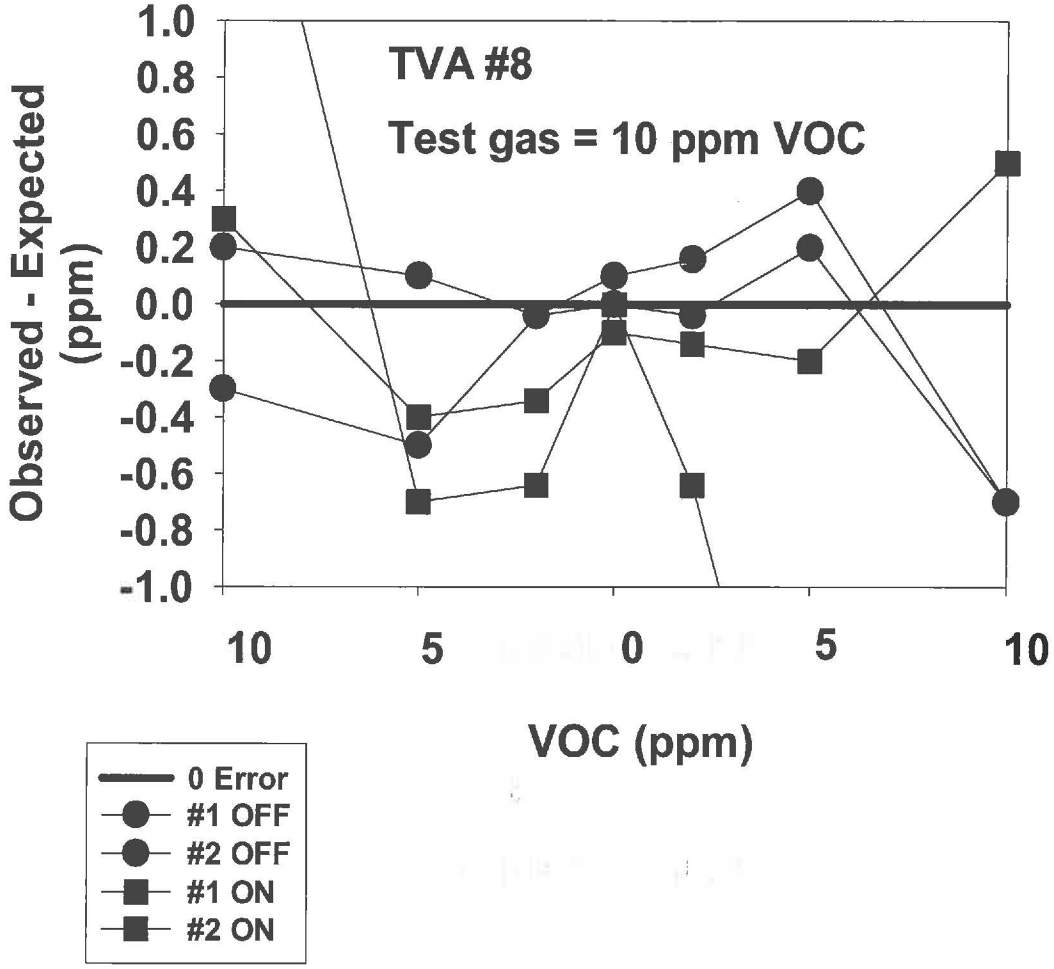


FIGURE 28. FID temp compensation testing.
TVA #3, FID (ppm)

N=2 tests for compensation OFF and ON

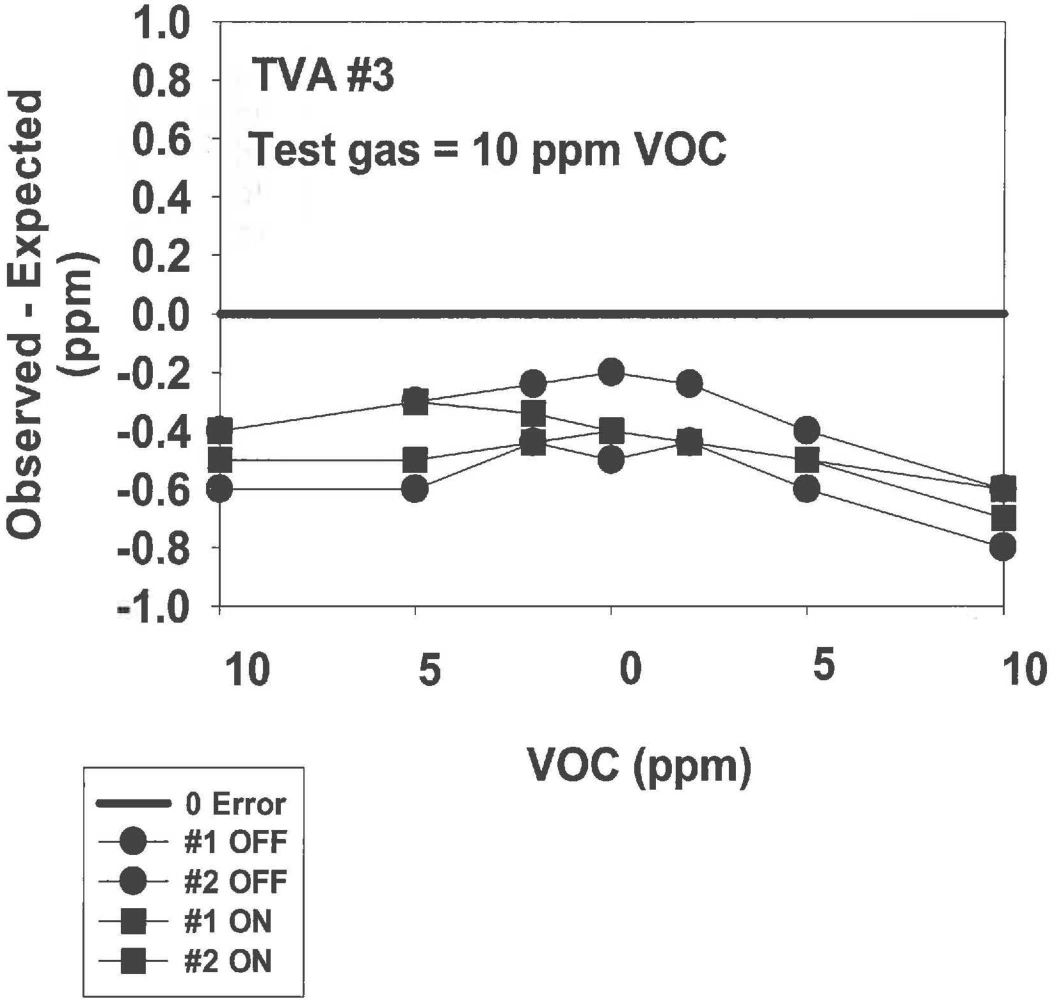


FIGURE 29. FID temp compensation testing. TVA #7, FID (ppm)

N=2 tests for compensation OFF and ON

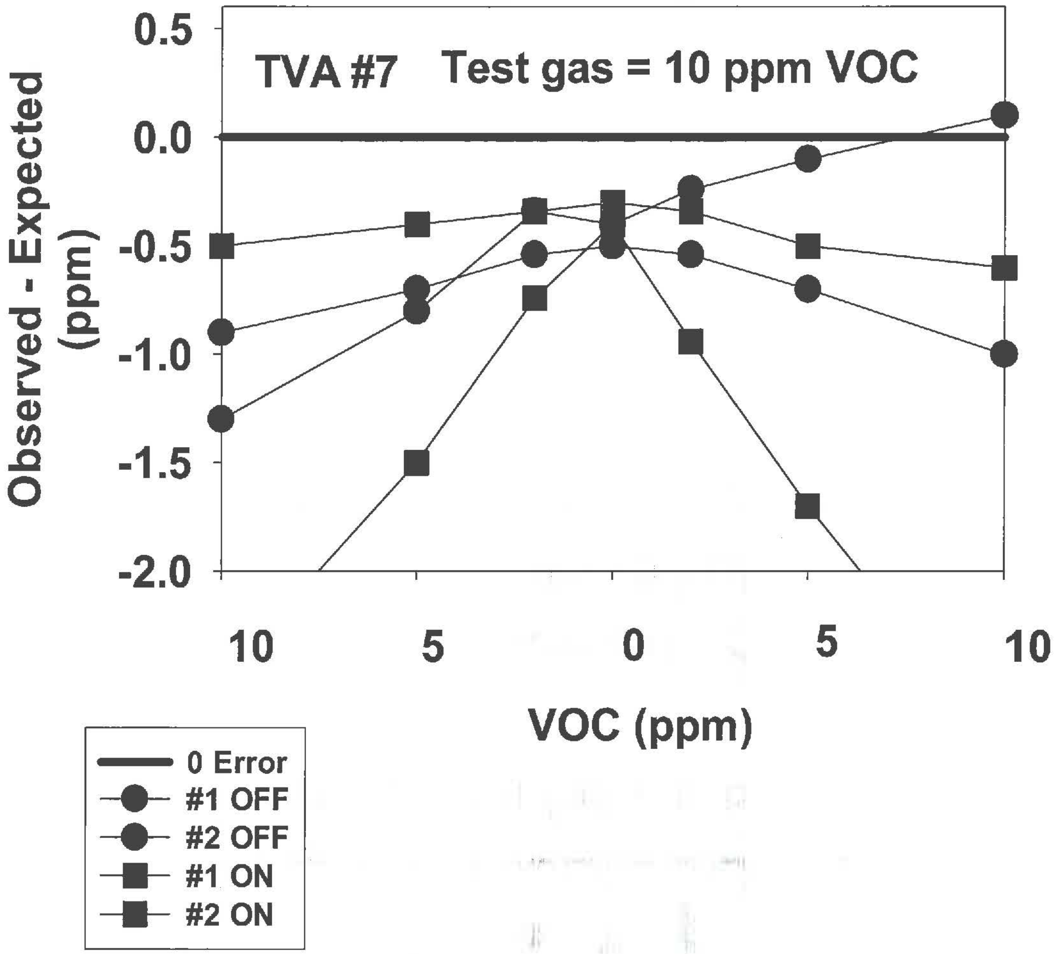
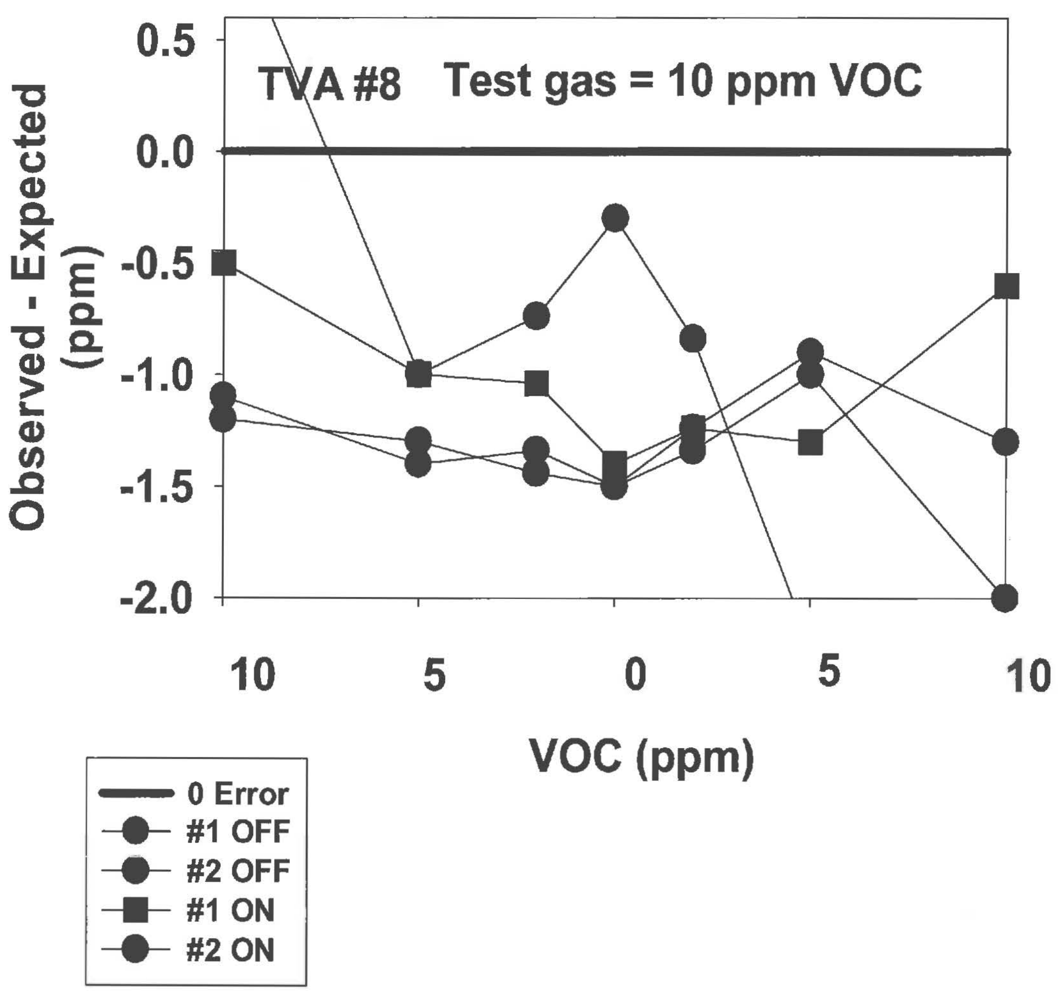


FIGURE 30. FID temp compensation testing. TVA #8, FID (ppm)

N=2 tests for compensation OFF and ON



APPENDIX A

OPERATING PROCEDURES FOR THE THERMO SCIENTIFIC TVA2020 TOXIC VAPOR ANALYZER

THESE PROCEDURES SHOULD BE CONSIDERED AS INTERIM UNTIL FIELD TESTING HAS BEEN COMPLETED

This document provides information for calibrating the Thermo Scientific TVA2020 toxic vapor analyzer gas monitor and using the monitor to screen diver quality air (DQA) for volatile contaminants. Using alternative operating procedures to those described in this Appendix will first need to be verified as producing acceptable results.

Although the TVA2020 manual provides a useful reference on the monitor features, configuring specific settings, troubleshooting, and maintenance, the operating procedures contained in the TVA2020 manual should not be used by the Navy for screening diving air.

Importantly, until field testing of the monitor has been completed and results evaluated, the procedures in this Appendix should be considered as interim, as field testing may reveal unexpected problems, issues, and concerns that may need to be addressed before transition of the monitor to the Fleet.

The manufacturer is replacing the TVA-1000B currently used by the Navy for DQA screening on submarines with the new TVA2020. This change requires that the current TVA-1000B procedures be replaced with those for the TVA2020. Like the TVA-1000B, the TVA2020 is equipped for Navy use with both a photoionization detector (PID) and a flame ionization detector (FID) allowing measurement of both organic and inorganic contaminants. The PID contains an internally sealed light source emitting at an energy (10.6 eV) that can ionize some, but not all, gases. This energy is slightly greater than the 10.2 eV of the shipboard PID (Trace Gas Analyzer (TGA)) used for routine screening of the submarine atmosphere. The total ion current is read on the digital display. Small, usually non-toxic gases (e.g., CO_2, CO, methane, many Freons) give little or no response. However, many toxic gases such as aromatic hydrocarbons are detected with high efficiency (i.e., can be detected down to 1 ppm). The PID also responds to many inorganic gases.

The FID uses the principle of H_2 flame ionization for detection and measurement of volatile organic compounds (i.e., those containing carbon) down to the ppm level. Electrically charged species are formed when organic compounds are introduced into a small H_2-in-air flame and are detected by a collecting electrode. Common gases (e.g., CO_2, CO) give no response. However, the FID has high sensitivity to most organic compounds including many species that are not sensed by the PID (e.g., methane, Freons). The O_2 for the flame combustion is provided by the air that is being sampled; thus, the FID can be used to sample only air.

A charcoal filter adaptor can be used with both the TVA-1000B and TVA2020 to remove trace organic vapors heavier than methane, ethane, and some related compounds. Filtering allows use of the span gas (containing ~10 ppm isobutylene) for zeroing both the PID and FID, as well as the determination in DQA samples of the relatively high level of methane that is often found in submarine atmospheres. Subtraction of the filtered from the unfiltered measurement will produce a total volatile organic reading that omits the non-hazardous methane contribution. Although the charcoal filter was used for both these functions with the TVA-1000B, the charcoal filter is not used in these procedures for the TVA2020 as past DQA screening reports suggested that charcoal readings taken with the TVA-1000B were often higher than those without charcoal for reasons unclear at this time. Also, laboratory testing suggested that charcoal filtering of the span gas may not be an effective approach in producing zero air for zeroing the TVA2020.

SIGNIFICANT DIFFERENCES BETWEEN TVA-1000B AND TVA2020

1. Weight (PID/FID version).

TVA-1000B: 11.9 lb. analyzer, 1.75 lb. enhanced probe.

TVA2020: 9.4 lb. analyzer, 1.5 lb. enhanced probe.

2. Size (analyzer).

TVA-1000B: 13.5" x 10.3" x 3.2".

TVA2020: 11.5 x 9.0 " x 4.0".

3. Battery.

TVA-1000B: NiCad. Per manufacturer specifications, minimum 8 hours continuous use, ~16 hours to recharge fully discharged battery.

TVA2020: Lithium ion. Per manufacturer specifications, minimum of 10 hours continuous use, maximum 10 hours to recharge a completely discharged battery.

4. H_2 supply.

TVA-1000B: on/off valve.

TVA2020: no on/off valve.

5. PC software (for downloading and other functions); data transfer mode.

TVA-1000B: Windows 8 compatible; RS-232.

TVA2020: No software required (TVA2020 functions as an external drive); USB-2.

Summary of differences. Compared to the TVA-1000B, the new TVA2020 is lighter, smaller, has a longer lasting battery that charges more quickly, and does not require special software for downloading and other functions. However, the TVA2020 does not have a valve to turn on and off the H_2 supply so care much be taken to remove or unscrew partially the H_2 tank after the monitor is turned off to avoid bleeding down the H_2 tank when the TVA2020 is not in use.

OPERATING PROCEDURES
(Some of the text in this section is adapted from the TVA2020 manual)

GENERAL INFORMATION

1. The TVA2020 should be procured along with its Nov 2019 upgraded battery charger, enhanced probe, extra H_2 tanks and refilling assembly as required, and spare parts and tools identified by Thermo to allow users in the Fleet to make limited repairs. All procured monitors should contain firmware up to versions 01.00.52S and 01.00.53S, but no future updates unless approved by PMS 399, as any future updates have not been tested by NEDU.

2. The following gases needed for calibration should be obtained commercially in pressure cylinders of suitable size:

a. High purity air (CO_2-free, hydrocarbon-free). For zeroing both the PID and FID during calibration; will be referred to in these procedures also as “zero air”.

b. Gas standard, containing nominal concentration of 10 ppm isobutylene, balance air; with accuracy guaranteed to +/-2% relative (or more accurate if available); for spanning both the PID and FID during calibration. If used also for calibrating the Geotech HYPB2.0 monitor, the gas standard instead should contain nominal concentrations of 10 ppm isobutylene, 15,000 ppm CO, 21% O_2, balance N_2 with accuracy for each of the three components guaranteed to +/-2% or better.

3. Calibration gas and DQA samples will be delivered to the monitor using the hardware and procedures used previously with TVA-1000B —unless other (or alternative) gas delivery procedures have been authorized by PMS 399.

4. Gas readings can be read on either of two displays, the monitor’s main LCD that cannot be backlit, or the LCD on the enhanced probe that may be backlit. However, the enhance probe is only active in the Run mode (where gas concentrations are displayed).

5. When the TVA2020 is not being used, the monitor and all associated gear should be stored indoors (at temperatures ranging between 19 and 25 °C [66–77 °F], "normal room temperature"), and thus protected from inclement weather.

6. The acceptable range in ambient temperatures for operating the monitor is from -10 to 45 °C (14 to 113 °F) — per Thermo Scientific specifications. However, despite the monitor's incorporation of correction to gas readings for changes in ambient temperature, both the PID and FID readings can be affected very substantially by changes in temperature from that at time of calibration. Thus, the TVA2020 should be allowed adequate time (at least 30 min) to equilibrate with the ambient temperature before calibration, and recalibrated if subsequently moved to sampling site at a much different temperature (e.g., a temperature 5 °C greater or lower than the calibration temperature), again after waiting at least 30 min.

7. Although the monitor has a data logging capability that was used extensively during laboratory testing and evaluation of the monitor, no data logging will be performed during air testing. NEDU is unsure whether data logging is a desired function for normal air sampling in the Fleet.

POWER / CHARGING

1. The TVA2020 is expected to be normally operated with power from its internal lithium ion battery, which is recharged between uses. The battery charger has three LEDs. The leftmost LED indicates power status: when plugged into line power, the leftmost LED turns green indicating the charger is ready to charge the battery. If the leftmost LED is orange or red, there is a problem with the charger and it should not be used.

2. When the TVA is connected to the charger, the center LED will initially turn orange for 5 to 10 sec while the temperature of the battery is being measured. If the battery temperature is acceptable, the center LED will turn green. If the center LED turns red, the battery temperature may be too hot or cold and will not charge. If the temperature is believed correct, then the battery or charger may be defective.

3. After the center LED turns green, the charger tests the battery and displays its correct charge state at the rightmost LED: (1) orange (constant current charge state), (2) orange/green alternating (constant voltage charge state), (3) steady green (fully charged), or (4) red (charge or battery defective and should not be used).

4. Per manufacturer specifications, a fully charged battery should provide a minimum of 10 hours of monitor use, and a completely discharged battery should require a maximum of 10 hours charging time — although use of the backlight in the enhanced probe will reduce battery life. Also, the battery charger is capable of operating the TVA2020 while simultaneously charging the battery although charging may take 14 hours. However, experience will show how long monitors can be operated between recharging in the field, including whether battery duration is affected if batteries are

used on multiple occasions without recharging, and how long recharging takes under field conditions.

TVA2020 MONITOR STARTUP AND CALIBRATION

Startup

1. Ensure that the monitor battery has been fully charged: charge monitor until the charging LED changes from the initial orange charging state to the green fully charged state.

2. Use the currently approved Air Purity Report data sheet for the correct class submarine to record information during testing.

3. If needed, refill H_2 tank(s) to no more than a maximum of 2200 psig using the refilling assembly. Record pressure(s). Per the TVA2020 manual, a fully charged H_2 tank will provide 10 hours of continuous operation.

4. Attach the TVA probe and electrical cable if needed.

5. Disconnect from battery charger.

6. Insert H_2 tank (this starts H_2 flowing).

7. Press ON causing TVA to beep and the display to appear.

8. Clear memory (OPTIONAL).

Main Menu. 4=Memory, 2=Clear memory, Enter, Exit to Main menu.

9. Check battery.

Main Menu. 3=Info, arrow down once, check battery (a fully charged battery should read ~7.7 to 7.8 V). If desired, the battery can be recharged. A low battery warning should appear on the display when the battery is at 6.5 V, and the TVA will shut off soon after. Exit to Main Menu.

10. Prior to first use, or if unsure about past history of the specific monitor being used, a number of recommended settings should be configured (or confirmed). However, once these settings have been configured, they should not need to be reset again. Although the keystrokes needed to configure these settings are not listed here, the TVA2020 manual describes how to make any needed changes in the following list:

a. Background correct= None.

b. Cal accept mode = Manual.

c. Cal save mode = Manual.

d. RF cal mode = factor.

e. Response factor = “RF0:DEFAULT” (1.00 for both FID and PID).

11. Turn OFF temperature compensation (FID). Once set, this setting should not need to be reset, but should be confirmed prior to each day’s use of the TVA2020.

Main Menu. 2=Setup, 5=Other, 4=User Options, 3=More, 1=Temp Comp, if needed set to 2=OFF, Exit, Exit, Exit, Exit to Main Menu.

12. Check/Set date and time (OPTIONAL).

Main Menu. 2=Setup, 5=Other, 2=Date, confirm date, Exit; OR press Enter, enter date (mm/da/yy) and press Enter.

3-Time, confirm time, Exit; OR press Enter, enter time and press Enter.

Exit, Exit to Main Menu.

13. Check/Set Logging (OPTIONAL).

Main Menu. 2=Setup, 3=Log, 2=Auto, Rate=10 s, Enter, Exit to Main Menu.

14. Set alarms to 0 to avoid triggering during calibration (once set, these settings will remain until changed).

Main Menu. 2=Setup, 2=Alarm, press1=STEL, confirm 0 ppm and then Exit back to Alarm levels. If need to set to 0, press 1=Both, enter 0, Enter.

Repeat for 2=Low ceiling, repeat for 3=High ceiling, then Exit, Exit back to Setup Menu, Exit to Main Menu.

15. Put into Run mode for sampling.

Main Menu. 1=Run, wait until completes initialization and the FID is ignited (~30 sec).

Enter (enter no characters), Enter to begin sampling.

IF “FID flameout” warning”, and “F” is displayed alongside of FID gas reading, return to main menu and retry 1=Run.

Calibration : Conserve Calibration Gas.

1. The monitor needs to be recalibrated at the beginning of each day that air testing will be done.

2. If necessary, move the monitor(s) and calibration gear (gases and needed hardware) to where calibration will be done. If possible, this location should be indoors, protected from inclement weather, and at temperatures similar to those where the monitor had been stored. However, if the calibration location is significantly hotter or colder than the temperature at which the monitor had been stored (e.g., a temperature 5 °C greater or lower than the storage temperature), wait at least 30 min, but preferably longer, before proceeding to the next step to allow at least partial temperature equilibration of the monitor with the new location. The calibration site may of course be the same location as the storage site.

3. If needed, put into Run mode for sampling.

Main Menu. 1=Run, Enter, Enter to begin sampling.

4. Confirm that at least 30 min has passed since the FID was first ignited before starting calibration. Exit to Main Menu.

5. Calibration involves zeroing both the PID and FID with zero air, followed by spanning both sensors with span gas (nominally 10 ppm isobutylene/balance air).

6. Exit, Exit to Main Menu.

7. Setting span gas (IF NEEDED).

Main Menu. 2=Setup,1=Calibrate, 6=Configure, 1=Number of span points

Set both span points for the PID and FID to 1 by pressing 1=Both, and then pressing 1 (span point for each).

If setting of span points is not needed, press Exit to Cal Configure Menu.

2=Span concentration, and if needed, enter span gas concentrations for both gases (e.g., 10.0 ppm for PID, 10.0 ppm for FID) by pressing 1=Both, and then entering the concentration (e.g., 10.0 ppm) and pressing Enter.

Confirm span gas concentration is displayed to the nearest 0.1 ppm; if needed use the up and down arrow keys to adjust the display. This setting will be the display format of both PID and FID readings. Exit to Cal Configure Menu.

If setting of span concentrations is not needed, press Exit to return to Calibration Menu.

CAUTION. If span gas concentrations are entered or changed, immediately following the change, re-span the TVA2020 to avoid lockup of the displayed gas readings by following the steps directly below.

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8. Span PID and FID (ONLY IF SPAN CONCENTRATIONS HAVE BEEN CHANGED).

After purging span gas regulator 3 times, dial in several psig delivery pressure, and sample span gas from the open syringe barrel for 1 min at an audible delivery rate. (Alternative gas delivery methods should ensure that at least 1.5 L/min is delivered to the TVA).

Calibration Menu. 2=Span, 1=Both, Enter (start), wait 10 sec, then press Enter to accept; then press 1 to save.

Exit to Calibration Menu.

---

9. Zero PID and FID.

Exit, Exit to Main Menu, 1=Run, Enter (enter no characters), Enter again to begin sampling.

After purging zero air regulator 3 times, dial in several psig delivery pressure, and sample zero air from the open syringe barrel for at least 1 min until stable at an audible delivery rate. (Alternative gas delivery methods should ensure that at least 1.5 L/min is delivered to the TVA).

Record pre-calibration zero readings.

Exit, Exit back to Main Menu, then 2=Setup, 1=Calibration.

Calibration Menu. 1=Zero, 1=Both, Enter (start), wait 10 sec, then press Enter to accept; then press 1 to save.

10. Check zero readings.

Exit, Exit to Main Menu, 1=Run, Enter (enter no characters), Enter again to begin sampling.

Both PID and FID zero readings should be no more than 0.2 ppm. Repeat zeroing if readings are greater than 0.2 ppm. Record final zero readings.

Shut off zero gas flow.

11. Span PID and FID.

If needed, purge span gas regulator 3 times, dial in several psig delivery pressure, and sample span gas from the open syringe barrel for at least 1 min at an audible delivery rate. (Alternative gas delivery methods should ensure that at least 1.5 L/min is delivered to the TVA).

Record pre-calibration span gas readings

Exit, Exit back to Main Menu, then 2=Setup, 1=Calibration.

Calibration Menu. 2=Span, 1=Both (check correct concentration), Enter (start), wait 10 sec, then press Enter to accept; then press 1 to save.

12. Check span gas readings.

Exit, Exit to Main Menu, 1=Run, Enter (enter no characters), Enter again to begin sampling.

Both PID and FID span gas readings should be within 0.2 ppm of the calibration value. Repeat spanning if readings are outside this range. Record final span readings.

Shut off span gas flow.

13. Leave in Run mode.

MONITOR USE DURING AIR TESTING

1. The TVA2020(s) can now be used to screen DQA per the current set of screening procedures authorized for use for (1) SSGN submarines (both DDS and HOSUB versions) and (2) for VA class submarines (again both DDS and HOSUB versions).

2. If the TVA2020 is moved to a new testing location that is significantly hotter or colder than the calibration temperature (e.g., a temperature 5 °C greater or lower than the calibration temperature), the TVA2020 should be allowed to equilibrate for at least 30 min to the ambient temperature of the new operational location and the TVA2020 recalibrated.

3.TVAs can be left on during the day until no longer needed, at which time monitors can be turned off by pressing and holding down the OFF key until the display turns off.

4. Unscrew partially, or remove, the H_2 tank to avoid depleting the tank H_2. Partially unscrewing the H_2 tank and leaving in place will help to keep debris from entering the space that accommodates the tank.

5. Ensure that the monitor and all testing gear are dry, and return all items to their storage area where monitors may, or may not, be reconnected to their chargers.

Downloading (OPTIONAL)

Downloading of logged data files does not require any special software to be installed on the computer. Rather, after putting the TVA2020 into the "USB mode" by several keystrokes, followed by using two standard USB cables to connect a USB barrier device (both supplied by the manufacturer) in line between the computer and the TVA, a set of TVA files (including a log.txt file with the logged data) is transferred into a TVA 2020 window that automatically opens on the computer.

1. Exit to Main Menu (if needed). If in Run mode, press Exit twice.

2. Press 4=Memory, 1=USB mode. "Creating files, please wait" should be displayed.

3. Wait until "USB mode, Exit=cancel" is displayed. Then connect TVA to PC.

4. XXXXXXXXXXXXLOG.TXT file (logged data) can then be found under the TVA2020 (E:)\log folder. This file should be saved somewhere else as this file will be overwritten during the next downloading.

If filename has been set (via monitor's menu) to include the TVA2020 serial number, filename will contain the 12 digit serial number followed by 'LOG" (e.g., "202017092753LOG"). The first 4 digits represent the 2020 product family, next 2 digits the year of manufacture (e.g., 17), next 2 digits the month of manufacture (e.g., 09), and the last 4 digits the sequential unit number (2753).

5. When ready, disconnect TVA from line to PC. Then press Exit twice to return to Main menu.