Greenhouse Gas Technology Verification Center

A USEPA Sponsored Environmental Technology Verification (ETV) Organization

Testing and Quality Assurance QA Plan for The Protectoseal Company's Pin-Tech Pressure Relief Valves

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1.0 BACKGROUND AND INTRODUCTION

The Environmental Technology Verification (ETV) program was established by the United States Environmental Protection Agency (EPA) in response to the belief that there are many viable environmental technologies which are not being used for the lack of credible third-party performance evaluation. With the performance data developed under the program, technology procurement and permitting personnel in the United States and abroad will be better-equipped to make informed purchasing decisions about environmental technology. In late 1997, EPA selected Southern Research Institute to manage the Greenhouse Gas Technology Verification Center (the Center), which is one of twelve ETV entities. Eleven other ETV entities are currently operating throughout the United States conducting third-party verification in a wide range of environmental media and industries.

In March of 1998, the Center met with members of the Executive Stakeholder Group. In that meeting, it was decided that the oil and gas industries were good candidates for third-party verification of methane mitigation and monitoring technologies. As a consequence, in June 1998, the Center hosted a meeting in Houston, Texas, with operators and vendors in the oil and natural gas industries. The objectives of the meeting were to: (1) gauge the need for verification testing in these industries, (2) identify specific technology testing priorities, (3) identify broadly acceptable verification and testing strategies, and (4) recruit industry specific stakeholders. Industry participants voiced support for the Center's mission, identified a need for independent third-party verification, and prioritized specific technologies and verification strategies. Since the Houston meeting, a 19-member Oil and Gas Industry Stakeholder Group was formed, vendors of greenhouse gas (GHG) mitigation devices have been solicited in several top-rated technology areas, and verification testing of some compressor leak mitigation devices has started.

The Protectoseal Company has committed to participation in an independent verification of their pressure relief valve (PRV) technology. Protectoseal's Pin-Tech is designed to reduce "fugitive" emissions (i.e., emissions from the relief valve under non-venting conditions) from low-pressure storage vessels, such as crude petroleum storage tanks at refineries. The background information supporting development of the national emission standards for hazardous air pollutants (NESHAP) from petroleum refineries estimated 9,779 storage tanks in operation in the United States, with 922 in crude oil service. These tanks release volatile constituents contained in the crude oil such as methane, ethane, hydrogen sulfide and other volatile species. If the relief device does not completely seal the tank from the atmosphere, significant amounts of methane and other compounds that are regulated, such as benzene, xylene, toluene, and the aggregate volatile organic compounds (VOC), can be emitted.

Refineries in the United States are subject to many emission regulations, and may be subject to certain federal regulations governing emissions from new or modified sources (new source performance standards or NSPS) and emissions of hazardous air pollutants (national emission standards or NESHAP). These regulations require pressure relief devices to operate in a condition of no detectable emissions when in normal non-venting mode, that is, have a maximum screening value at the leak interface of less than 500 ppmv (40 CFR Part 60 Subpart GGG).

An evaluation of this Pin-Tech device is scheduled for August 1999 and will be conducted at a testing laboratory that offers experience in calibrating relief valves (i.e., provides equipment capable of precisely controlling pressures to the relief valve), has testing equipment, and can conduct the screening phase of the program. This test plan describes the technology to be tested, and outlines the Center's plans to conduct the verification in a laboratory setting. It has been prepared to allow timely evaluation, comment, and recommendation by Protectoseal (the vendor), the Oil and Gas Stakeholder Group, and the EPA.

Verification testing will take approximately two weeks. After the testing is completed, the Center will issue a report with its findings. The specific verification parameters to be determined are listed below. Section 2.1 provides a deeper discussion of each of these parameters.

- Measurement of the emissions at the PRV when in the non-venting mode to ensure that the device meets the <500 ppmv limit set by equipment leak requirements in Parts 60, 61, and 63 of Title 40 in the Code of Federal Regulations.

- Accuracy to set pressure. Verify that it is ±5% of that value.

2.0 TECHNOLOGY DESCRIPTION AND VERIFICATION APPROACH

2.1. PIN-TECH DESCRIPTION

The Pin-Tech PRV is designed for use on any type of low-pressure storage vessel. It protects the vessel from becoming damaged from over pressurizing, either through routine service (upper, Figure 1) or during an abnormal condition (lower, Figure 1). This PRV design incorporates a steel buckling pin that serves to set the relief pressure and keep the valve tight and not leaking when the unit is in the non-venting mode. If the pressure inside the vessel rises to the set point, a pressure at which the tank could be damaged, the relief pin is designed to buckle allowing the valve's piston to rise and release the pressure to keep from destroying the tank.

Traditionally designed PRVs typically vent an appreciable amount of the gaseous contents contained in the tank as the tank undergoes normal pressurization cycles. The Pin-Tech device uses a rigid pin that locks the valve's piston in place. This minimizes the fugitive leaks, until the pressure in the tank reaches the valve release set pressure, (an non-standard operating condition) which corresponds to the amount of force needed to buckle the rigid pin allowing the piston to rise from its seat and vent.

There are two types of Pin-Tech PRVs, one is the direct-acting type (foreground) and the other is the diaphragm-assisted model (background, Figure 2). Both PRVs operate on the same principle: the valve opens when the pin buckles at the design set pressure. The diaphragm-assisted PRV is used for very low release set pressures where there may be insufficient pressure in the vessel to buckle the pin; the diaphragm magnifies the small pressure increase in the vessel, generating sufficient force to buckle the pin and lift the piston.

Upon overpressure, the pin buckles and the valve lifts from the seat. Gas escapes from the entire 360 degrees of the periphery of the valve and seat. The design of the valve uses a pin, constructed of aircraft grade stainless steel (or other metal), which buckles at the relieving pressure. Based on preliminary assessments, the pin remains intact and secure until the set pressure is reached. Although a slight deflection can be seen immediately before failure, initial trials indicate that the pin "springs back" if the pressure subsides before the set pressure is achieved.

The Pin-Tech design reportedly provides positive sealing of the process from the atmosphere if the device has not relieved. To ensure the effectiveness of the buckling pin technology, the pin will have to be replaced to return the valve to the secure "no detectable emission" operation during non-vent mode after the pin has failed (i.e., the valve has relieved during an overpressure vent episode). This scenario is similar to use of a rupture disk, except that the relief valve will "close" after the overpressure has subsided.

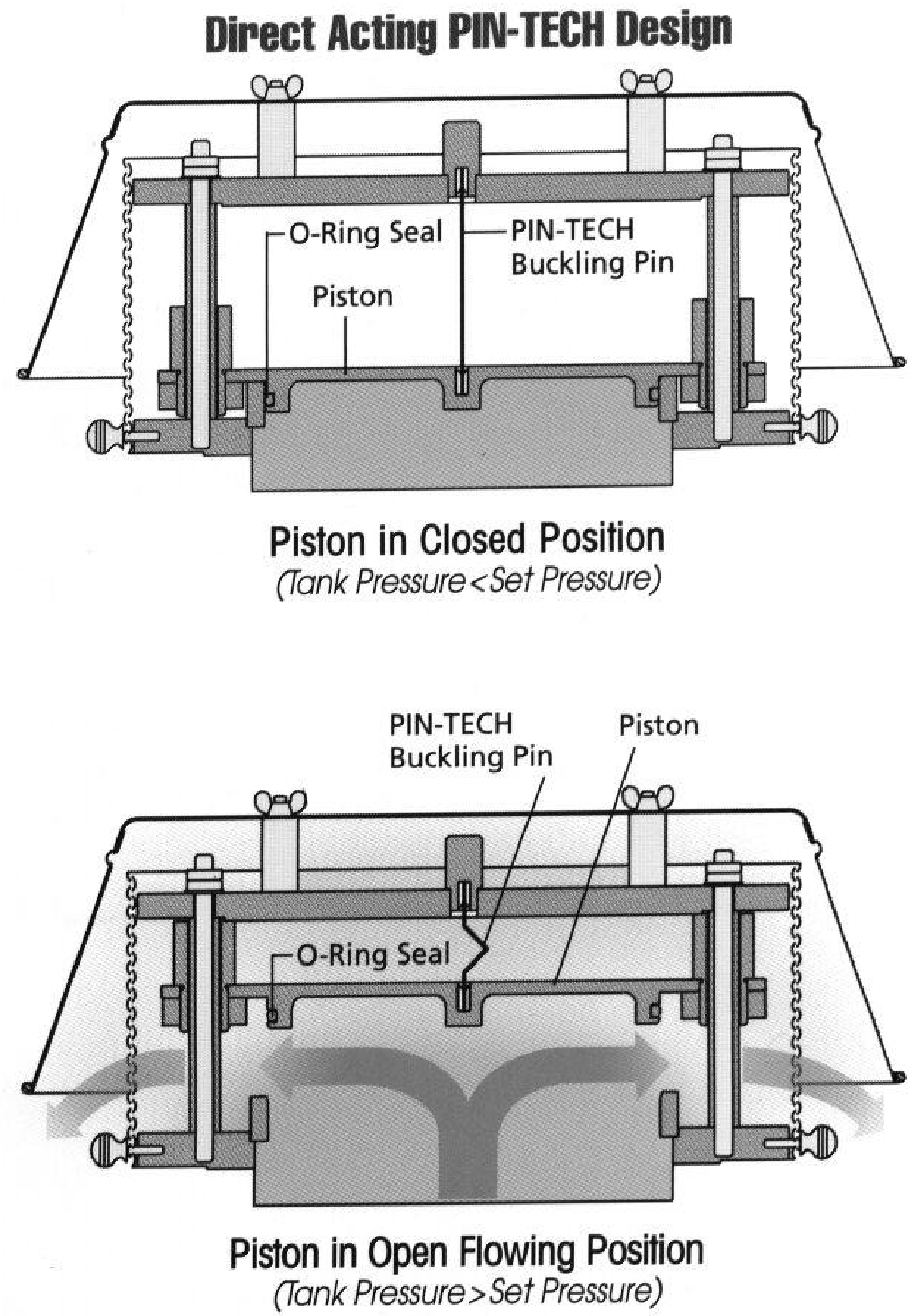

Figure 1: Cross-sectional view of Pin-Tech (direct-acting type)

Figure 2: Examples of Pin-Tech pressure relief valves

2.2. VERIFICATION PARAMETERS AND THEIR DETERMINATION

The design of the Pin-Tech device is intended to reduce overall emissions by maintaining "no detectable emissions" (500 ppmv) when in the non-venting mode. The goal of the evaluation, therefore, is to verify that this device operates with no detectable emissions during normal tank operations. Following the protocol of EPA Method 21 (40 CFR 60, Appendix A), measurements will be made at the potential leak interface of the PRV during the simulation of standard tank duty cycles (Section 2.5). An independent laboratory (Section 2.3) will conduct the test with a variety of valve sizes to ensure consistent performance throughout the product line. The valves will be randomly selected to ensure further credibility of the testing.

The tank cycle will be represented by a pressure cycle that will mimic that of a typical refinery crude oil tank daily cycle, assuming crude oil transfer into the tank and routine diurnal changes for various locations in the United States. The tests will also include an assessment of relieving by increasing pressure to the PRV until the PRV opens; this relief pressure will be recorded for comparison to the set pressure.

After testing the Pin-Tech devices, the same test cycle will be repeated with several conventional PRVs that represent the types available to industry. These devices will reflect the performance of conventional PRVs and provide a baseline against which the Pin-Tech device may be compared.

2.2.1. Pin-Tech Evaluation

The Pin-Tech evaluation will be conducted in a laboratory because the tests could be more effectively controlled than in the field on actual tanks. A laboratory study allows a greater variety of conditions to be tested and certain parameters (such as release pressure) can be more easily controlled and, thus, evaluated. A field program would be subject to greater variability in the actual conditions experienced and would hamper the effective evaluation of the devices under study.

To evaluate the Pin-Tech device, a small-diameter direct-acting Pin-Tech PRV will be subjected to a pressure cycle defined to simulate a typical daily tank duty cycle (Section 2.5). The pressure in the vessel will be monitored throughout the duty cycle. The potential leak interface, that is, the area around the valve seal, will also be monitored using a portable hydrocarbon instrument, in accordance with Method 21 to identify any potential emissions from the circumference of the PRV. The test will continue through the cycle until the preset release of the valve is attained; the release pressure for the cycle will be recorded. This will constitute a single test. This test will be repeated to ensure reproducibility of the results.

The overall test will continue using a larger-diameter, direct-acting Pin-Tech device, repeating the entire process described above. The entire evaluation program will then proceed to comparable tests for a small-diameter diaphragm-assisted PRV and a larger-diameter, diaphragm-assisted PRV.

A similar test cycle will be performed on multiple conventional PRVs representative of this same service in the oil industry. These tests on conventional equipment will serve as a baseline for this type of service. The multiple conventional PRVs will be chosen randomly and anonymously. Efforts will be made to reflect a significant percentage of those devices used in the industry. The averaged data recorded during the similar cycles will be compared with the results of the testing of the Pin-Tech equipment.

To complete the evaluation of the Pin-Tech equipment for this service, data regarding cost of devices, ease of installation, maintenance issues (including ease to reset pin), operating and maintenance (O & M) costs, and any specific characteristics encountered during testing will be reported.

An integral part of the assessment will be the potential reduction in methane emissions that would be achieved from the implementation of this type of technology. The testing will determine the effectiveness in "sealing" the storage tank from the atmosphere and eliminating the semi-continuous simmering of the relief valve, which contributes greater levels of emissions. The test will provide side-by-side comparison of the performance of conventional relief valves used for this service and the Pin-Tech design. Leak frequencies for the two types of relief valves will provide a clearer indication of the relative emissions associated with use of the different equipment. A complete evaluation of the results will be made using the EPA Protocol for Equipment Leak Emission Estimates that will provide a comparison of projected emissions from the two types of relief valves.

2.3. LABORATORY SELECTION

The following criteria were used to determine the lab selection.

- Experience with tanks and tank testing,
- Available pressure vessels, measuring equipment, and testing rigs,
- Experienced personnel that can execute the test, and
- Familiarity with calibrating relief valves and with the Method 21 test method.

Typically, manufacturing sites that have equipment operating in liquid or vapor service will require pressure relief equipment for safety and insurance purposes. Accordingly, a manufacturing site may have calibration and test equipment for pressure relief valves on site to facilitate routine relief valve testing (e.g., annual testing typical of most process industries). The calibration and test equipment are precisely the kind of equipment needed for the successful simulation of the tank duty cycle. Also, some manufacturing sites may use outside services to provide this important service for the relief valves at the site. These services may be at a fixed location or provided from a travelling trailer equipped with the requisite calibration and test facilities.

Candidate sites for this test include:

- Existing manufacturing sites with equipment for calibration and testing,

- Calibration and test service companies, and

- Outside laboratories with capabilities to set up equipment for the tank duty cycle simulation and testing of the valves for “no detectable emissions”.

The firm selected for this program is Southeast Valve of Charlotte, North Carolina. Southeast Valve is an independent firm that services relief valves for the process industries. They have calibration and test equipment in a stationary laboratory in Charlotte and a mobile calibration trailer. The firm was selected because:

- They have experience in calibrating relief valves,
- They have valve calibration equipment that can accommodate the gas that simulates a crude oil tank,
- They have portable equipment that can be brought to a local location for the duration of the test,
- They have personnel that can complete the calibration cycle (i.e., simulated tank duty cycle) and the monitoring using Method 21, and
- They have never done work directly for Protectoseal or any other manufacturer of PRVs

2.4. OPERATION, CONSTRUCTION, AND INSTALLATION OF THE PIN-TECH DEVICE

The Pin-Tech device uses a novel and patented buckling pin to ensure that the valve piston remains firmly seated when not venting. Should the pressure inside the vessel reach the set pressure of the relief valve, the pin, being sacrificial, buckles under the pressure allowing the piston to rise and vent the excess pressure. The buckling pin is configured to sense the axial force caused by the tank pressure acting on the piston. The force required to buckle the pin is governed by Euler's Law and is a function of the metallurgy, length, and diameter of the pin.

After the pin has buckled and the excess pressure is relieved, the pin can be easily replaced while the vent remains in service. An instrument can be installed as an option to the valve to indicate remotely (e.g., in a control room) that the valve has actuated. The pin will have to be replaced to return the valve to an assured condition of no detectable emissions during non-venting mode. The valves are available in sizes ranging from 2-in diameter to 24-in diameter, and are designed for set pressures from 1 oz./in^2 to 15 psig.

The standard material of construction of the body of the valve is either stainless steel or Alloy C (C276), although special materials are also available upon request. The buckling pin is fabricated from 304 stainless; again, other materials are available upon request. The valve is designed with a "soft" seat that can be fabricated from various elastomers, such as Viton®, Neoprene®, Buna-N, EPDM, Kalrez®, and Chemraz®.

Installation and sizing of the valve is relatively simple. All units mate with either a standard flanged 150# ANSI, API (20-in or 24-in only), or DIN PN 16 connections. To size the valve for the proper application, the following formula is used:

$$K_{eff} = Q_{CFH}/P^{0.5}$$

Where: K_{eff} = calculated number for effective sizing factor

Q_{CFH} = venting requirement in cubic feet per hour

P = maximum pressure that the tank may experience in inches water column

After determining the appropriate K-factor for the relief requirements, the size of the valve that can accommodate the relief demands is selected from a valve sizing table (Table 1).

Table 1: Table of K-Values for Valve Sizing

K-Value	Size (inches)	K-Value	Size (inches)
4,250	2	96,000	10
9,800	3	113,500	12
16,180	4	145,970	16
36,200	6	254,550	20
62,050	8	354,170	24

2.5. DEVELOPMENT OF TANK CYCLE

The evaluation of the Pin-Tech relief valve will be done over a series of pressures that simulate a storage tank over daily cycle. The tank duty cycle is a series of pressures that would be expected in a storage vessel during normal operations or merely standing. The pressure cycle that defines the tank duty cycle is developed from tank characteristics. The pressures are determined from models that estimate emissions; the same models estimate concentrations of hydrocarbons in the gas phase that would be emitted, also part of the test design. The model (described later) uses known tank dimensions, parameters, colors, and crude oil composition to the tank. The total pressure increase in the storage tank was estimated from (1) the transfer rate into the tank was estimated and (2) the pressure increase resulting from the diurnal temperature increase.

Information on the population of crude oil storage tanks in refineries in the United States was obtained from the EPA's Office of Air Quality Planning and Standards (OAQPS). The tank capacities range from less than 25,000 bbl to greater than 200,000 bbl with diameters ranging from 30 to 210 feet. For the purposes of designing the tank cycle for this evaluation, the crude oil transfer rates were assumed to be as great as 3,200 gal/min, and the tank color is typically white to off-white.

A model tank approach was used in designing this test program to simulate the pressures inside a large crude oil tank, i.e., pressure that might be seen by a relief valve. The tank characteristics are the first step in designing the model tank duty cycle. A single model tank cycle was defined for this test:

Capacity (MMgal)	8
Diameter (ft)	150
Color	White
Transfer rate (gal/min)	3,200

The same resources were used to obtain data on typical crude oil compositions, especially volatile hydrocarbon constituents that are flashed from the crude oil when fed to the initial storage vessel at the refinery. These data were derived from the American Petroleum Institute (API) and other published data. A single crude oil content was used in the design of the tank duty cycle; this was based on typical contents for the domestic refineries (Table 2).

Table 2: Constituents in "Model" Crude Oil

Compound	Content (%)	Compound	Content (%)
Methane	0.19	Hexanes	4.76
Ethane	0.23	Heptanes	3.90
Propane	0.75	Octanes	6.81
Butanes	2.06	Nonanes	4.01
Pentanes	3.44	BTEX	0.82

A model was used to estimate the effect of temperature on the pressure in the vapor space of the storage tank and to estimate the concentration of vapor constituents. The model used was the stable oil tank model, a component of the Production Tank Emissions Model (E&P TANK version 1.0). The model provides flash calculations and calculations that incorporate non-equilibrium systems, a refinement over the standard vapor-liquid equilibrium systems simulated by the EPA TANKS model. The E&P TANK model allows use of built-in data for oil composition and meteorological data for specific locations.

The E&P TANK model requires the physical parameters of the tank (the model tank), the inlet crude oil composition data (model crude oil), and the meteorological data for the location of interest to project the vapor-phase compositions. These vapor phase concentrations provide the bounds for the concentration of the gas to be used as the motive fluid in the tank experiments (Table 3). The total hydrocarbon concentrations ranged from 3,300 to 22,900 ppmv. However, considering the cases to be tested and the relative response of the monitoring instruments to the various compounds, a methane concentration of 15,000 ppmv should be used for the pressurized fluid in the valve calibration equipment. Methane was selected for use in the tank simulation for ease of preparation and use.

Table 3: Concentrations Projected by E&P Model

Compounds	Concentration (ppmv)		
	Maximum	Minimum	Average
C1	12,171	1,900	5,470
C2	2,112	883	1,668
C3	3,220	137	1,670
i-C4	1,327	67	568
n-C4	2,777	95	1,183
i-C5	577	82	304
n-C5	387	68	232
Hexanes	168	43	104
Heptanes	115	32	67
Octanes	53	13	33
Nonanes	22	4	11
Benzene	2	1	1
Total	22,931	3,325	11,311

The duty cycle is defined by the operating pressures in the tank, which can be also estimated from the model and from meteorological data. The meteorological data considered for development of the tank duty cycle were obtained from the National Oceanic and Atmospheric Administration (NOAA). Monthly data were downloaded from Internet available archives and compiled to determine the statistical average, maximum, and minimum values. These extremes, plus the maximum diurnal temperature change, were used to define the typical and worst case tank duty cycles (Table 4).

- The maximum temperature and the maximum diurnal temperature change defined the worst-case temperature change for the vapor space of the model storage tank. The increase in vapor space volume (resulting from the temperature increase) was converted to a pressure increase, assuming constant volume of the vapor space.

- The pressure increase resulting from transfer into the crude oil tank was estimated from the assumed initial tank level and assumed transfer quantity into the tank.

Table 4: Summary of Temperature Data for Four Typical Locations (°F)

		Maximum Daily	Minimum Daily	Diurnal Change
Midland, TX	Average	80.9	53.9	27.0
	Standard Deviation	15.9	16.6	7.4
	Maximum	109.4	82.9	43.2
	Minimum	46.4	12.2	3.8
Delaware City, DE	Average	68.2	47.0	21.2
	Standard Deviation	16.1	15.0	7.2
	Maximum	93.9	78.8	44.1
	Minimum	28.4	12.9	1.8
Kenai, AK	Average	44.6	28.3	16.2
	Standard Deviation	15.6	17.5	7.5
	Maximum	74.1	57.2	39.6
	Minimum	-4.0	-26.0	1.8
Bakersfield, CA	Average	75.9	51.1	24.7
	Standard Deviation	16.2	12.8	6.5
	Maximum	109.9	80.6	45.9
	Minimum	51.1	21.2	9.0

The tank pressure cycles (Table 5) to be evaluated are based on temperature increases, transfers into the tank, and a combination of both transfers into the tank with daily temperature increase. The temperature cycle assumes the greatest diurnal temperature change of any of the sites evaluated and the maximum temperature noted for that same site. The temperature cycle indicates a pressure increase of about 8 percent. The transfer episode assumes about 3/4-million-gallon transfer into an 8-MMgal tank with a starting tank level of about 50 percent. Another assessment could have been included in the design of the tank duty cycle, namely the effect of solar radiation effects on the storage tank. Because the effect of the transfer into the tank is large, however, the effect of solar radiation was not pursued. This effect was believed to be within the envelope of pressures described by the temperature increase and transfer cycle.

Table 5: Description of the Tank Pressure Cycle

Test Cycle	Description
Temperature Cycle	1.29 psia increase Basis: 64F to 109.9F
Transfer Cycle	3.49 psia increase Basis: 768,000 gal transferred into an 8MMgal tank starting at 50% level
Synergistic Cycle	5.09 psia increase Basis: 64F to 109.9F Basis: 768,000 gal transferred into an 8MMgal tank starting at 50% level

The cycles will last from one to three hours in duration, depending upon the complexity of the changes being evaluated. Data will be collected periodically throughout the test period. At the initiation of the test program, measurements will be made at 0.5-psi increments in the pressure vessel. The system pressure will be incremented and allowed to stabilize for at least 20 seconds before recording the pressure and making the Method 21 measurement.

The 0.5-psi increment was selected based on the number of measurements to be made over a maximum pressure cycle of 5 psi (10 intervals total). This interval may be adjusted during the test program if warranted based on assessment of the data collection activities. For example, a smaller increment is warranted for smaller pressure increases, such as those associated with the diurnal temperature increase only. Another modification to the increment size would result from the identification of the release pressure. If the relief valve opens during a pressure increase (between measurements) a smaller increment will be used to refine the determination of the relief pressure and the leak characteristics near the relief pressure.

2.6. SCHEDULE OF ACTIVITIES

Laboratory selection, planned for mid-May 1999, is the first step in the evaluation program. Testing is scheduled for early August 1999, to be completed by the mid of August 1999. After data analysis is completed, a draft report should be available for review by Protectoseal, the oil and gas industry stakeholders, and the EPA by the end of August 1999. The final report is scheduled to be available by October 1999.

3.0 DATA QUALITY OBJECTIVES AND INDICATORS

This section specifies data quality indicators (Table 6) that will be used as measures of data quality for the test data and states how values for each indicator will be determined through calibrations, quality control (QC) checks and other appropriate methods (Table 7).

Table 6: Data Quality Indicators

Measurement	Method	Range	Frequency	Accuracy & Precision	Method to Verify
Screening concentration	EPA Method 21	0-1,000 ppmv	Continuously throughout the cycle	±5% of span	Calibrate initial and check twice for each test
Pressure at relief	In-line pressure gauge	0-15 psig	Twice per valve	±0.5%	NIST standard

Table 7: Summary of Calibration and Quality Control Checks

Measurement	Cal/QC Check	Frequency	Allowable Results	Response to Check
Methane gas leaked at valve	Calibrate initially, check against certified methane concentrations	Daily prior to taking data	Feasible	Identify problem and correct
Pressure in tank	Calibrate initially, sensor diagnostics	Startup, when taking data	No error indication	Replace sensor

4.0 SAMPLING AND ANALYTICAL QC/QA PROCEDURES

The goal of the testing program is to assess the performance of the Pin-Tech PRV design with respect to "no detectable emissions" or no screening value greater than 500 ppmv. The sampling and quality control techniques used to ensure the generation of high quality, reliable data are divided into two sections: those associated with screening value measurements and those associated with measurement of process parameters. The quality control and assurance techniques and measures for the EPA reference method are provided in the method.

4.1. METHOD 21 - VOLATILE ORGANIC COMPOUND LEAKS

Method 21 (40 CFR 60, Appendix A) is the reference method specified by standards of performance for equipment leaks to determine the need for maintenance or to assess conformance with the allowable leak frequency provisions of the equipment leak regulations. Method 21 (Appendix A) was borne from the early research efforts to characterize the potential for emissions from fugitive emission sources (now known as equipment leaks) in the petroleum and chemical process industries.

4.1.1. Instrument Selection

Method 21 identifies performance specifications for portable hydrocarbon monitoring instruments that can be used by this method (Table 8). The method also specifies performance criteria for a portable hydrocarbon monitoring instrument that can be used to determine the concentration of organic compounds near the leak interface for various equipment such as valves, pumps seals, compressor seals, agitator seals, flanges and other connectors, and pressure relief devices (Table 9).

Table 8: Specifications for Method 21 Monitoring Instruments

Performance Parameter	Acceptable Range
Instrument response	Instrument responds to the compounds to be measured; candidate instrument technologies include: Catalytic oxidation Flame ionization Infrared absorption Photoionization
Measurement range	Capable of measuring the concentrations, less than 1,000 ppmv
Instrument scale	Readable to ±5% of leak definition
Sample flow rate	0.5-3 L/min
NFPA rating	Intrinsically safe in explosive atmospheres

Table 9: Performance Criteria for Method 21 Monitoring Instruments

Performance Parameter	Acceptable Range
Response factors	10 (maximum)
Response time	30 seconds (maximum)
Calibration precision	10 percent (maximum) of calibration gas value

Several candidate instruments have been qualified and have been in routine use since the requirements for routine leak detection and repair in the process industries (Table 10). All candidate instruments are capable of detecting 500 ppmv hydrocarbon concentrations, and therefore are suitable for this program. The Foxboro OVA 128 was selected for this test because (1) it meets all the performance specifications in Method 21, (2) this series of instrument has been used throughout the development of equipment leak data by the EPA, and (3) it can be calibrated with a span of 0 to 1,000 ppmv, placing the critical measurement at mid-scale.

Table 10: Candidate Monitoring Instruments

Candidate Instrument	Detector Type
Foxboro Organic Vapor Analyzer (OVA) Model 108	Flame ionization
Foxboro Organic Vapor Analyzer (OVA) Model 128	Flame ionization
Heath Detecto-Pak II	Flame ionization
HNu Systems HW-101	Photoionization
Rae Systems	Photoionization
Miran 1B2	Non-dispersive infrared

4.1.2. Instrument Calibration

The instrument will be calibrated before the sampling begins and then daily during the sampling program in accordance with Method 21. Section 3.2 of the method specifies the calibration gas to be used for Method 21 screening programs. Cylinder gas standards will be used for this program that adequately bound the leak definition from the regulations. An air standard containing less than 10 ppmv hydrocarbon will be used as the zero gas and a 1,000-ppmv-methane-in-air standard (nominal) will be used as the span gas. An intermediate standard (mid-scale) is not deemed necessary for this program given the small range of concentrations to be studied in this program. The vendor will provide certified analyses for each gas standard.

> **3.2 Calibration Gases.** The monitoring instrument is calibrated in terms of parts per million by volume (ppm) of the reference compound specified in the applicable regulation. The calibration gases required for monitoring and instrument performance evaluation are a zero gas (air, less than 10 ppm VOC) and a calibration gas in air mixture approximately equal to the leak definition specified in the regulation. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within ± 2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life. Alternatively, calibration gases may be prepared by the user according to any accepted gaseous preparation procedure that will yield a mixture accurate to within ± 2 percent. Prepared standards must be replaced each day of use unless it can be demonstrated that degradation does not occur during storage.

Each calibration will determine the instrument response time (Table 11), precision (Table 12), and drift (Table 13). The procedures from the methods describe the procedure for calibrating the instrument and evaluating its performance (presented below). These performance evaluations will be made daily during the test program.

4.2 Calibration Procedures. Assemble and start up the VOC analyzer according to the manufacturer's instructions. After the appropriate warm-up period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value. (Note: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.)

4.4.2 Calibration Precision. Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

4.4.3 Response Time. Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. Measure the time from switching to when 90 percent of the final stable reading is attained. Perform this test sequence three times and record the results. Calculate the average response time.

Although the method does not include an evaluation of instrument drift, it does call for routine checks to ensure that the instrument remains in calibration throughout the screening program. For this test, drift checks of the instrument will be made. The drift checks are essentially calibration checks at the start, middle, and end of the testing day (Table 13).

Table 11: Instrument Response Time Test Log Sheet

Response Time Test				
Test No.	Calibration Conc'n (ppmv)	Conc'n at 90 Percent	Time to 90 Percent Reading (sec)	<30 sec?
1				
2				
3				
Average				

Table 12: Calibration Precision Test Log Sheet

Calibration Precision Test					
Test No.	Calibration Gas Mixture (ppmv)	Instrument Meter Reading (ppmv)	Difference (ppmv)	Percent Difference	Passed?
1					
2					
3					
Average					

The logged data provide documentation of the veracity of the screening data produced.

Table 13: Drift Test Log Sheet

ETV/Southern Research Institute Pin-Tech Evaluation
Drift Test Log Sheet

Instrument ID ______________________

Analyst Name/Initial ______________________

Date	Nominal Gas Concentration (ppmv)	Pre-Test		Mid-Test		Post-Test	
		Concentration (ppmv)	% Error	Concentration (ppmv)	% Error	Concentration (ppmv)	% Error

4.1.3. Screening Procedure

Implementing Method 21 for determining the screening value for a pressure relief valve generally requires the extraction of the sample from the exhaust of the relief valve or from the horn attached to the exhaust from the relief valve. For a low-pressure device, such as a conservation vent or the equipment tested in this program, the instrument probe will be traversed around the circumference of the valve seat at the seal interface. (As presented below, the Method requires only that measurements be made within 1 inch of the leak interface. This provision allows measurements at static seals, such as that for a valve, and dynamic seals, such as those found on compressors, pumps, or agitators. Because the relief valves on the test stand will have a static seal, measurements can be made at the potential leak interface.). No interference to this approach (as might be experienced in field measurements at an operating facility) is expected during the controlled testing of this program.

> **4.3.2 Type II - "No Detectable Emission"**. Determine the ambient concentration around the source by moving the probe randomly upwind and downwind around one to two meters from the source. In case of interference, this determination may be made closer to the source down to no closer than 25 centimeters. Then move the probe to the surface of the source and measure as in 4.3.1. The difference in these concentrations determines whether there are no detectable emissions. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are: (a) Pump or Compressor Seals - Survey the local area ambient VOC concentration and determine if detectable emissions exist. (b) Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices - Determine if any VOC sources exist upstream of the device. If such ducting exists and emissions cannot be vented to the atmosphere upstream of the control device, then it is presumed that no detectable emissions are present. If venting is possible sample to determine if detectable emissions are present.

The screening data will be recorded for each test run on prepared data forms (Table 14). The maximum screening value from the complete traverse will be recorded as the concentration at each step (i.e., pressure increment) of the tank duty cycle test. After two runs have been completed, the data will be reviewed for completeness and to assess consistency across the two test runs. If the data are not consistent, meaning that the two values are not within 20 percent of each other, a third test run will be made.

4.2. MEASUREMENT OF RELIEVING PRESSURE

The test equipment will be designed to provide an accurate pressure to the PRV. The equipment will likely be a calibration test rig used for calibration and annual testing of relief valves, so an accurate pressure sensor will be available (± 0.5 percent of span). The test rig will necessarily have certified instruments. Copies of the most recent calibrations will be included in the report. The testing group providing the equipment to perform these evaluations will provide the instrument certifications. The pressure will be monitored throughout the test cycle and recorded as noted above.

When the relief valve lifts and the pressure to the device relieves, the final pressure in the test equipment will be recorded. This pressure will be compared in the report to the set pressure of the PRV. If the valve relieves before the next pressure increment, the test will be repeated with a smaller pressure increment nearer the relief pressure. This additional test will aid in evaluating valve performance nearer the set pressure, the pressure region thought to be most problematic for conventional relief valves.

When testing the Pin-Tech devices, the pressure will be increase up to a point where there is visible deflection in the pin, then the pressure will be lowered then increased again to verify that a leak does not develop. This will be noted in the comment section of Table 14.

Table 14: Test Run Log Sheet

Test Data Log Sheet			Valve/Size	
Instrument ID				
Analyst Name/Initial				
Test Number				
Date	Time	Pressure	Maximum Screening Value (ppmv)	Comments

5.0 REDUCTION OF DATA, VALIDATION, AND REPORTING

There will be little data to reduce in this test program. Unlike other program where emission rate data are generated, this evaluation will target the effectiveness of equipment in maintaining a condition of "no detectable emissions" during periods that the relief device is not actuated. This evaluation does not require the calculation of concentration or flow rates. It only requires an observation of the results obtained with a properly calibrated monitoring instrument over the course of a simulated tank duty cycle.

There will be a few calculations to assess instrument performance.

5.1. MANUAL MEASUREMENTS

The data generated from the implementation of manual methods require computation of percent difference for calibration precision and percent error for calibration drift. These calculations are simple, difference of measured value and actual concentration divided by the actual concentration.

5.2. DATA REVIEW, VALIDATION, AND REPORTING

The concentration measurements over the simulated tank duty cycle and calculated data will be compiled in tabular format for ease of comparison. Outliers will be identified from the observation. Then, the data for each test will be summarized and recorded in a test data summary log sheet (Table 15). The summary table will allow quick comparison of the performance of all devices tested.

Table 15: Test Data Summary Sheet

		Date		
Device	**Valve Size (in)**	**Screening Value - maximum (ppmv)**	**Relief Pressure (psia)**	
			Obs.	Design
Pin-Tech direct action (small)				
Pin-Tech direct action (large)				
Pin-Tech diaphragm assisted (small)				
Pin-Tech diaphragm assisted (large)				
Conventional PRV#1				
Conventional PRV#2				
Conventional PRV#3				
Conventional PRV#4				
Conventional PRV#5				

The summary results will compare the effectiveness of the Pin-Tech and conventional PRVs. The report will consider the effectiveness over the entire simulated tank duty cycle. The relative performance of the traditional relief valves and the newer Pin-Tech technology will be reviewed.

6.0 AUDITS

A data quality audit (DQA) is planned for this test. The DQA will be conducted by SRI's independently managed QA staff. This will include verification of data, checking calculations, and documenting data handling has been done correctly as the basis for the audit. An external audit may be performed at EPA's discretion by EPA QA staff or a qualified contractor. A performance audit on the measuring equipment used in this test will not be necessary due to the types of instruments and their inherent reliability and their ability to be lab verified during usage. The internal audit of data quality will be conducted once the data collection and analysis are complete. The final report will contain a summary of results from any audits.

7.0 CORRECTIVE ACTION

Section 3.0 lists the allowable values for each calibration and quality checks and also indicates actions to be taken in response to an out of control condition. Other issues may arise that require corrective actions or plan changes to ensure that the data quality objectives are met. SRI's Quality Management Plan provides general procedures for corrective action that will be followed for any such instances.

8.0 PROJECT ORGANIZATION

Southern Research Institute's Greenhouse Gas Technology Verification Center has overall responsibility for planning and ensuring successful implementation of the verification test. The Protectoseal Company is providing the Pin-Tech devices and guidance in the test installation. The laboratory is providing the testing site, the test equipment, and the measuring instruments and trained personnel to execute the test program. The Center and Protectoseal have signed a formal agreement (the Commitment Letter) specifying the responsibilities and obligations of each party.

9.0 TEST PROGRAM HEALTH AND SAFETY

This section applies to Center personnel only. Other participating organizations should have their own Health and Safety Programs-specific to their respective roles in this project.

A basic safety precaution to consider when working with pressurized vessels is care must be taken to avoid over-pressurizing the vessel causing it to rupture where injury may occur. Because the test will be conducted in an independent laboratory, the Center will adhere to the laboratory's safety program.

10.0 REFERENCES

US Patents held by Protectoseal Company for the Pin-Tech design: 4,724,857; 4,787,409; 4,896,689; 5,577,523; 5,577,524; 4,896,690; et al.

Method 21 - Determination of Volatile Organic Compounds Leaks. Code of Federal Regulations, Title 40, Part 60, Appendix A. (Posted at Emission Measurement Technology Information Center, February 9, 1993.)

Production Tank Emissions Model (E&P TANK Version 1.0), Report and User's Manual. A Program for Estimating Emissions from Hydrocarbon Production Tanks. Software Number 4660. American Petroleum Institute and Gas Research Institute. (Prepared by DB Robinson Research Ltd.) October 1997.

1995 Protocol for Equipment Leak Emission Estimates. US Environmental Protection Agency. (Prepared by Radian Corporation.) Document. No. EPA-453/R-95-017. November 1995.

Memorandum to James Durham, EPA:CPB, from Patrick Murphy, Radian Corporation. Summary of Nationwide Volatile Organic Compound and Hazardous Air Pollutant Emission Estimates for Storage Tanks at Petroleum Refineries. October 15, 1992. (Docket No. A-93-48-II-B-4)

Letter to James Durham, EPA:CPB, from Marco Zarate, Radian Corporation. Transmittal of Section 114 storage tank data summary report for petroleum refineries. March 3, 1992. (Docket No. A-93-48-II-B-1)