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**VACUUM VAPOR AND PASSIVE CRYOGENIC VAPOR
EXTRACTION TECHNOLOGY COMPARATIVE FIELD TEST
FOR SUBSURFACE SOIL VAPOR SAMPLING**

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Vacuum Vapor and Passive Cryogenic Vapor Extraction Technology Comparative Field Tests for Subsurface Soil Vapor Sampling

Introduction: Under a cooperative agreement, (Reference 1 and 2) Westinghouse Idaho Nuclear Company (WINCO) and Petro Site Assessment (PSA) compared field testing of WINCO's passive cryogenic vapor extraction (PCVE) and PSA's vacuum/vapor (VV) technologies. The tests were to demonstrate the equivalence of the two technologies for collecting soil vapor samples. Reference 3 details an initial experimental plan for the comparative tests at the Wilcox and Associates Test Site. Due to limitations of the Wilcox and Associates Test Site identified during preliminary background testing, a modified test plan employing a new test location and a specially fabricated test apparatus was formulated (Reference 4).

Comparative field testing of the PCVE and VV technologies was conducted the week of July 26, 1993 in a tent-covered, open-field area located adjacent to Highway 291, approximately one-half mile north of PSA offices. Presented below are overviews of the PCVE and VV technologies and the comparative test protocol. These overviews are followed by a description of the test apparatus and the results of scoping tests. Lastly, the results of the comparative tests are presented.

Vacuum/Vapor and Passive Cryogenic Vapor Extraction Technologies: Sampling equipment used by the VV technology is shown schematically in Figure 1.0. Major components consist of a vacuum pump, a vacuum-volume tank, a volume-pressure gauge, a control panel and ancillary valving and sample lines. The system is isolated by valving off the sample line, evacuation of the system with the vacuum pump, and isolation of the system from the vacuum pump from the system upon achieving the desired level of vacuum. In use, the sample line is connected to the sample source, the sample line valve is opened to pull sample air into the vacuum-volume tank, and the sample line valve is closed following a predetermined sample collection interval or collection of the desired air volume (maximum volume 8 liters). Following sample collection, a small sample is withdrawn from the sample line by inserting a syringe through the wall of a short section of sample line. The sample is then injected into a gas chromatograph for analysis. The above process is repeated to collect another sample.

Sampling equipment used by PCVE technology is shown schematically in Figure 2.0. Major components consist of stainless steel sample cylinder, a liquid nitrogen reservoir, and a sample inlet with shutoff valve. The sample cylinder is evacuated, the liquid nitrogen reservoir is filled, and the sample cylinder is immersed in the liquid nitrogen. In use, the sample line is connected to the sample source, the sample line valve is opened to pull sample air into the sample cylinder, and the sample line valve is closed following a predetermined sample collection interval or collection of the desired volume of air (maximum volume 120 to 130 liters). Following the collection of the sample, the sample cylinder is removed from the liquid nitrogen reservoir and returned to the laboratory for analysis. Alternately, a small sample aliquot can be removed from the sample cylinder by the use of a sampling manifold, a smaller sample transfer cylinder, or simply a syringe. Prior

VACUUM/VAPOR

FIGURE 1.0

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PASSIVE CRYOGENIC VAPOR EXTRACTION

FIGURE 2.0

to collection of a small aliquot for field analysis, the sample cylinder is warmed to ambient temperature, typically by letting the sample cylinder set overnight under ambient conditions.

Test Apparatus and Scoping Tests: The test apparatus for the VV and PCVE comparative tests is shown schematically in Figure 3.0. The components of the apparatus fabricated of PVC consists of: a 2-ft long, 1/2-in ID sample riser; two 5-ft long, 1-in ID horizontal pipe runs; a large 8-in outside diameter "T" connector; and various other smaller connectors. The assembly of the PVC components of the apparatus was achieved by the use of a PVC cleaner, primer, and cement. In addition, component assembly was performed in sequence to ensure all components were totally filled with a medium grade silica sand.

Globe shutoff valves are located on the sample riser, the large "T", and the test apparatus inlet line. In addition, a sampling port equipped with a septum is located on the top of the large "T". Other test components were a gasoline reservoir; an ice bath; a mass flow controller/ totalizer, and a 25-foot long, 3/16-in ID FEP sample line for connection to the VV or PCVE sampling equipment.

Scoping tests were initially performed to evaluate the test apparatus. The tests included evaluations of the volume of the test apparatus with and without sand fill, the air in-leakage rate of the test apparatus, and the potential measurement interferences of the PVC cleaner, primer and cement. The tests were followed by introduction of both very small and large quantities of gasoline into the test apparatus to evaluate the measurement responses.

The internal volume of the test apparatus without sand fill was determined by calculating the volume from precise measurement of the dimensions of the various components. The internal volume of the test apparatus with sand fill was determined by measurement of the medium grade sand void volume. The void volume was measured by the volume of water required to fill a 6-in section of piping filled and unfilled with sand.

The measured void volume of the sand 38.6 percent. This corresponds to an internal volume for the apparatus with sand fill of 2.3 liters.

Measurement of the apparatus air in-leakage rate was performed by isolation of one end of the system by closing a valve, evacuation the entire apparatus (including sample line), isolation of the opposite end of system by closure of a valve, and recording the increased in pressure within the system with time. The measured average rate of air in-leakage was 0.053 L/min. This corresponds to a leakage rate of 2.3 percent of the internal volume of the apparatus with sand fill.

The measurement of potential measurement interferences associated with the PVC cleaner, primer and cement were determined prior to the introduction of gasoline into the test apparatus. Initially, potential interferences with the same or very

WINCO/PSA APPARATUS

FIGURE 3.0

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similar retention times of benzene and toluene were detected. Purging of the test apparatus with ambient air for a period of 1 hour, however, reduced the potential interferences to nondetectable levels.

To evaluate the relative gas chromatographic responses to the normal 0.1-cc sample size; 100 microliters of gasoline was introduced into the system. This quantity of gasoline yielded measurement responses only slightly above background levels. Secondly, 40-mL of gasoline was added to the gasoline reservoir. Following a period of equilibrium, measurement responses were readily distinguishable from background responses. This quantity of gasoline, nonleaded regular, was used in the gasoline reservoir for subsequent comparative tests.

Test Protocol: The protocol for VV comparative tests entailed pulling a stream of ambient air for a predetermined period of time at a known flowrate through an ice-cooled, gasoline-containing reservoir (Figure 3.0). Out of the gasoline reservoir the gasoline-laden air stream passed through a mass flow controller-totalizer into the sand-filled test apparatus. The gasoline-laden air stream was then directed from the test apparatus through a sample line into the VV sampling equipment, described above. At the end of the predetermined sampling interval, the sample flow was stopped, and the test apparatus and sample line were returned to ambient pressure. Upon return to ambient pressure, a 0.1-cc sample was withdrawn with a gas tight syringe from a short section of FEP sample line at sample port 1-A, or alternately from the septum at sample port 1-0. The sample was then introduced into a Shimadzu GC-14A gas chromatograph equipped with photoionization detector for analysis. The gas chromatograph was mounted in a van-style vehicle located on-site during the comparative tests.

The protocol for PCVE comparative tests as similar to the VV comparative test protocol. A stream of ambient air was pulled for a predetermined period of time at a known flowrate through an ice-cooled, gasoline-containing reservoir (Figure 3.0). The gasoline-laden air stream passed through a mass flow controller-totalizer into the sand-filled test apparatus. The gasoline-laden air stream was then directed from the test apparatus through a sample line into the PCVE sampling equipment, described above. At the end of the predetermined sampling interval, the sample flow was stopped, and the test apparatus and sample line were then returned to ambient pressure. A 0.1-cc sample was then withdrawn with a gas tight syringe from a short section of FEP sample line at sample port 1-A, or alternately from the septum at sample port 1-0. The sample was then introduced into a Shimadzu GC-14A gas chromatograph equipped with photoionization detector for analysis.

In addition, an aliquot of each sample cylinder was expanded into a sample transfer manifold. A portion of the sample aliquot was then transferred from the manifold into a smaller, secondary sample cylinder, and a 0.1-cc portion of the sample was withdrawn from the manifold with a syringe for field gas chromatographic analysis. Then, the large cryogenic sample cylinder was vented and the small secondary sample cylinders were returned to the laboratory for analysis.

Comparative Test Measure Results: The primary objective was to demonstrate the equivalency of the VV and PCVE technologies. The results are shown in Table 1 and Table 2. In phase one of the first test, VV sampling methodology was employed to collect a set of three samples in succession (designated with VV-XX-1-0, Table 1). Each of the three samples were collected by pulling an air stream through the gas

reservoir into the sand filled test apparatus and then through a sample line into the VV sampling equipment. Following the collection of each sample, a 0.1-cc sample was withdrawn from the test apparatus from Sample Point 1-0 and analyzed at the test site by gas chromatography.

In the second phase the first test following VV technology sampling, PCVE sampling methodology was employed to collect a second set of three samples in succession (designated with CS-X-1-0, Table 1). Each of the three samples were collected by pulling an air stream through the gas reservoir into the sand filled test apparatus and then through a sample line into the VV sampling equipment. Following the collection of each sample, a 0.1-cc sample was withdrawn from the test apparatus from Sample Point 1-0 and analyzed at the test site by gas chromatography.

Comparison of the average measurement results from the first test of VV and PCVE technologies for the collection of soil vapor sampling indicates excellent agreement between the two sampling technologies. All results are well within the 68% confidence interval. These data indicate the two technologies provide equivalent collection of soil vapor samples.

The data, however, indicated wide variability between individual measurements of both technologies. Individual measurement, however, were less widely distributed for PCVE technology than the individual measurement of the VV technology. This is possibly associated with the more uniform flow rates employed in PCVE technology. Individual benzene, toluene, ethylbenzene, p/m xylene and o-xylene VV measurements ranged from 26.2-75.2, 54.2-102.6, 5.8-8.0, 13.6-20.6, and 6.3-9.0 ppm (volume/volume), respectively. Individual benzene, toluene, ethylbenzene, p/m xylene and o-xylene PCVE measurements ranged from 40.4-62.2, 79.3-95.5, 6.4-9.4, 16.2-23.4, and 6.9-10.1 ppm (volume/volume), respectively. From examination of all test data, the ranges of variability can not be attributed to sample duration, sample flowrate, or total sample volume, with the possible exception for PCVE sample uniformity as noted above.

In phase one of the second test, VV sampling methodology was employed to collect a set of three samples in succession (designated with VV-GRS-X, Table 2). Each of the three samples were collected by pulling an air stream through directly through the gas reservoir, through a sample line, and into the VV sampling equipment. Following the collection of each sample, a 0.1-cc sample was withdrawn from the sample line adjacent to the VV sampling equipment and analyzed at the test site by gas chromatography. Sample durations, sample flowrates, and total sample volumes for the three samples were nominally 60 seconds, 3.0 liters/min., and 3.0 liters, respectively. The temperature of the ice bath was held constant between 2.1 and 2.3 °C.

In the second phase the second test following VV technology sampling, PCVE sampling methodology was employed to collect a second set of three samples in succession (designated with CS-GRS-X, Table 2). Each of the three samples were collected by pulling an air stream directly through the gas reservoir, through a sample line, and into the VV sampling equipment. Following the collection of each sample, a 0.1-cc sample was withdrawn from the sample line adjacent to the VV sampling equipment and analyzed at the test site by gas chromatography. Sample durations and total sample

volumes for the three samples ranged from 140-199 seconds and 5.0-5.1 liters, respectively. The sample flowrate was maintained nominally constant at 2.2 liter/min. The temperature of the ice bath was held constant between 2.1 and 2.3 °C.

Again, comparison of the average measurement results from the second test of VV and PCVE technologies for the collection of vapor sampling indicates excellent agreement between the two sampling technologies. All results are well within the one sigma level of confidence. These data also indicate the two technologies provide equivalent collection of vapor samples.

Individual measurement of both technologies again exhibited wide variability. Individual benzene, toluene, ethylbenzene, p/m xylene and o-xylene VV measurements ranged from 31.2-69.7, 49.3-134.0, 4.2-9.2, 10.6-34.2, and 4.8-15.1 ppm (volume/volume), respectively. Individual benzene, toluene, ethylbenzene, p/m xylene and o-xylene PCVE measurements ranged from 21.5-77.9, 47.8-143.8, 5.9-15.7, 13.8-34.9, and 6.2-16.6 ppm (volume/volume), respectively. Again, an examination of all test data cannot attributed the variability to sample duration, sample flowrate, or total sample volume.

Another objective of the field tests was to demonstrate that soil vapor samples collected in small portable sample cylinders by PCVE technology are applicable for subsequent in-field and/or laboratory analysis. In Table 3 are the results of actual measurement results for samples collected in four individual small portable samples cylinders. Shown for each sample cylinder are the inlet sample concentrations determined from the analysis of three or more aliquots of sample air entering the individual PCVE cylinders, and corresponding sample cylinder concentrations determined from the analysis of an aliquot of the sample cylinder following the expansion of a portion into a sample manifold.

As shown in Table 3, the sample inlet concentration and sample content concentration data are not consistent. In general, the sample inlet concentrations are higher than the sample cylinder concentrations in sample cylinder of lowest total sample pressure, and the sample inlet concentrations are lower than the sample cylinder concentrations in cylinders of the higher total pressure.

The variability of the sample cylinders concentrations for the four cylinders is further demonstrated in Table 4, which presents the concentrations of the individual constituents normalized to ethylbenzene. Also shown in Table 4 are concentrations of the individual constituents of a gasoline vapor sample at ambient conditions normalized to benzene. As shown there is relative small variability in the p/m-xylene and o-xylene ratios and considerable variability in the benzene and toluene. The benzene ratios range from 19.0 to 3.7 and the toluene ratios range from 19.6 to 10.1. This large range of variability is related to the total sample cylinder pressure. At the lower sample cylinder pressures, both benzene and toluene are enriched in comparison to gasoline. At the higher sample cylinder pressure both benzene and toluene are depleted in comparison to gasoline.

These results are attributed to phase changes within the pressurized sample cylinders (Reference 5). At the lower sample cylinder pressures, the sample constituents are present in both a vapor and condensed liquid phase. The more volatile benzene and toluene are present in the vapor phase; the less volatile

ethylbenzene and p/m/o-xylene are present in the condensed liquid phase. As a result, the resultant sample upon withdrawal of a portion of the contents is enriched in the more volatile benzene and toluene components in comparison to gasoline. At the higher sample cylinder pressures, benzene and toluene are also present in the condensed liquid phase. As a result, the resultant sample upon withdrawal of a sample is depleted in benzene and toluene in comparison to gasoline.

Two possibilities exist to overcome the deficiency associated with alteration of sample composition upon the withdrawal of the sample contents. The first is to limit the pressure within the sample cylinder to prevent the formation of two phases. The other more desirable process would pass the entire sample through an adsorber for the selective collection of the components of interest. Although both options for overcoming the deficiency require further investigation, adsorption media (special charcoals) for the collection of constituents of this study are known.

References

1. R. R. Sense, letter to S. J. Fernandez, "Passive Cryogenic Vapor Extraction (PCVE)", dated April 22, 1993.
2. S. J. Fernandez, Fer-53-93, "Petro Site Assessment/WINCO Field Tests - Cooperative Agreement", dated May 28, 1993.
3. B. G. Motes, Moe-12-93, "Petro Site Assessment - Environmental Test Plan", dated June 21, 1993.
4. R. R. Sense, letter to S. J. Fernandez, "Pilot Test", dated June 29, 1993.
5. "Hydrocarbon Mixtures", Scott Tech News Letter, Vol 8, No 1.

Table 1

Measurements Results for VV and PCVE Technologies
(Soil Vapor Extraction From Sand-Filled Test Apparatus)

<u>Sample ID</u>	<u>Benzene</u> ppm v/v	<u>Toluene</u> ppm v/v	<u>Ethyl- Benzene</u> ppm v/v	<u>para/meta- Xylene</u> ppm v/v	<u>ortho- Xylene</u> ppm v/v
VV-9-1-0	26.6	60.0	7.3	20.6	8.6
VV-11-1-0	51.7	54.2	5.8	14.8	6.9
VV-13-1-0	75.2	70.6	5.8	13.6	6.3
VV-15-1-0	58.9	102.6	8.0	20.0	9.0
CS-4-1-0	47.5	79.3	6.4	16.2	6.9
CS-6-1-0	40.4	81.6	7.9	19.7	9.0
CS-8-1-0	62.6	95.5	9.4	23.4	10.1
VV Average	51.2	71.8	6.7	17.3	7.7
1-Sigma	24.3	21.6	1.1	3.6	1.3
CS Average	50.2	85.4	7.9	19.8	8.7
1-Sigma	11.3	8.7	1.5	3.6	1.6

Table 2

*Measurements Results for VV and PCVE Technologies
(Vapor Extraction Directly From Gasoline Reservoir)*

<u>Sample ID</u>	<u>Benzene</u> ppm v/v	<u>Toluene</u> ppm v/v	<u>Ethyl- Benzene</u> ppm v/v	<u>para/meta- Xylene</u> ppm v/v	<u>ortho- Xylene</u> ppm v/v
VV-GRS-1	52.1	93.0	9.2	20.9	8.7
VV-GRS-2	69.7	134.0	15.0	34.2	15.1
VV-GRS-3	31.2	49.3	4.2	10.6	4.8
CS-GRS-1	21.5	47.8	5.9	13.8	6.2
CS-GRS-2	41.1	73.1	7.4	18.9	8.4
CS-GRS-3	77.9	143.8	15.6	35.9	16.6
VV Average	51.0	92.1	9.5	21.9	9.5
1-Sigma	19.3	42.4	5.4	11.8	5.2
CS Average	46.8	88.2	9.6	22.8	10.4
1-Sigma	28.6	49.8	5.2	11.6	5.5

Table 3

*Measurements Results for VV and PCVE Technologies
Sample Inlet Concentrations Versus
Cryogenic Cylinder Content Concentrations*

<u>Sample ID</u>	<u>Benzene</u> ppm v/v	<u>Toluene</u> ppm v/v	<u>Ethyl- Benzene</u> ppm v/v	<u>para/meta- Xylene</u> ppm v/v	<u>ortho- Xylene</u> ppm v/v
<i>Cylinder 1917</i>					
<i>Inlet</i>	92.1	122.6	8.7	20.9	5.8
<i>Contents</i> <i>(750 PSIG)</i>	55.1	56.9	2.9	6.8	2.6
<i>Cylinder 1201</i>					
<i>Inlet</i>	46.8	88.2	9.6	22.8	10.4
<i>Contents</i> <i>(900 PSIG)</i>	70.4	95.0	5.6	12.4	4.2
<i>Cylinder 1191</i>					
<i>Inlet</i>	41.4	74.4	6.9	17.1	7.6
<i>Contents</i> <i>(1600 PSIG)</i>	32.9	54.4	4.2	9.9	4.1
<i>Cylinder 1200</i>					
<i>Inlet</i>	5.5	18.8	3.4	11.7	5.1
<i>Contents</i> <i>(2200 PSIG)</i>	74.2	190.0	17.9	46.6	18.1

Table 4

Measurements Results for VV and PCVF Technologies
Cylinder Content Ratios Versus Sample Cylinder Pressures
(Ratios Normalized to Ethylbenzene)

<u>Sample ID</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Ethyl- Benzene</u>	<u>para/meta- Xylene</u>	<u>ortho- Xylene</u>
Cylinder 1917 (750 PSIG)	19.0	19.6	1.0	2.3	0.9
Cylinder 1201 (900 PSIG)	12.6	17.0	1.0	2.2	0.8
Cylinder 1191 (1600 PSIG)	7.8	13.0	1.0	2.5	1.1
Cylinder 1200 (2200 PSIG)	3.7	10.1	1.0	2.6	1.0
Gasoline	8.7	13.3	1.0	2.8	0.9

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