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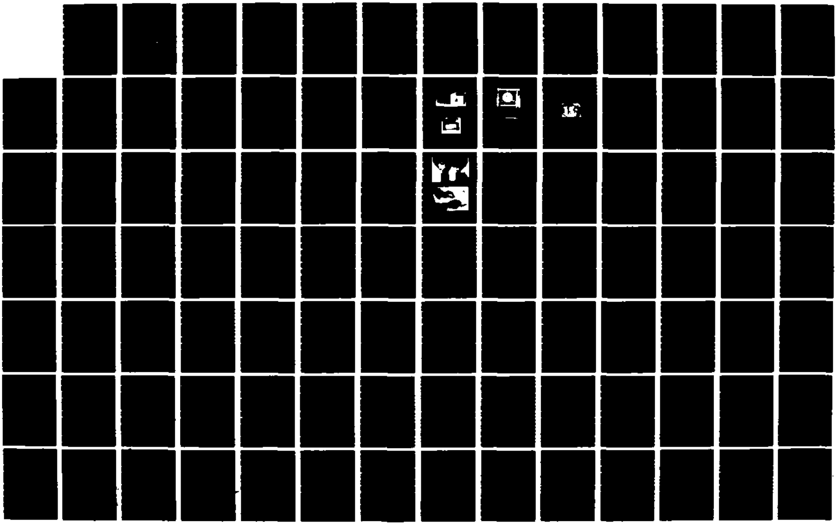

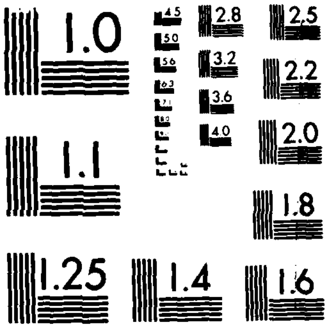

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Task 8. Bench-Scale Investigation of Low Temperature Thermal Removal of TCE from Soil

FINAL REPORT

Walter L. Lambert, Ph.D.
Lawrence J. Bove
David Burkitt
Scott Birk
David J. Russell
Peter J. Marks

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ROY F. WESTON, INC.
West Chester, Pennsylvania 19380

March 1985

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Bench-scale studies were performed to demonstrate the viability of the concept of low temperature thermal volatilization of TCE from soils. A factorial experimental design using multi-way Analysis of Variance (ANOVA) for data analysis was employed. Factors were type of soil (3 levels), TCE concentration (2 levels), operating temperature (3 levels), and moisture content (2 levels). Duplicates were run.

The concept was demonstrated. TCE can be stripped from contaminated soils under the conditions of this study. Complete removal of TCE is dependent on operating conditions.

Statistically significant factors influencing the rate of volatilization were operating temperature, soil moisture (dominant factor), and an undefined interaction between them. Kinetics were proportional to both temperature and soil moisture.

Varying amounts of TCE were not stripped from the tested soil at all experimental conditions at temperatures less than 120°C. The content of these residuals was verified by independent analysis to be TCE. Only TCE was displayed as output traces by the experimental apparatus.

All of the experimental factors and each of their binary combination were statistically significant to the magnitude of TCE residual concentrations. Operating temperature was the dominant factor.

Engineering data implications based on experimental results are:

(a) Operating temperatures for pilot-scale equipment should be greater than or equal to 120°C for complete removal of TCE in less than 20 minutes.

(b) Pilot-scale equipment should be of sufficient flexibility to permit verification of the results of this study and experimentation to optimize operating parameters.

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1. EXECUTIVE SUMMARY

1.1 Volatilization kinetics. Volatilization kinetics, as related to this study, is defined as the rate of volatilization of TCE from the three selected soils. Volatilization kinetics was dependent upon a subset of experimental factors tested. Statistically significant factors were:

(a) Operating temperature.
(b) Soil moisture (dominant factor).
(c) Interaction between (a) and (b).

Relationships indicated by the experimental data were:

(a) Kinetics proportional to operating temperature.
(b) Kinetics proportional to soil moisture.
(c) Kinetics proportional to a combination of temperature and moisture.

1.2 TCE residuals. A residual did exist under most of the experimental conditions of this study. Evaluation of residuals was made on the basis of residual proportion to total TCE volatilized so that direct comparison of data could be made without reference to specific soil properties (e.g., sample weight and soil density). Statistically significant factors were:

(a) Operating temperature (greatest stripping of TCE at operating temperature of 120°C).
(b) Soil type.
(c) Soil moisture.
(d) Interaction between temperature and soil type.
(e) Interaction between temperature and soil moisture.

Operating temperature was the dominant factor.

Relationships indicated by statistical analysis of the data were:

(a) Residual fraction inversely proportional to temperature.
(b) Residual fraction inversely proportional to soil moisture.
(c) Residual fraction inversely proportional to one or more soil parameters which placed the three soils in the following order of increasing residual, other conditions remaining constant: Letterkenny, Pennsylvania > Twin Cities, Minnesota > Sharpe, California.

(d) Residual fraction inversely proportional to an undefined interaction between soil type and operating temperature.
(e) Residual fraction inversely proportional to an undefined interaction between soil moisture and operating temperature.

TCE concentration was not statistically significant to the behavior of residual fractions.

1.3 Engineering implications. The obvious and consistent patterns in temperature dependency of both kinetics and residuals implies that significant residuals should remain from attempts to air strip TCE from soils at ambient temperatures and treatment times less than 20 minutes. The kinetics factor must be taken into account. Pilot studies may reveal that ambient temperatures merely prolong the stripping process and the end result is the same regardless of temperature. This has to be verified. Data from this study imply that ambient stripping will leave an undesirable residual.

Temperatures above ambient are required to improve stripping kinetics and to minimize residuals. The operating temperature should reach 110 to 120°C for complete stripping of TCE. Co-volatilization of water vapor with the TCE may assist in completely scrubbing the TCE residual. This has to be verified.

Machinery for stripping TCE from soil may be of two types. The first is a single chamber device operating at the appropriate temperature throughout. The second is a two-stage device having a low temperature first stage and a high temperature second. A comparative evaluation is required to be able to recommend which generic type may be most applicable.

Equipment most readily adaptable to pilot testing of thermally induced volatilization comes from the field of commercial drying.

The protocol for pilot testing should be designed to verify the conclusions of this study and to provide answers to engineering questions of optimization.

Machinery employed for pilot testing should have sufficient controls to permit parametric testing of both design and operational parameters. Compromises will be required to avoid the necessity of custom construction. Parameters include feed rate, TCE concentration, operating temperature, soil moisture, feed preparation, agitation rate, and air recycle rate.

Options for equipment include actual pilot-scale machinery and small-scale commercial machinery. A brief survey of the equipment market revealed that both options are conceptually viable. Actual selection will depend on availability, configuration, cost, and dependency on proprietary designs.

2. PURPOSE AND OBJECTIVES

2.1 Reference. The primary reference for this report is, "Test Plan for a Bench-Scale Investigation of Low Temperature Thermal Removal of TCE from Soil," prepared by Roy F. Weston, Inc. for the U.S. Army Toxic and Hazardous Materials Agency, January 1984. Full text is presented as Appendix A.

2.2 Purpose. Low temperature stripping of TCE from aqueous solutions has been demonstrated to be an economical and practical process. However, information concerning low temperature removal from a soil medium is limited. The purpose of this investigation was to determine the factors that would affect removal efficiency.

This experimentation was the first component of a phased developmental scheme for promising soil decontamination technologies. Results of this testing will be applied to pilot-scale investigations for verification of the concept and for evaluation of engineering design and performance parameters.

2.3 Objectives. The primary objective of the investigation was to decide if the concept of low temperature thermal removal of TCE merits pilot-scale testing.

Secondary objectives included the following:

(a) Identification of process sensitive parameters, including an analysis of sensitivity.
(b) Indications of optimum ranges of operational parameters.
(c) Indications of the type of pilot- and full-scale equipment that may be most applicable.

2.4 Criteria for positive test of concept. A positive test of concept is volatilization (stripping) of TCE from soils to nondetectable levels of the instrumentation employed for this study.

This criterion is based on anticipated requirements for volume production through commercial equipment. The available equipment itself demands an operating temperature in the range of ambient to 400°F. Economical throughput requires a soil residence time measured in minutes. The absence of a universally acceptable residual level of TCE in soils, and the exploratory testing for potential engineering performance (mass balance on TCE around the test system) require that all detectable levels of TCE be removed for positive test of concept.

3. PARAMETERS AND TEST CONDITIONS

3.1 Test parameters.

3.1.1 Definitions.

(a) Parameter. This is a measurable property or characteristic that may be quantified as part of bench-scale testing. The word is also used for constants, coefficients, and exponents that describe statistical populations. Both uses of the word will be applied in this test plan.

(b) Experimental variable. This is a parameter that is under investigation. Experimental variables are either dependent or independent. The latter are controlled, and their values are predetermined. The former are uncontrolled, and their values are monitored and measured.

3.1.2 Relevant test parameters. Thirty-seven parameters were identified as having relevance to this study. Of those, 18 were soil characteristics that were fixed by the source and type of soils to be used. The remainder were associated with either experimental or full-scale operation of potentially adaptable commercial equipment. Each of the parameters was considered to be a candidate experimental variable. An analysis of each was conducted, and the results are shown in Table 1.

All of the parameters in the list were either controllable or not. Some had relevance to bench testing, and all had relevance to full-scale operations. All were measurable. If used as an experimental variable, some were judged to be dependent in that they were judged to be products of a commercial operation. Others were judged to be independent because they were either fixed by materials to be used or could be controlled independently of one another.

Experimental variables were identified as parameters meeting the following set of criteria:

(a) Controllable.
(b) Relevant to bench-scale investigations.
(c) Measurable.
(d) Not fixed by preservation method, source of material, or condition of supply, e.g., TCE-free purge gas supplied in that condition in cylinders.

TABLE 1. ANALYSIS OF EXPERIMENTAL VARIABLES

Parameter, characteristics, descriptor, variable, or condition	Controllable?	Relevance to phases of testing				Measurable/ method	As an experimental parameter		Sample type		Test plan classification of parameter		
		Bench	Breadboard	Pilot	Production		Independent	Dependent	Discrete	Continuous	Dependent	Independent	Experimental parameter, but not a variable
1. Moisture content, soil, initial	Yes	X	X	X	X	Yes -- ASA 7-2.2	X		X			X	
2. Moisure content, soil, final	No			X	X	Yes -- ASA 7-2.2		X	X				
3. Moisture content, soil, interim	No			X	X	Yes -- Mass balance calculation - ASA 7-2.2		X	X				
4. Moisture content, purge gas, inflow	Yes -- bench Yes -- production			X	X	Yes -- fixed-dry	X		X				
5. Moisture content, purge gas, outflow	No -- bench No -- production			X	X	Yes -- GC		X	X				
6. Temperature, oven environment	Yes	X	X	X	X	Yes -- thermocouple, direct reading	X			X		X	
7. Temperature, soil sample, initial	Yes	X	X	X	X	Yes -- thermocouple, direct reading, fixed	X		X				X
8. Temperature, soil sample, interim	No			X	X	Yes -- thermocouple, direct reading		X		X			X
9. Temperature, soil sample, final	Yes			X	X	Yes -- thermocouple, direct reading		X	X				X
10. Temperature, purge gas, inflow	Yes	X	X	X	X	Yes -- fixed at oven temperature	X			X			X

TABLE 1. (CONTINUED)

	Parameter, characteristics, descriptor, variable, or condition	Controllable?	Relevance to phases of testing				Measurable/ method	As an experimental parameter		Sample type		Test plan classification of parameter		
			Bench	Breadboard	Pilot	Production		Independent	Dependent	Discrete	Continuous	Dependent	Independent	Experimental parameter, but not a variable
11.	Temperature, purge gas, outflow	Yes			X	X	Yes -- fixed at oven temperature		X		X			
12.	TCE concentration, soil, initial	Yes	X	X	X	X	Yes -- method-	X		X			X	
13.	TCE concentration, soil, interim	No	X	X			Yes -- computed by mass balance		X	X		X Computed		
14.	TCE concentration, soil, final	No	X	X	X	X	Yes -- method-		X	X		X Computed		
15.	TCE concentration, purge gas, inflow	Yes			X	X	Yes -- fixed at zero	X		X				X
16.	TCE concentration, purge gas, outflow	No	X	X	X	X	Yes -- GC sample method		X	X		X Measured		
17.	Weight, soil sample, dry	Yes	X	X	X	X	Yes -- ASA 7-2.2 "fixed"	X		X				X
18.	Time of volatilization	No	X	X	X	X	Yes -- elapsed time, GC computer	X			X			X
19.	Flow rate, purge gas	Yes	X	X	X	X	Yes -- mass flowmeter, GC	X			X		X	
20.	Soil characteristics	Fixed source	X	X	X	X	Yes	X		X			X	

Independent experimental variables for consideration in this study were the following:

(a) Moisture content, soil, initial.
(b) Temperature, oven.
(c) TCE concentration, soil, initial.
(d) Flow rate, purge gas.
(e) Soil characteristics (18 characteristics).

Dependent experimental variables were the following:

(a) TCE concentration, purge gas, outflow (measured), continuous.
(b) TCE concentration, soil, interim (computed).
(c) TCE concentration, soil, final (measured).

Experimental parameters for monitoring were the following:

(a) Temperature, soil sample, initial.
(b) Temperature, soil sample, interim.
(c) Temperature, soil sample, final.
(d) Temperature, purge gas, inflow.
(e) TCE concentration, purge gas, inflow.
(f) Weight, soil sample, dry.
(g) Time.

3.2 Test apparatus.

3.2.1 Background. Thought was given to the types of commercial-scale equipment that might be used for volatilization of TCE from soils. A brief review of chemical and metallurgical processing equipment resulted in industrial dryers being the prime candidate for full-scale operations. A brief survey of dryer manufacturers and vendors was completed. It was evident from discussions with vendors that a bench-scale study using a general apparatus could not simulate the engineering performance of a full-scale unit. Therefore, the thrust of the bench study was proof of concept.

Considerations for selection, design, configuration, and operation of bench-scale apparatus included the following:

(a) A soil sample size in the 1 to 10 gram range.
(b) A flow-through purge gas.
(c) Temperature control to within 1-degree Celsius.
(d) Analytical equipment to determine quantities of TCE.

3.2.2 Test apparatus. Based on the considerations discussed above, it was concluded that all of the requirements for control, sample size, and detection could be satisfied if the tests were run using the assembly shown in Figure 1.

Figures 2, 3, and 4 are detailed photographs of various components of the test apparatus. Major subsystems of a Hewlett-Packard Model 5880A gas chromatograph (GC) were adapted for use as a simulation system for through-circulation volatilization of TCE from a variety of soils.

The GC oven (Figure 1, item 9) provided a controlled, isothermal environment. It also provided ramped temperatures for TCE residuals volatilization, and for drying soil samples at the end of a run.

Purge gas was dry helium (Figure 1, item 3) which will not interfere with operation of the Hall cell. In a commercial dryer, it would be most economical to operate with ambient air that would have a variable relative humidity. A dry purge gas maximizes the rate of water evaporation, which may cause the slowest rate of TCE volatilization.

Four to six gram samples of spiked soil were held in glass-wool stoppered tubing (Figure 1, item 6) at oven temperature. The sample tube was fitted on either end with swageloc fittings for mating to the purge gas tubing. Inside the sample tube, and imbedded in the soil sample, was a thermocouple (Figure 1, item 5) for recording the temperature of the soil sample during the experiment.

Off-gas carrying TCE and moisture was valved (Figure 1, item 10) to a Hall furnace (Figure 1, item 13) and a Hall detector (Figure 1, item 14) for quantification of TCE. The heated valve assembly (Figure 1, items 10, 11, and 12) provided a series of short duration samples. The series of TCE peaks expected to be generated during a stripping simulation run provided a TCE mass evolution rate (i.e., flux). Integration of the area under the set of curves quantified the total mass of TCE evolved.

Temperatures in the oven and of the soil sample were monitored by thermocouples connected to the GC's real-time clock with printer.

1. Hydrogen flow control
2,3. Nitrogen flow control
4. Divert valve
5. Thermocouple
6. Sample column
7. Glass wool
8. 1/10 in. SS tubing
9. Forced air oven
10. 6 port 3 cross valve
11. Valve oven
12. Valve driver
13. Hall furnace
14. Hall conductivity cell

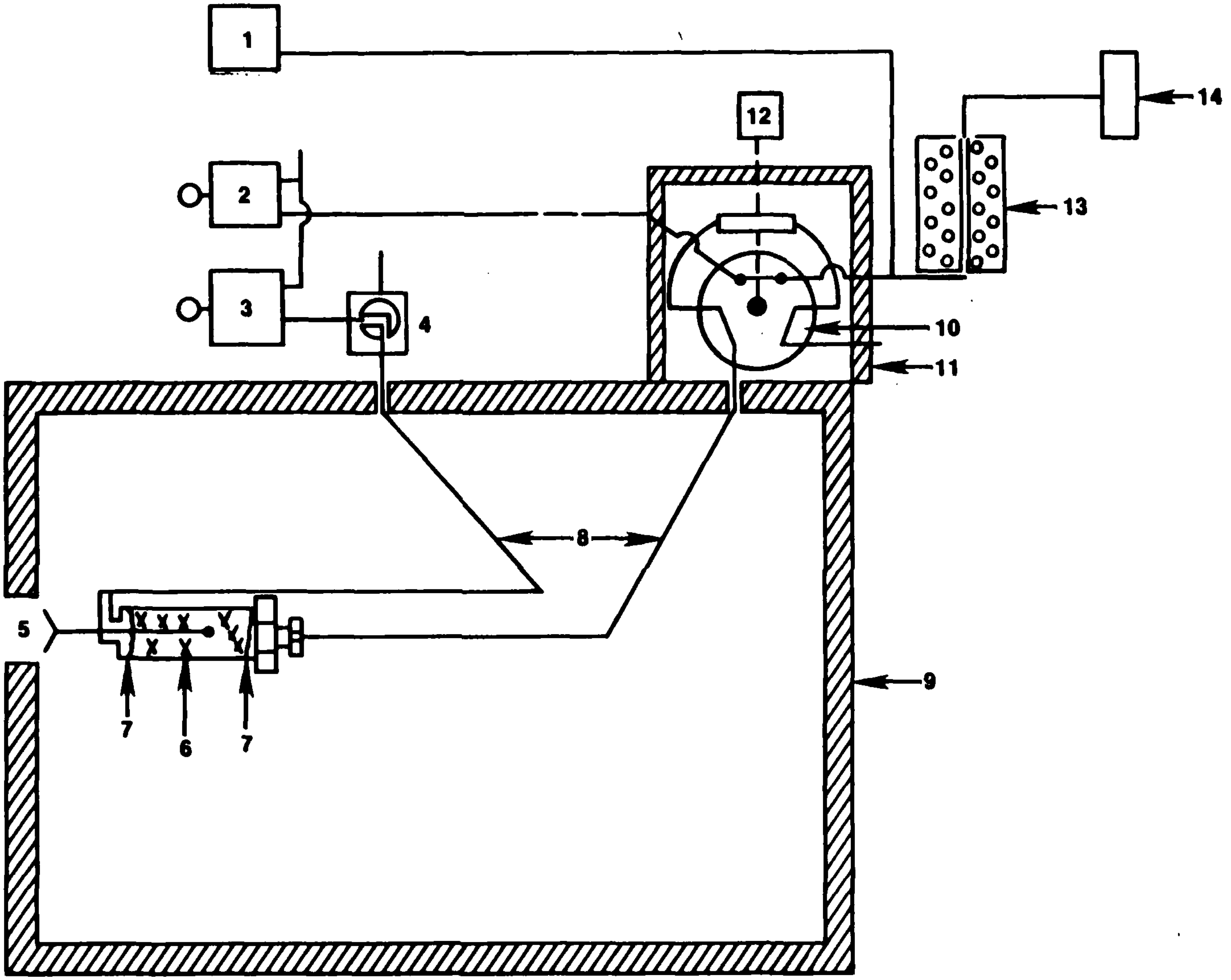


Figure 1. Schematic of the apparatus to measure the volatilization of TCE from soil.

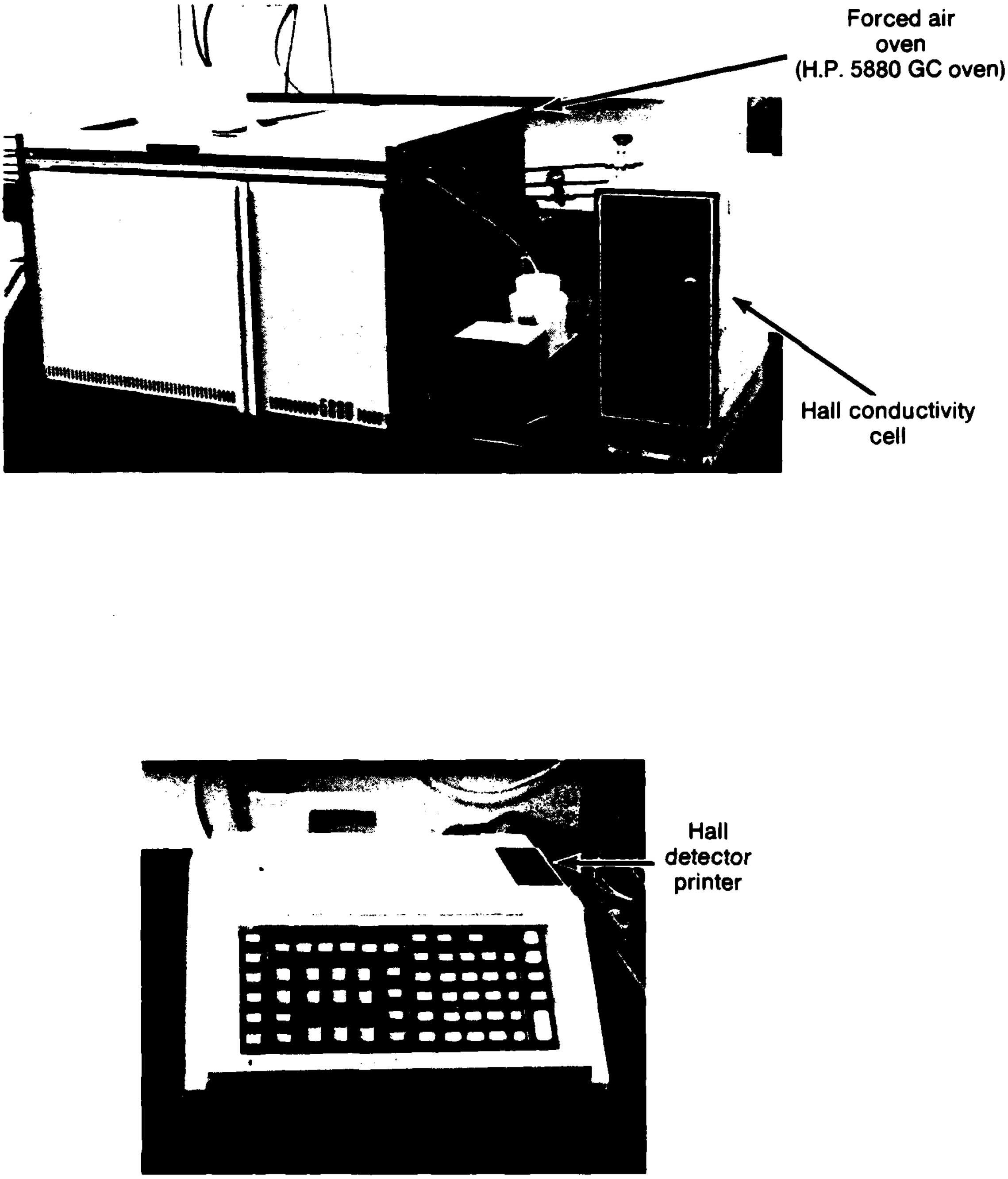


Figure 2. Experimental appartus.

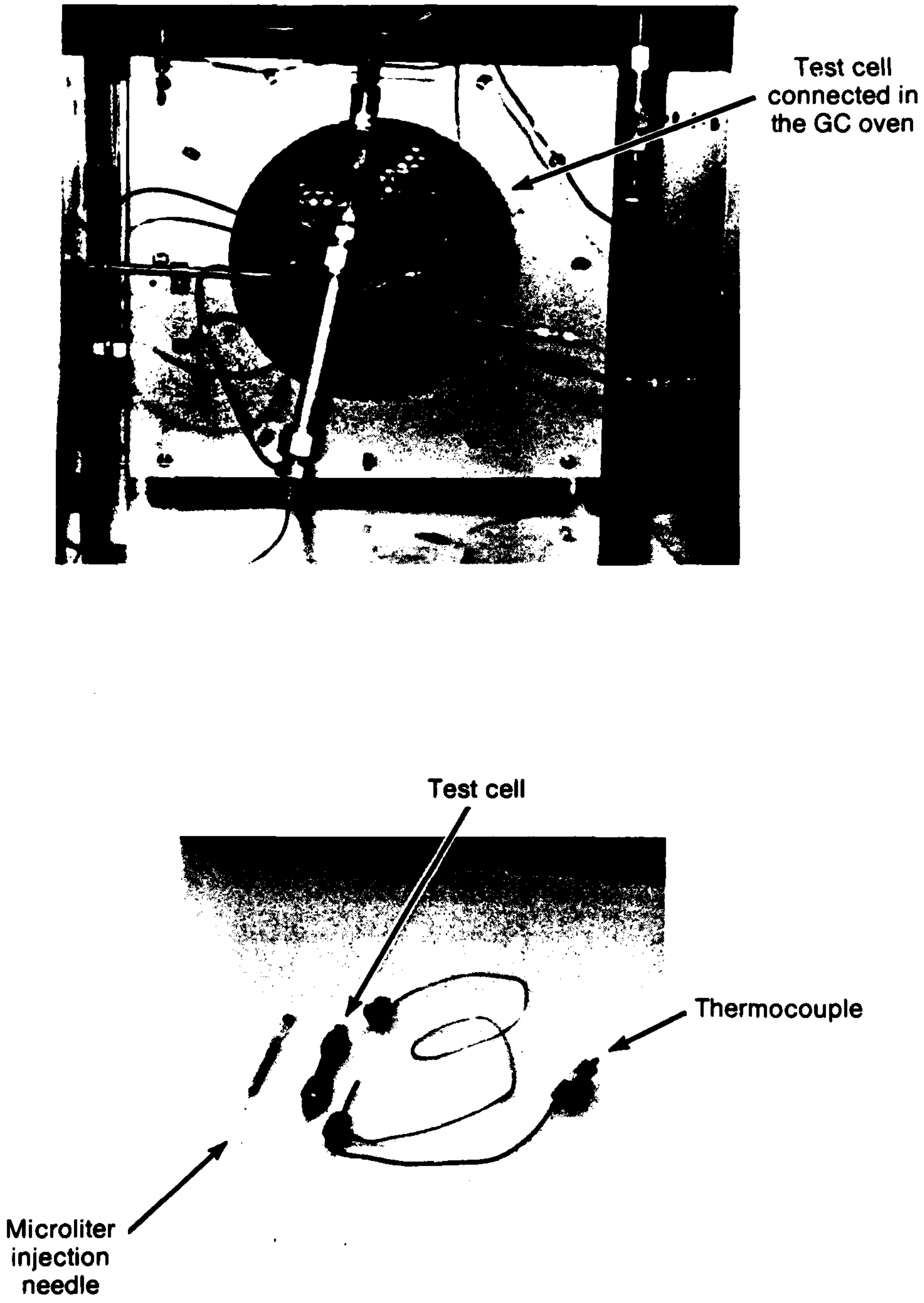


Figure 3. Experimental test cell.

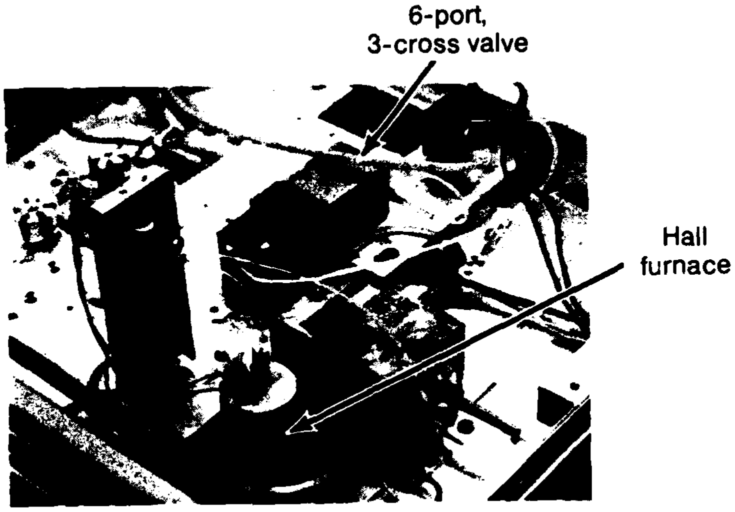


Figure 4. Hall furnace.

3.3 Initial experimental design. A full factorial design with three replicates per test case was originally planned prior to shakedown and operation of the test apparatus. The number of runs was:

(2 levels of soil moisture) x (3 drying temperatures) x (3 TCE concentrations) x (3 soil types) x (3 replicates) = 162 runs.

Identification of each run is provided in Figure 5. Each run is identified by a four-digit number. Each digit denotes one of four experimental variables (factors), and the value of the digit denotes the level (value) of that factor.

The values shown in Figure 5 for each level of the experimental factors were tentative and were based on best estimates at the time of the initial test plan preparation. The final experimental design was determined during the shakedown phase of the project.

The selected sites for sources of test soils were as follows:

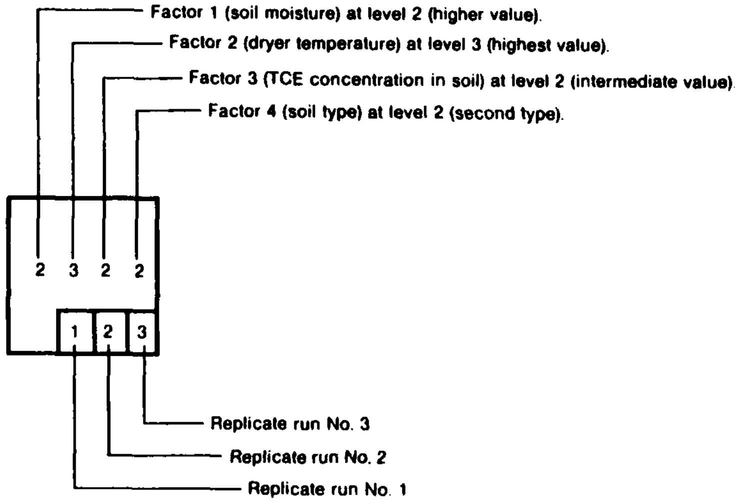
(a) Location 1: Sharpe Army Depot, California (SH).
(b) Location 2: Twin Cities Army Ammunition Plant, Minnesota (TC).
(c) Location 3: Letterkenny Army Depot, Pennsylvania (LK).

These selections were made based on known contamination onsite and anticipated differences of the soil structure at each site. Uncontaminated soils were collected for use in these tests.

		Soil moisture level 1			Soil moisture level 2		
		Dryer temp. level 1	Dryer temp. level 2	Dryer temp. level 3	Dryer temp. level 1	Dryer temp. level 2	Dryer temp. level 3
TCE concentration level 1 in soil	Soil type 1	1111 1 2 3	1211 1 2 3	1311 1 2 3	2111 1 2 3	2211 1 2 3	2311 1 2 3
	Soil type 2	1112 1 2 3	1212 1 2 3	1312 1 2 3	2112 1 2 3	2212 1 2 3	2312 1 2 3
	Soil type 3	1113 1 2 3	1213 1 2 3	1313 1 2 3	2113 1 2 3	2213 1 2 3	2313 1 2 3
TCE concentration level 2 in soil	Soil type 1	1121 1 2 3	1221 1 2 3	1321 1 2 3	2121 1 2 3	2221 1 2 3	2321 1 2 3
	Soil type 2	1122 1 2 3	1222 1 2 3	1322 1 2 3	2122 1 2 3	2222 1 2 3	2322 1 2 3
	Soil type 3	1123 1 2 3	1223 1 2 3	1323 1 2 3	2123 1 2 3	2223 1 2 3	2323 1 2 3
TCE concentration level 3 in soil	Soil type 1	1131 1 2 3	1231 1 2 3	1331 1 2 3	2131 1 2 3	2231 1 2 3	2331 1 2 3
	Soil type 2	1132 1 2 3	1232 1 2 3	1332 1 2 3	2132 1 2 3	2232 1 2 3	2332 1 2 3
	Soil type 3	1133 1 2 3	1233 1 2 3	1333 1 2 3	2133 1 2 3	2233 1 2 3	2333 1 2 3

Note. This is a full factorial experimental design in which there are four factors (experimental variables), three of which are at three levels (three values), and one of which is at two levels (two values).

Each block in the design represents one set of experimental conditions. Each condition is to be run in three replicates. An explanation of the diagram blocks is shown below



Variable	Level 1	Level 2	Level 3
Soil moisture	20%	40%	
Dryer temperature	25°C	90°C	150°C
TCE concentration in soil	10 mg/kg (dry)	100 mg/kg	1,000 mg/kg
Soil type	Location 1	Location 2	Location 3

Figure 5. Initial experimental design for investigating low temperature thermal removal of trichloroethylene from soils.

3.4 Shakedown protocol.

3.4.1 Objectives. The shakedown protocol consisted of a series of experiments performed to acquire data which would identify operational shortcomings of the experimental apparatus at test conditions specified in the original test plan. Listed below were the objectives of the shakedown protocol:

(a) Verify soil handling procedures which included moisture and solvent addition.
(b) Verify integrated experimental apparatus operability at experimental conditions.
(c) Finalize all experimental operating parameters.
(d) Revise initial experimental design to reflect results of shakedown.

3.4.2 Execution. Table 2 summarizes the experiments performed during the shakedown protocol. It is important to note that the protocol was continually revised as new information was generated.

3.4.3 Conclusions. Following are the major conclusions of the shakedown procedure:

(a) The moisture contents originally specified resulted in a sludgelike mud which would result in poor operation of the test apparatus.
(b) Soils must not be air-dried before moisture is added.
(c) Moisture should be added to soil at ambient moisture content and mixed thoroughly by hand to avoid uneven distribution.
(d) Experimental apparatus successfully detected and quantified TCE when the solvent was spiked into an empty test cell.
(e) Purge gas flow-rate was determined to be 20 cubic centimeters per minute.
(f) The third experimental temperature was determined to be 120^{o}C.
(g) Recovery of TCE was best quantified when solvent was directly spiked into a test cell filled with soil and held overnight.
(h) TCE spike volumes were limited by the spiking apparatus to no less than 0.5 uL.
(i) TCE recovery and spike reproducability were best effected when solvent was directly spiked into a test cell and held for at least 16 hours before testing.
(j) Soil moisture adversely affected the detection of TCE by the Hall cell at specified experimental conditions. This resulted in TCE recoveries of over 100 percent (based on the Hall cell readings). This resulted in the modification of the test plan to include dried soils ranging from 0.5 to 1 percent moisture by weight.

TABLE 2. SUMMARY OF SHAKEDOWN TESTING

Purpose of experiment	Description of experiment	Results of experiment	Analysis of results
Verification of soil condition at moisture levels for experiment (20% and 40% moisture content)	Approximately 500 grams of soils from SH, TC, and LK were air-dried and sieved. A predetermined amount of water was added to the soils resulting in 20% and 40% moisture content mixtures. The soils were placed on a rotary mixing device for 24 hours.	Both 20% and 40% mixtures formed muds that would not be acceptable in the planned experimental test cell.	Both 20% and 40% moisture eliminated as the experimental conditions. Decision: Additional testing for both mixing and moisture addition need to be initiated.
Determination of ambient moisture content of the soils	Soils from SH, TC, and LK were sieved. Standard moisture content tests were performed.	Native soil moistures: SH: 7.5% TC: 11.5% LK: 17%	Ambient moisture would constitute a moisture level to be tested. Decision: Further testing would be initiated to increase moisture on SH to 10% and TC and LK to 20%.
Verification of moisture addition technique for upper level moisture content for all soils (using new moisture addition technique)	Approximately 500 grams of soil from SH, TC, and LK were sieved. Moisture was added to SH, TC, and LK resulting in moisture contents of 10%, 20%, and 20%, respectively. Moisture was added slowly with hand mixing of soils using a hand trough. (This process was used so that mud balls would not form during rotary mixing.) Soils were mixed 24 hours on the rotary mixer.	SH at 10% moisture produced a soil mixture with an apparent even distribution of moisture. TC and LK at 20% moisture produced many ball-like structures.	SH soils can be spiked to 10% moisture content and produce a mixture with properties acceptable for testing. TC and LK at 20% moisture were unacceptable due to apparent uneven moisture distribution evidenced by the formation of the ball-like soil stuctures. Decision: Further testing to raise TC soil to 14% moisture content and to lower LK to 12 to 13% moisture.
Verification of moisture addition technique for upper level moisture content for TC soils	Approximately 500 grams of TC soil (ambient condition 11.5% moisture) was sieved. A calculated amount of water was added which resulted in a mixture containing 14% moisture. The mixing technique described above was utilized for this test.	Mixing produced a soil mixture with an apparent even distribution of moisture.	14% was accepted as the upper level moisture level in the experimental test plan.

TABLE 2. (CONTINUED)

Purpose of experiment	Description of experiment	Results of experiment	Analysis of results
Verification of moisture reduction technique for LK soil	Approximately 500 grams of LK soil (ambient condition 17% moisture) was sieved and air-dried for 1 hour. A portion of this sample then underwent standard %-moisture test.	Resultant soil moisture content of LK soil was 13%.	LK soil would be tested at 13% and 17% moisture content. The procedure in this test will be used for reducing moisture content in LK soils.
Verification of operability of experimental equipment	An experimental test cell was filled with approximately 5 grams of SH soil at ambient moisture conditions and placed in the GC oven, which had been modified to the desired experimental scheme pictured in Figure 1. An operating temperature of 90°C was established. Test was repeated for all soils.	Hall detector results indicated presence of detectable compound in the ambient soil. In addition, system plagued by short circuit at GC.	Soils were submitted for a GC/MS fraction for volatile compounds. Short circuit was caused by thermocouples. As a result insulated thermocouples have been ordered to prevent this from occurring.
Identification of compounds which resulted in interferences on the Hall detector	All soils submitted for GC/MS fraction for volatile compounds.	No compounds which may be detected on a Hall detector were identified. Test results in Appendix A.	Soils contain no interference. Experimental equipment needs further testing.
Identification of source of interferences observed on Hall detector	An experimental test cell using SH soil was filled and tested as described above. In addition, an empty test cell was tested at the same conditions.	Detectable compounds were observed by the Hall detector for both test cells.	The ambient soil is not the cause of the interference. Test cells and Hall detector system need further investigation.
Identification of source of interferences observed on Hall detector	All test cells were baked at 400°C in order to volatilize any potential compound causing interference on the Hall detector. Selected empty cells were tested on the experimental apparatus at 90°C as described above.	Detectable compounds were observed on the Hall detector for all selected test cells.	Test cells are not a source of interference detected by the Hall detector. Decision: Hall detector was taken out-of-service for routine maintenance.
Identification of source of interference observed on Hall detector	Empty cell tested on experimental apparatus at 90°C using method described above. Repeated for three additional cells.	No detectable compound observed.	Contaminated Hall detector system caused observed detected material. System now operates with all components connected.

TABLE 2. (CONTINUED)

Purpose of experiment	Description of experiment	Results of experiment	Analysis of results
Verification of operability of system with soils at experimental moisture conditions	Soils at ambient moisture conditions were placed in test cells and tested on the experimental apparatus at 90°C. One run for each soil.	No detectable compound observed.	Experiment operates properly in the presence of soil at an experimental moisture level.
Establishment of purge gas rate through test cell	A test cell was filled with approximately 5 grams of soil at ambient moisture levels. The loaded cell was baked at 175°C to remove moisture from soil. The cell was spiked with 0.05 microliter (uL), 0.5 and 5 uL[1] of TCE (at 25°C). Purge gas rate set at 20 cm^3/minute. Test repeated for 40 cm^3/minute, 60 cm^3/minute, and 80 cm^3/minute.		20 cm^3/minute was established rate for helium purge gas.
Establishment of valve opening rate	Experimental protocol same as above. Valve tested at various speeds ranging from 0.02 minute per opening to 0.1 minute per opening.		
Verification of operability of system with TCE at experimental quantities; production of TCE standard	Empty test cells were spiked directly with 0.05 uL, 0.5 uL, and 5 uL of TCE (at 25°C). Test cells were immediately tested in experimental apparatus at 27°C for 15 minutes followed by ramping of temperature to 175°C with an additional 15-minute hold time. Each spike was run in triplicate.	Hall detector verified presence of a detectable material. Only 0.5 uL and 5 uL spikes resulted in consistent reading on Hall cell.	Results using 0.5 uL and 5 uL TCE spike were used to produce a TCE standard line. This relates unit area detected by the Hall cell with actual TCE concentration. Observation: It is evident that performance of a standard curve at 0.05 uL will be difficult due to the accuracy of the spiking apparatus.

---

[1] 0.05 uL is equivalent to a TCE concentration of 15 ppm, 0.5 uL equivalent to 150 ppm, 5 uL equivalent to 1,500 ppm, assuming sample size was 5 grams. Sample sizes varied from 4 grams to 6 grams depending on the test cell and the type of soil.

TABLE 2. (CONTINUED)

Purpose of experiment	Description of experiment	Results of experiment	Analysis of results
Verification of equipment performance at anticipated experimental moisture levels and TCE concentrations	Soil samples spiked with TCE and water in 1 liter amber glass jar. All jars spiked at 4°C. 5 grams of soil of known moisture content and TCE concentrations is fed into a test cell in a refrigerated area. The cell is held 24 hours before testing. During testing sample is held at operating temperature for 10 minutes before system ramps temperature to 175°C at a rate of 25°C per minute. Multiple soil samples plus standards were executed (operating temperatures: 27°C and 90°C; moisture levels were SH: 7.5% and 10%; TC: 11.5% and 14%; LK 13% and 17%).	Hall detector readings indicated specific patterns of TCE emissions at a specific operating temperature. Results indicated inconsistencies when comparing Hall detector readings during experimental runs versus TCE recovery standards. These inconsistencies ranged from 2% recovery to 800% recovery.	Further shakedown testing necessary to determine third temperature based on data acquired. It is likely that TCE is volatilizing in the headspace of the soil stock bottles. TCE may be lost in an inconsistent manner during this time period. At this time it has not been established that TCE is homogeneously present in the spiked soil stock bottle. As a result of this test it has been decided to abandon initial spiking technique. From this time all test cells will be spiked directly. This decision eliminates 10 ppm as an experimental test condition.
Development of temperature profile curves	Approximately 5 grams of soil was spiked with 1 uL of TCE (at 25°C) and was tested immediately. (3 soils) x (2 temperatures -- 27°C, 90°C) x (1 TCE concentration) x (2 moistures). Operating temperature was maintained for 10 minutes before ramping occurred (as described above).	Data acquired allowed plot of operating temperature and soil temperature versus time. In addition, data indicated at which time last traces of detectable materials were observed on the Hall detector.	Plots established that the third temperature for this experiment would be 120°C. In addition, moisture content appears to be an important factor in temperature differences between operating temperature and actual soil temperature observed.
Verification of ambient moisture levels	All soils were tested for moisture levels using the standard test method.	Moisture levels -- SH: 4.0% TC: 7.5% LK: 15.0%	Due to increased human handling, air contact with soils has lowered moisture levels. No adverse effects are expected as a result of the lower ambient moisture.

TABLE 2. (CONTINUED)

Purpose of experiment	Description of experiment	Results of experiment	Analysis of results
Determine TCE recovery patterns versus time	Test conditions: SH soil in test cell, 5 uL TCE spike directly into cell at refrigerated temperatures. Cells to be held from 0 to 24 hours. Two temperatures -- 27°C and 90°C. TCE recovery (in unit area) to be observed. Operating temperature to be maintained for 10 minutes followed by ramping to 175°C.	Hours / 27°C / 90°C T=0 / 62,000 / 108,800 T=1 / 66,600 / 3,900,900 T=4 / 61,400 / 192,900 T=8 / 66,400 / 56,900 T=24 / 76,900 / 36,700 STANDARD = 60,100	Data do not indicate any clear patterns. Several parts in this test are much greater than the standard, indicating an operational difficulty with the experimental system. As a result of this test, hold time for test cells directly spiked will remain 24 hours. Decision: Future testing will study recovery of TCE in more detail.
Verification of third temperature and finalization of operating time before ramping	LK soil at ambient moisture is spiked in the test cell and held for 24 hours. System was operated at 120°C. No ramping occurred. Sample run in duplicate.	In both tests, 90% removal of TCE occurred at *10 minutes and* 12 minutes, respectively.	Decision: Operating time will be 14 *minutes for all samples. New temperature* profile curves are required for this operating condition.
Determination of TCE concentrations to be used during experimentation	SH soil at ambient moisture to be spiked at refrigerated conditions in test cell and held for 24 hours. Concentrations in cell to range from 100 ppm to 1,500 ppm. Tests to be performed at 120°C using time scheme determined above. Samples run in duplicate.	No results from any test cell.	Investigations which occurred following this test indicated that test cells were not spiked due to pluggage in *microliter hypodermic* needle. Decision: A similar test should be executed at a later date.
Determination of TCE concentrations to be used during experiment	LK soil at ambient moisture to be spiked at refrigerated conditions in test cell and held for 24 hours. Spike volumes of 0.2, 0.3, and 0.5 uL correspond to concentrations of 40, 60, and 100 ppm TCE in the test cell, assuming a 5 gram sample. Test to be performed at 27°C using operating time scheme of 14 minutes at operating temperature *followed* by ramping to 175°C.	TCE Spike Volume / % Recovery 0.2 uL / 183 0.3 uL / 69 0.5 uL / 54 Percent recovery based on standards run during the experiment.	Inconsistencies remain. Data inconclusive. Decision: Additional testing necessary to determine experimental concentrations.

TABLE 2. (CONTINUED)

Purpose of experiment	Description of experiment	Results of experiment	Analysis of results
Verification of TCE recovery and spike reproducability	All soils at ambient moistures were spiked with 1 uL of TCE directly into a test cell (resulting in a TCE concentration of 300 ppm) and held for 24 hours. Experiment executed at 120°C using operation scheme mentioned above. Samples run in duplicate. Data indicated the SH soils percent recovery ranged from 160 to 200%. TC and LK ranged from 20% to 700% recovery.	TCE was volatilized before ramping occurred. For all cases time for 90% removal was between 1.63 and 2.13 minutes. Results for all soils indicated a percent recovery of 160% to 700% for all soils tested as observed on the Hall detector. Data indicated the SH soil percent recovery ranged from 160% to 200%. TC and LK ranged from 200% to 700% recovery.	There is evidence that results are consistent in terms of time of volatilization, but at this period a material balance cannot be developed. There is some factor, or combination of factors, which causes recovery to consistently exceed 100%; this factor has yet to be determined.
Determination of moisture effect on function of Hall detector	All soils were oven dried for 1 hour at 110°C. Once soil cooled it was placed into test cells and spiked directly with TCE at 27°C. Spike amounts were 1 uL and 5 uL. Test conditions were at 120°C using above operating conditions.	System yielded TCE recoveries of 120 to 160% of spike.	Data indicated that moisture has an effect on the operation of the experimental test apparatus, but other factors cause yield of over 100%. Spiking errors may account for these errors. In addition, volatilization of TCE in dry soil was slowed as compared to test runs at ambient moisture levels. Decision: Operating times for experimentation would be increased to 20 minutes.

3.5 Experimental design. Information learned during the shakedown phase was applied against the original experimental design for 162 runs. It was evident that a modified test plan was appropriate. A two-phase design using the same factorial concepts as the original design was formulated. Phase I was:

(1 level of soil moisture) x (3 operating temperatures) x (2 TCE concentrations) x (3 soil types) x (2 replicates) = 36 runs

Phase II was:

(1 level of soil moisture) x (3 operating temperatures) x (1 TCE concentration) x (3 soil types) x (2 duplicates) = 18 runs

A summary of the experimental design is illustrated in Figure 6.

3.6 Experimental procedure. The shakedown protocol produced data which directly affected the experimental procedure. The following subsections outline the procedures used to perform this experiment.

3.6.1 Soil handling. Approximately 2.0 kilograms of soil collected from the designated site at ambient moisture conditions was sieved through a 2-millimeter screen. The resultant soil was mixed and divided into two approximately equal volumes. One volume was immediately stored in a 1-liter amber glass container. The remaining soil was dried overnight at 60°C. At 60°C, soil is dried to less than 2 percent (weight percentage) of the mixture while minimizing the potential for changing organic properties. Moisture content was determined using standard tests for both dried and ambient soils before execution of the experiment.

3.6.2 Preparation of test cells. Prefabricated test cells were filled with soil of a specific type and moisture content using a metallic laboratory spatula as pictured in Figure 7. The soil was packed into the tube using a pipe cleaner.

Cells were spiked with either 1 uL or 5 uL of TCE via hypodermic needle injection directly into the test cell at room temperature. Once spiked, the cell was immediately sealed and stored at room temperature for at least 16 hours before testing. The spiking technique is pictured in Figure 7.

		Soil moisture level 1			Soil moisture level 2		
		Dryer Temperature 1	Dryer Temperature 2	Dryer Temperature 3	Dryer Temperature 1	Dryer Temperature 2	Dryer Temperature 3
TCE Concentration Level 1	Soil 1	1111 1 2	1211 1 2	1311 1 2	2111 1 2	2211 1 2	2311 1 2
	Soil 2	1112 1 2	1212 1 2	1312 1 2	2112 1 2	2212 1 2	2312 1 2
	Soil 3	1113 1 2	1213 1 2	1313 1 2	2113 1 2	2213 1 2	2313 1 2
TCE Concentration Level 2	Soil 1	1121 1 2	1221 1 2	1321 1 2			
	Soil 2	1122 1 2	1222 1 2	1322 1 2			
	Soil 3	1123 1 2	1223 1 2	1323 1 2			

Variable	Level 1	Level 2	Level 3
Soil moisture	Dried at 60°C	Ambient	
Dryer temperature	27°C	90°C	120°C
TCE Concentration	1μL[a]	5μL[a]	
Soil type	Sharpe	Twin Cities	Letterkenny

[a] Concentrations of TCE in soil are 300 ppm for the 1μL spike and 1,500 ppm for the 5μL spike assuming a 5 gram test sample of soil.

Each block in the design represents one set of experimental conditions. Each condition is to be run in two replicates. An explanation of the diagram blocks is shown below.

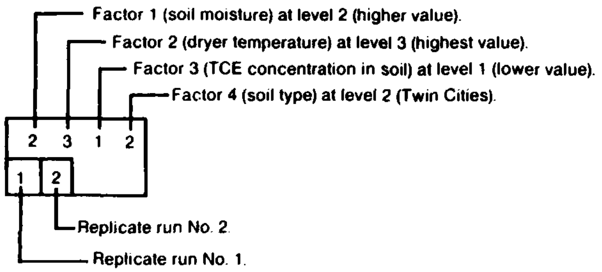
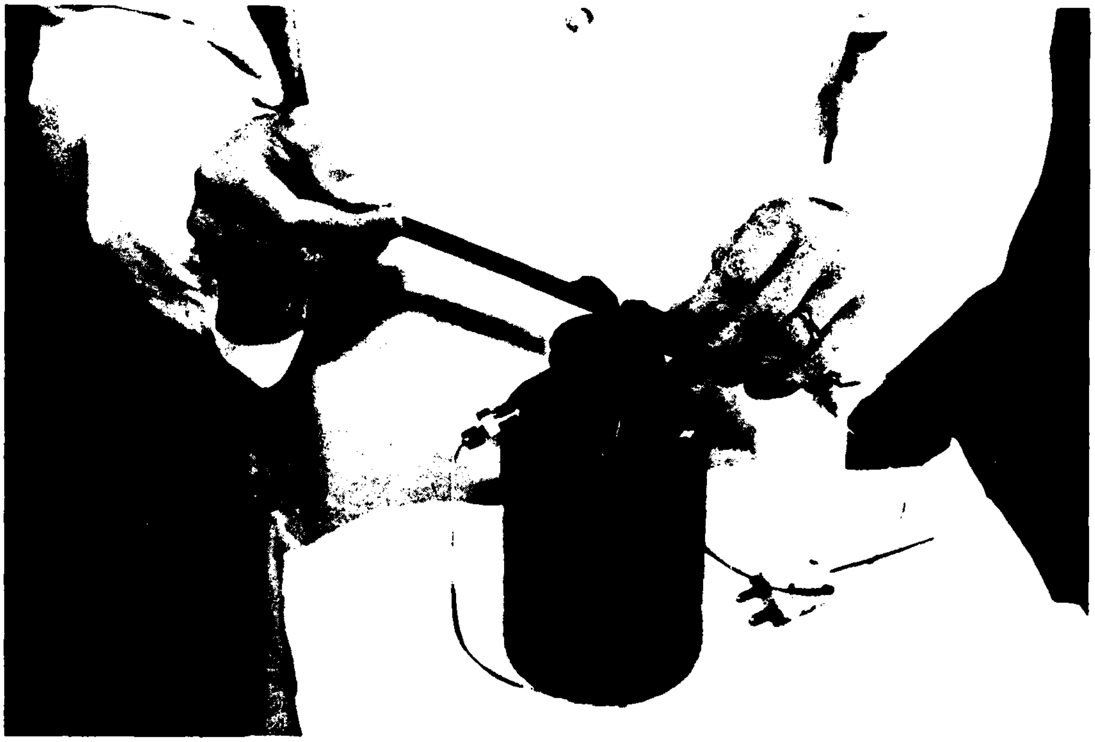
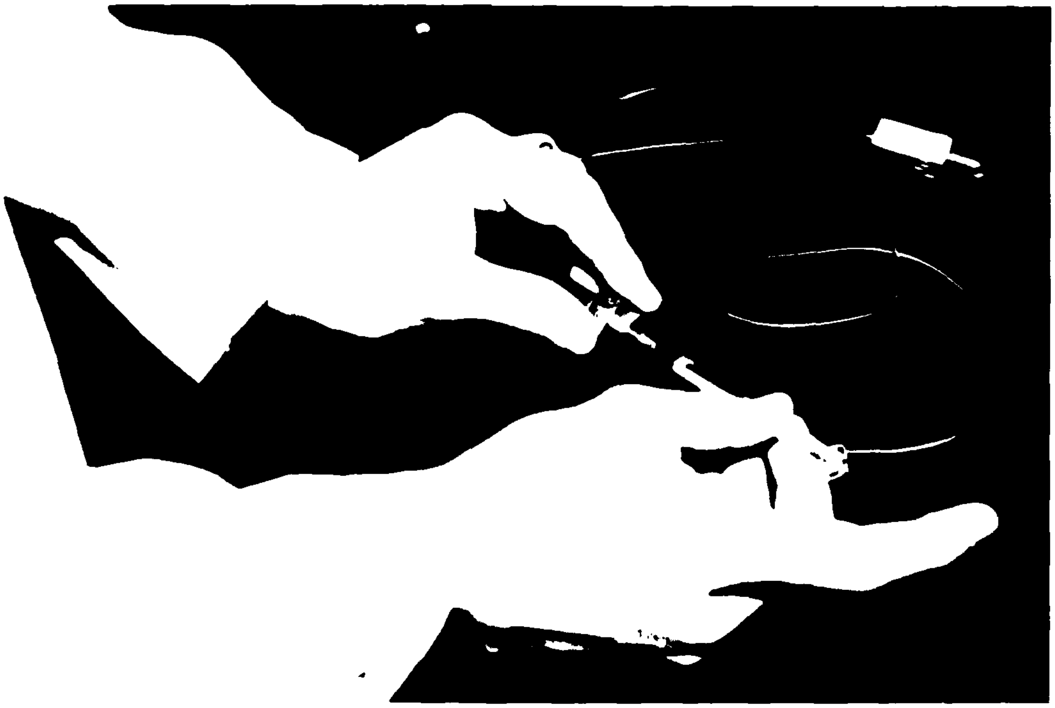


Figure 6. Revised experimental design for investigating low temperature thermal removal of trichloroethylene from soils.



Filling test cell with soil.



Spiking test cell with TCE.

Figure 7. Preparation of test cell.

3.6.3 Experimental apparatus preparation. The experimental apparatus required daily standardization to determine equipment operability. TCE spikes of 1 uL and 5 uL were directly injected into an empty test cell. The cell was immediately placed into the GC oven where it was subjected to experimental conditions at 27°C for 15 minutes. The amount recovered was observed on the Hall cell printout. This test was performed in duplicate.

The resultant Hall cell readings were used as the daily standard to determine the recovery percentages during the execution of the experiment. Typical standard results and their application during data analysis are explained in Section 4.

In addition, several procedures were performed on an as-needed basis for maintenance purposes. These procedures included replacing the Hall reaction chamber, replacing tubing which feeds Hall reaction chamber, and replacing the n-propanol solvent used as part of the Hall detection cell.

3.6.4 Execution of experimental design. A prepared test cell was connected to the purge gas inlet and outlet lines inside the GC oven. Once connnected, the test cell was subjected to the specified experimental temperature for 20 minutes, followed by temperature ramping to 175°C. The ramping proceeds at a rate of 25°C per minute. The system operates in the ramping mode for 15 minutes.

Effluent purge gas from the test cell was automatically sampled every 30 seconds via the 6-port, 3-cross valve. Twice each minute the valve opened for approximately 1 second to collect effluent purge gas. The sample was directed to the Hall furnace which operated at temperatures exceeding 800°F. These conditions converted the chlorines of the TCE to hydrochloric acid (HCl). The effluent of the Hall furnace was fed into a Hall detector cell. This cell used the electrochemical properties of HCl in conjunction with a standard solvent (in this case n-propanol) to measure the amount of HCl in the Hall cell. These readings were displayed on a strip chart.

Upon completion of a run, the test cell was removed from the GC oven. The cell was emptied of the test soil and cleaned for re-use using a nylon brush and a water/detergent solution. Once cooled (if necessary) the test apparatus was ready for the next experimental run.

3.6.5 Temperature profile. At the completion of experimentation, additional data were needed which compared oven temperature and test cell temperature versus time. These profiles were generated using the experimental apparatus. A test cell was filled with soil at its ambient moisture level. Oven temperature was programmed to operate at an experimental temperature for 20 minutes, followed by temperature ramping to 175°C at a rate of 25°C per minute. In addition, soil temperature within the cell was recorded every 4 minutes.

This process was repeated for all three soils at ambient moisture levels at the specified experimental operating temperatures.

3.6.6 TCE verification test. During experimentation, it was observed that the Hall cell would detect what was thought to be TCE during the ramping process. It was decided that an additional test should be performed to verify the presence of residual TCE in the effluent gas from the test cell during the ramping process.

A test cell was filled with SH soil at the ambient moisture level and connected to the experimental apparatus. An experiment was performed at 27°C using the procedures discussed in Subsection 3.6.4. At 20 minutes temperature was ramped and effluent gas was collected in a gas bag typically used during air sampling. The collected gas was then submitted for a GC/MS (mass spectroscopy) scan.

3.6.7 Soil characterization. During shakedown and experimental procedures, physical properties of all test soils were characterized. Table 3 lists tests performed on all soils.

TABLE 3. CHARACTERIZATION PARAMETERS FOR EACH SOIL TYPE

Parameter	Method
Soil pH	ASA 60-3 (glass electrode pH meter)[a]
Total organic carbon	ASA 90-2 (wet combustion)
Total exchangeable bases (base saturation)	ASA 59-2 (residual carbonate method)
Sand	Hydrometer
Silt and clay	Hydrometer
Particle size distribution	Standard sieve analysis
Kaolinite	ASA 49-4 (X-ray diffraction)
Illite	ASA 49-4
Vermiculite	ASA 49-4
Montmorillonite	ASA 49-4
Chlorite	ASA 49-4
Interstratified combinations of 2:1 type components	ASA 49-4
Carbonate ($CaCO_3$)	ASA 91
Aluminum, total	ASA 67-2
Cation exchange capacity	ASA 57-3 (sodium saturation)
Exchange acidity	ASA 59-2 (residual carbonate)

[a] Black, C.A. (Editor-in-chief), D.D. Evans, J.L. White, L.E. Ensminger, F.E. Clark, and R.C. Dinauer. Methods of Soil Analysis, Part 1: Physical and Mineralogical Properties, Including Statistics of Measurement and Sampling and Part 2: Chemical and Microbiological Properties. Madison, Wisconsin; American Society of Agronomy, Inc., 1965.

4. RESULTS

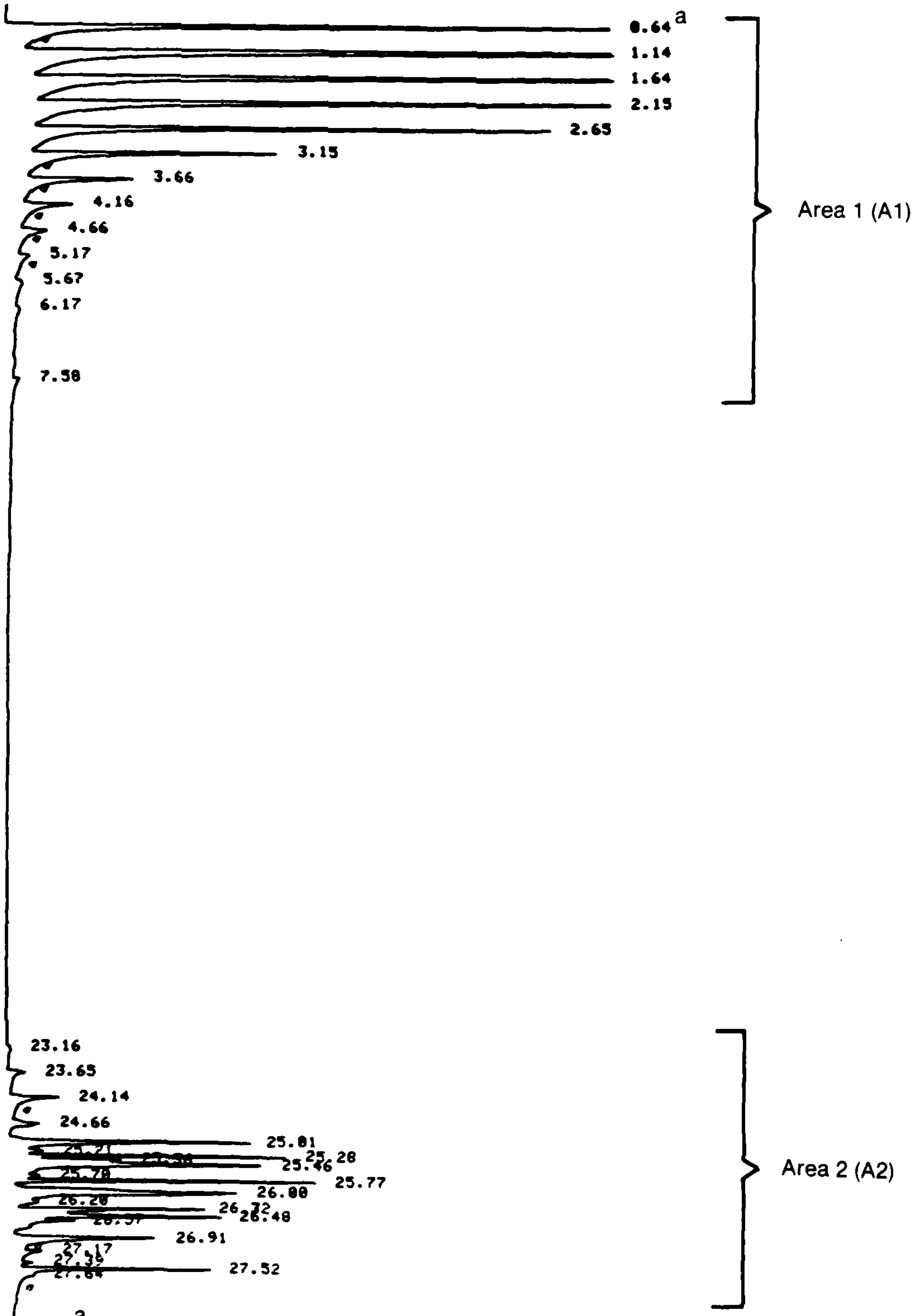
4.1 Typical data output.

4.1.1 Experiment. Figure 8 and Table 4 present characteristic output for an experiment. Figure 8 presents a Hall cell TCE trace during periodic sampling of sample tube off-gas. The number at the top of each peak is the time in minutes at which the peak was measured. Table 4 presents individual and total areas under the traces of Figure 8. Areas are proportional to TCE volatilized.

The experimental protocol described in Subsection 3.6 specified that the test operating temperature was to be maintained for 20 minutes before the temperature was ramped at a rate of 25°C per minute to 175°C. This procedure often resulted in two sets of peaks, as seen in Figure 8. A certain amount of TCE was volatilized at experimental operating conditions, but a TCE residual remained in the soil and required higher temperatures to volatilize.

The total area under the peaks observed between Time 0 and 20 minutes is Area 1 (A1). The total area under peaks observed during temperature ramping (between 20 minutes and completion of the experiment) is Area 2 (A2). Total area for the experiment is the sum of A1 and A2. For the experimental results presented in Figure 8, A1 was 8,114.0 area units and A2 was 3,744.1 area units. Total area was 11,858.1.

4.1.2 Standard. In order to determine estimations of amounts of TCE volatilized, standard curves were produced on a daily basis. Standards were run for 1 uL and 5 uL volumes of TCE.



[a] Time in minutes at which peak was measured.

Note: Temperature ramped to 175°C (25°C per minute) after 20 minutes of this experimental run.

Figure 8. **Typical curve produced during the execution of an experiment. This output is from experiment 2112 (Twin Cities soil, 1µL TCE, 27°C at 7.5 percent moisture) performed on 10 November 1984.**

TABLE 4. TCE MEASURED BY HALL DETECTOR DURING EXPERIMENT 2112.

```
  RT              AREA   TYPE   WIDTH        HEIGHT     BASELINE     AREA %

 0.00                          BASELINE @ START RUN = -0.07
 0.00                          THRESHOLD @ START RUN =  2
 0.00                          PEAK WIDTH @ START RUN = 0.04
 0.13             7.26   BB     -----          2.19        -0.02      0.061
 0.64          1214.29   BV     0.06 *       336.10         0.91     10.240
 1.14          2044.75   BB     0.06 *       579.86         7.75     17.244
 1.64          1869.04   BB     0.06 *       511.59        11.25     15.762
 2.15          1315.41   BB     0.06 *       332.38        11.50     11.093
 2.65           811.94   PB     0.06 *       198.86        11.19      6.847
 3.15           419.28   BV     0.07 *        95.46         9.53      3.536
 3.66           202.97   BV     0.08 *        41.12         8.29      1.712
 4.16           110.98   BV     -----*        19.19         6.92      0.936
 4.66            68.22   BV     -----*        10.73         5.45      0.575
 5.17            32.18   BV     -----          4.61         4.66      0.271
 5.67            10.67   BB     -----          2.60         4.20      0.090
 6.17             1.60   BB     -----          0.84         4.34      0.013
 7.58             5.37   BB     -----          2.75         2.61      0.045
23.16             4.43   BB     -----          1.21         0.59      0.037
23.65            31.93   BB     -----          6.93         0.83      0.269
24.14           107.34   BV     -----*        19.88         1.18      0.905
24.66            66.66   BP    *-----         11.80         1.72      0.562
25.01           371.93   PV     -----         91.71         0.77      3.136
25.21            66.22   VV     -----         13.85         0.92      0.558
25.28           271.17   VV     -----        106.71         0.98      2.287
25.36           116.99   VV     -----         44.04         1.05      0.987
25.46           559.77   VV     -----         97.43         1.11      4.721
25.70            58.59   VV     -----         12.18         1.31      0.494
25.77           269.49   VV     -----        117.67         1.36      2.273
26.00           608.50   VV    *-----         87.49         1.53      5.131
26.20            66.06   VV     -----         10.84         1.69      0.557
26.32           248.44   VV     -----*        72.74         1.78      2.095
26.48           312.60   VV     -----         80.62         1.90      2.636
26.57            89.18   VV     -----         24.36         1.97      0.752
26.91           222.93   PV     -----*        54.61         3.50      1.880
27.17            26.74   BP     -----          7.34         6.66      0.225
27.39            14.14   PV     -----          5.35         5.28      0.119
27.52           203.01   VV     -----         73.44         4.96      1.712
27.64            27.98   VP     -----          6.07         4.69      0.236

TOTAL AREA = 11858.10
```

NOTE: TCE detection is the total area under the integrated curve in Figure 8.

The daily standard at 1 uL TCE is presented in Figure 9. Total standard area is 20,524 for that day. This indicated that recovery (following ramping to 120°C) for experiment 2112 was 11,858.1/20,524.3 x 100 = 57.8 percent, or 42.2 percent of the TCE was lost during spiking and storage of the test cell before experimentation. Examples of other relevant calculations follow:

$$1 \times 10^{-6} \text{ liter (1 uL)} \times \frac{1.466 \text{ grams}}{\text{mL}} \times \frac{1{,}000 \text{ mL}}{\text{L}} = 1.47 \text{ mg}$$

$$\left(\text{TCE spike volume}\right) \left(\begin{array}{l}\text{TCE density} \\ \text{at } 68^{\circ}\text{F}\end{array}\right) = \begin{array}{l}\text{TCE spike} \\ \text{weight}\end{array}$$

$$\begin{aligned} \text{TCE loss} &= 1.47 \text{ mg} \times 0.422 \\ &= 0.62 \text{ mg lost} \end{aligned}$$

$$\text{Total sample at time of sampling} = 0.85 \text{ mg}$$

$$\text{Sample weight} = 4.5 \text{ g}$$

$$\begin{aligned} \begin{array}{c}\text{Initial concentration} \\ \text{(dry weight basis)}\end{array} &= \frac{0.85 \text{ mg}}{0.0042 \text{ kg soil}} \\ &= \frac{202.4 \text{ mg}}{\text{kg}} \\ &= 202.4 \text{ ppm} \end{aligned}$$

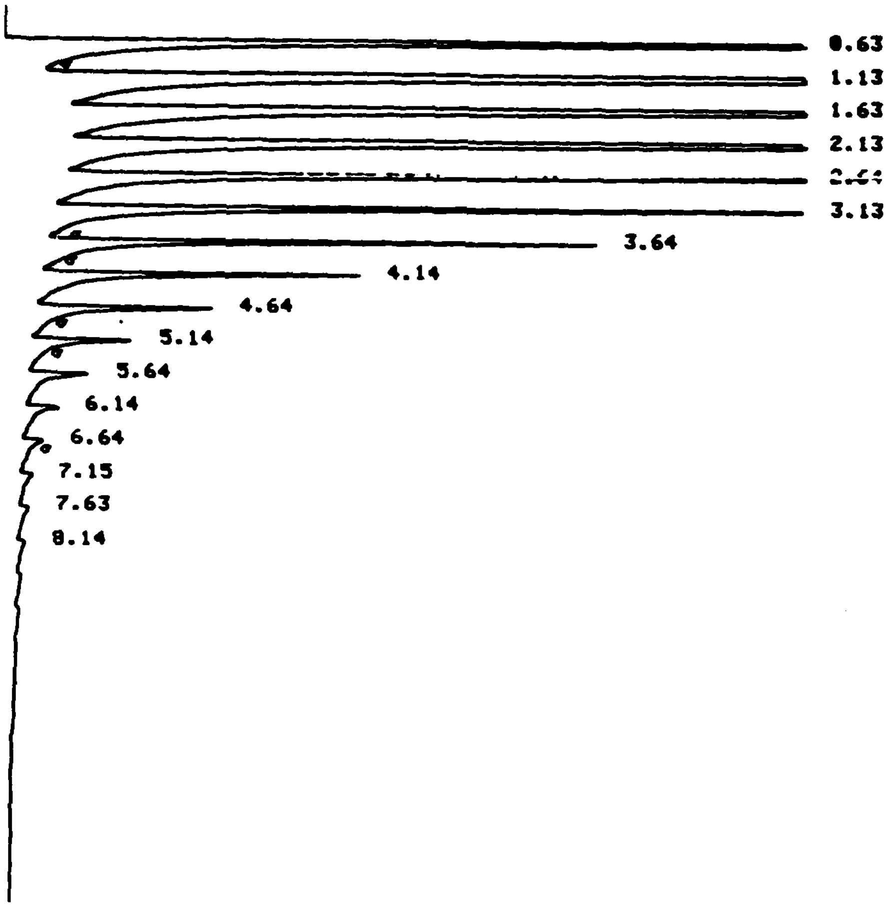
$$\frac{\text{A1 Area}}{\text{Total Area}} \cdot 0.85 \text{ mg TCE} = \begin{array}{l}\text{Amount removed during} \\ \text{first 20 minutes at} \\ \text{operating temperature}\end{array}$$

or

$$\frac{8{,}114}{11{,}858.1} \times 0.85 \text{ mg} = 0.58 \text{ mg TCE removed}$$

$$\begin{aligned} \text{Residual TCE} &= 0.85 - 0.58 \\ &= \begin{array}{l}0.27 \text{ mg residual TCE} \\ \text{(detected by ramping} \\ \text{temperature)}\end{array} \end{aligned}$$

$$\begin{aligned} \begin{array}{c}\text{Residual concentration} \\ \text{(dry weight basis)}\end{array} &= \frac{0.27 \text{ mg TCE}}{0.0042 \text{ kg soil}} \\ \begin{array}{l}\text{(detected by ramping} \\ \text{temperature)}\end{array} &= \frac{64.3 \text{ mg TCE}}{\text{kg soil}} \\ &= 64.3 \text{ ppm} \end{aligned}$$



```
 RT                 AREA  TYPE   WIDTH          HEIGHT      BASELINE     AREA %

0.00                            BASELINE @ START RUN = -0.07
0.00                            THRESHOLD @ START RUN =  2
0.00                            PEAK WIDTH @ START RUN = 0.04
0.63              2378.62  BV    0.05 +         752.62          0.96     11.589
1.13              5936.87  BV   *0.05 +        1899.70         11.89     28.926
1.63              4569.48  VV    0.05 +        1372.17         11.71     22.264
2.13              3089.10  VV    0.06 +         869.30         11.53     15.051
2.64              1767.16  VV    0.06 +         465.53         11.35      8.610
3.13              1054.10  VV    0.06 +         256.78         11.18      5.136
3.64               687.48  VV    0.07 +         162.21         11.00      3.350
4.14               424.56  BV    0.07 +          92.96         10.58      2.069
4.64               265.05  PV   ------+          51.56          8.76      1.291
5.14               152.91  BV   ------+          29.30          7.50      0.745
5.64                95.88  BV   ------+          17.95          6.29      0.467
6.14                36.97  BB   ------+           8.85          6.50      0.180
6.64                35.89  BV   ------+           6.32          4.73      0.175
7.15                16.65  BB   -----             3.30          4.37      0.081
7.63                 7.73  BB   -----             2.43          4.20      0.038
8.14                 5.88  BB   -----             1.95          3.69      0.029

TOTAL AREA = 20524.30
```

Figure 9. Standard curve for 1 µL spike of TCE performed on 10 November 1984.

4.2 Experimental results.

4.2.1 Experimental moisture levels. Moisture levels of the soils at ambient and dried at 60°C were determined using standard procedures. Table 5 lists those results.

4.2.2 TCE removal rate at operating temperature - kinetics. This was the time (in minutes) when 90 percent of A1 was observed. This was calculated using the data described in Subsection 4.1. These data are presented in Figure 10.

4.2.3 TCE residual percentage. This variable was calculated as (Area of A2/Total Area) x 100. These data are presented in Figure 11.

4.2.4 Temperature profiles. Figures 12, 13, and 14 illustrate temperature versus time profiles for soils at Level 2 moistures for 27°C, 90°C, and 120°C, respectively.

4.2.5 TCE verification test. Data generated from the execution of the test plan indicated that TCE volatilization occurred at the operating temperature and during temperature ramping. TCE was verified as the material comprising A2 by GC/MS and GC/IR analysis. Water vapor and carbon dioxide were also identified, but neither contributed to the Hall cell trace.

4.2.6 Soil characterization. Volatile organic scans were performed on all soils prior to TCE spiking to identify any compound(s) which may cause interferences in the execution of the test plan. These results indicated that no volatile organics were present above detection limits (0.1 ug/g) in the background soils.

Following the initial volatile organic scans soils were characterized per original test plan. Table 6 presents these results.

TABLE 5. EXPERIMENTAL MOISTURE LEVELS FOR EACH SOIL TESTED

	Soil Moisture Levels Used During Experimentation	
	Level 1	Level 2
Soil Type	Dried at 60°C (% Moisture)	Ambient (% Moisture)
Sharpe	0.3	4
Twin Cities	0.5	7
Letterkenny	1.0	15

		Soil moisture level 1 A_1, lower			Soil moisture level 2 A_2, higher		
		Dryer Temperature 1 B_1	Dryer Temperature 2 B_2	Dryer Temperature 3 B_3	Dryer Temperature 1 B_1	Dryer Temperature 2 B_2	Dryer Temperature 3 B_3
TCE concentration 1 C_1	**Soil 1** D_1	1111 18.16 18.18	1211 15.64 16.14	1311 8.63 8.13	2111 3.65 3.16	2211 1.63 19.63	2311 1.63 1.63
	Soil 2 D_2	1112 16.17 18.15	1212 17.14 17.14	1312 4.13 9.63	2112 2.64 3.15	2212 19.13 19.13	2312 1.63 1.63
	Soil 3 D_3	1113 50[a] 18.68	1213 17.14 17.14	1313 9.14 9.64	2113 3.15 3.65	2213 1.63 1.13	2313 2.13 1.63
TCE concentration 2 C_2	**Soil 1** D_1	1121 18.15 15.65	1221 15.64 15.63	1321 7.63 6.13			
	Soil 2 D_2	1122 18.16 50[a]	1222 16.13 16.13	1322 9.63 10.13			
	Soil 3 D_3	1123 18.21 18.66	1223 17.14 17.13	1323 5.13 3.63			

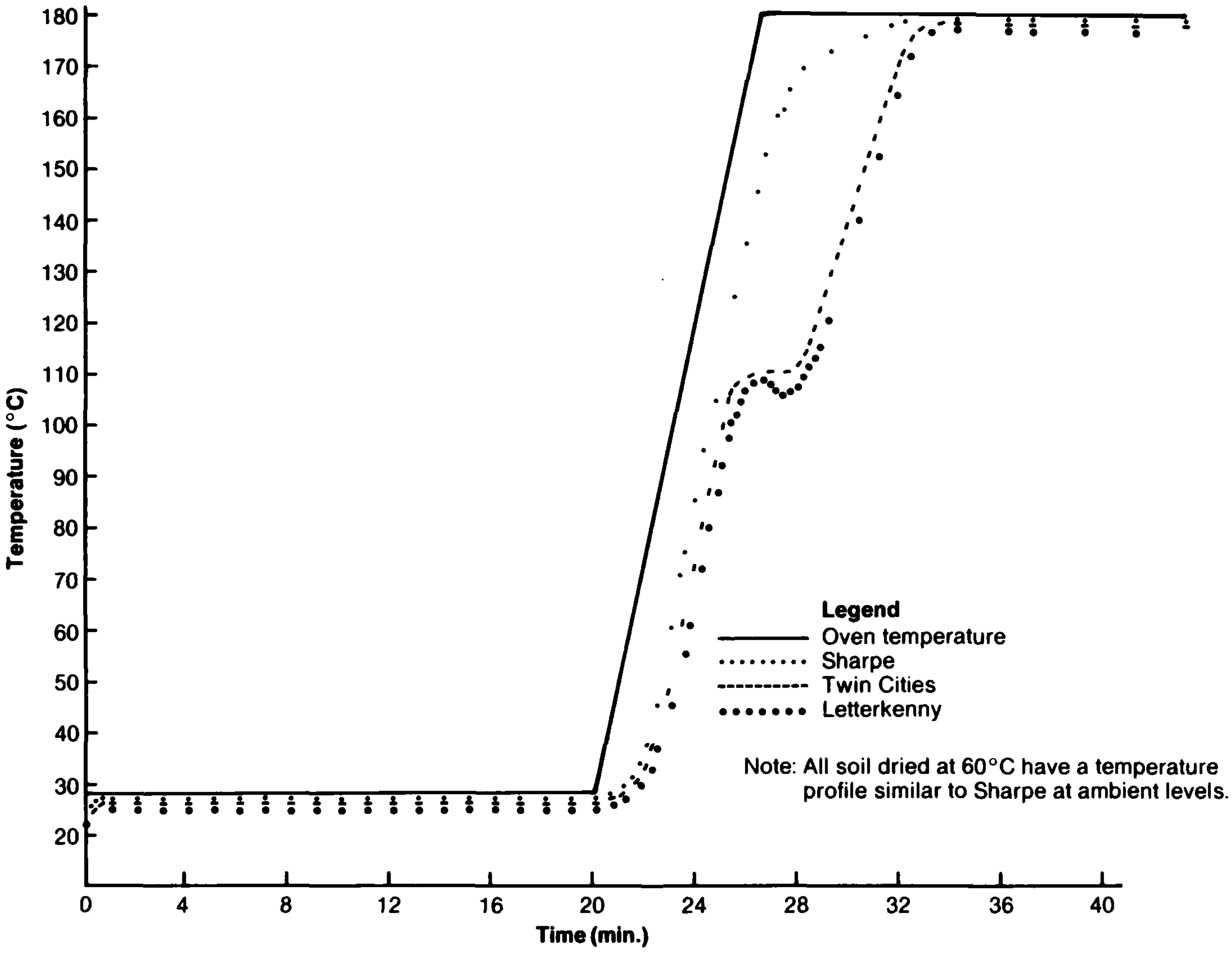
[a] 50 was used to indicate that no TCE was detected at the specified operating temperature.

Figure 10. Time (minutes) for 90 percent of TCE removed at the operational temperature to be volatilized.

		Soil moisture level 1 A_1, lower			Soil moisture level 2 A_2, higher		
		Dryer Temperature 1 B_1	Dryer Temperature 2 B_2	Dryer Temperature 3 B_3	Dryer Temperature 1 B_1	Dryer Temperature 2 B_2	Dryer Temperature 3 B_3
TCE concentration 1 C_1 1µl	Soil 1 D_1	1111 99.53 97.60	1211 20.02 16.70	1311 0.96 0.65	2111 12.59 71.78	2211 3.36 80.70	2311 0^a 0^a
	Soil 2 D_2	1112 99.86 99.95	1212 49.63 55.37	1312 0.71 1.86	2112 54.27 31.58	2212 91.06 91.63	2312 0^a 0^a
	Soil 3 D_3	1113 100 99.35	1213 37.17 54.67	1313 0^a 0.44	2113 77.69 35.45	2213 8.42 7.61	2313 0^a 2.16
TCE concentration 2 C_2 5µl	Soil 1 D_1	1121 93.38 35.87	1221 12.97 15.26	1321 1.02 0.74			
	Soil 2 D_2	1122 100 96.40	1222 36.29 40.18	1322 3.10 2.62			
	Soil 3 D_3	1123 99.88 99.26	1223 51.09 65.23	1323 0.01 0.01			

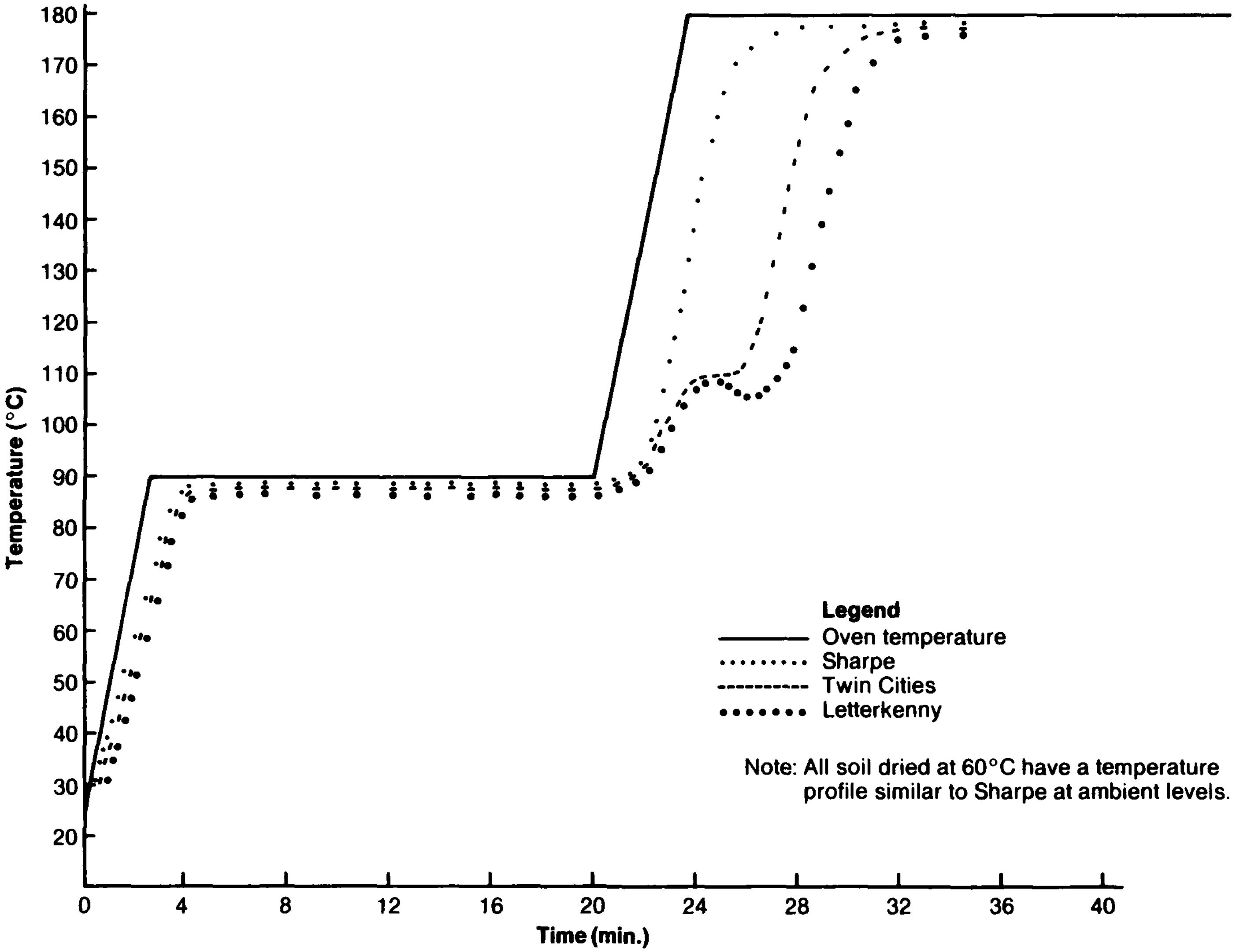
[a] No second peak was observed.

Figure 11. Residual percentages of TCE to total TCE volatilized.



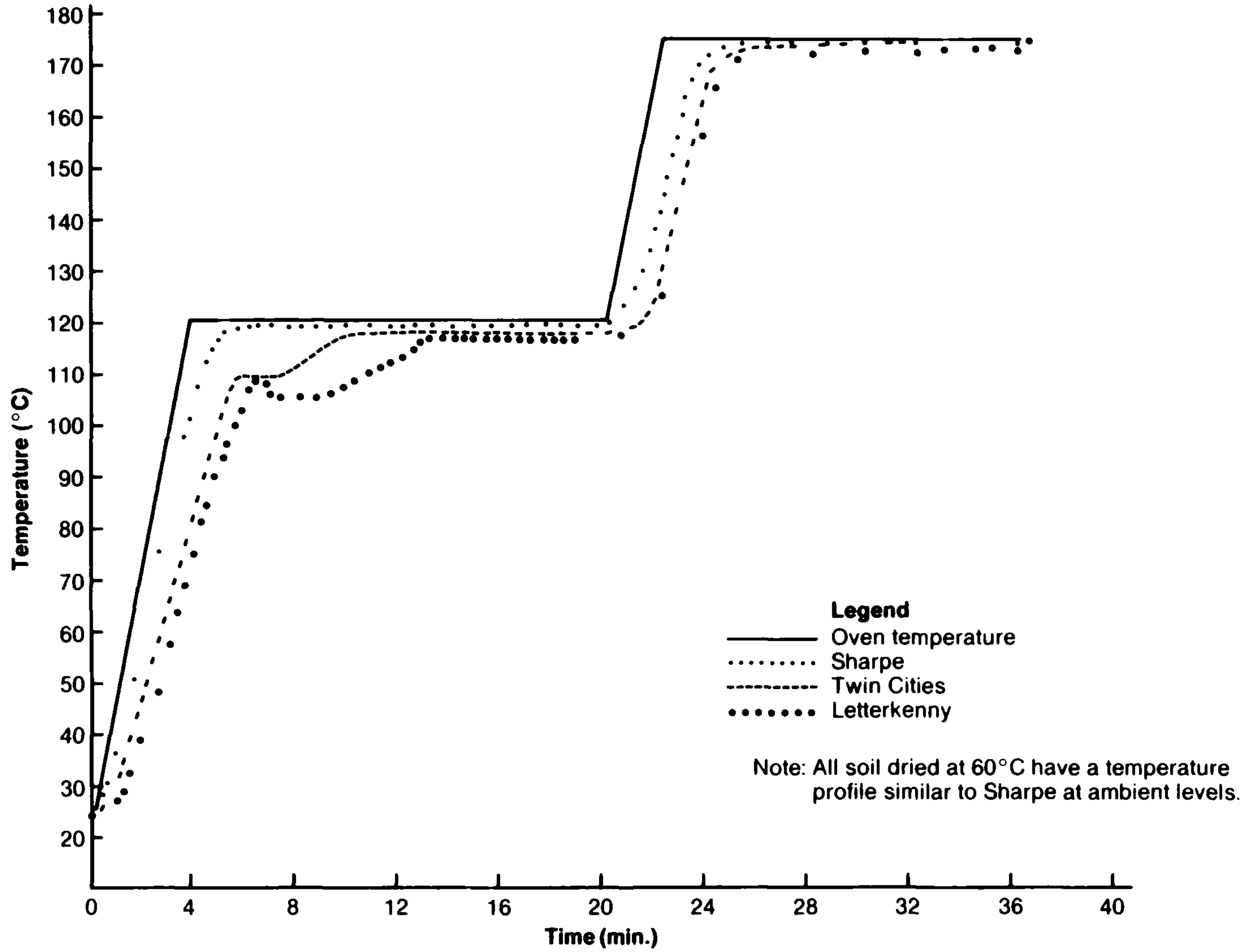
Note: All soil dried at 60°C have a temperature profile similar to Sharpe at ambient levels.

Figure 12. Temperature versus time profile for soils at ambient moisture levels for 27°C experimentation.



Note: All soil dried at 60°C have a temperature profile similar to Sharpe at ambient levels.

Figure 13. Temperature versus time profile for soils at ambient moisture levels for 90°C experimentation.



Note: All soil dried at 60°C have a temperature profile similar to Sharpe at ambient levels.

Figure 14. Temperature versus time profile for soils at ambient moisture levels for 120°C experimentation.

TABLE 6. SOIL CHARACTERIZATION

	Sharpe	Twin Cities	Letterkenny
Concentration of minerals[a]			
Phosphorous (total)	81	72	4
Potassium	200	50	60
Magnesium	424	192	85
Hydrogen (meq/100 g)	0	0	0.5
Calcium	1,020	1,560	1,920
Sodium	260	35	47
Aluminum (total)	<1	<1	<1
Percent calcium carbonate	1.79%	1.96%	6.07%
Percent total organic carbon	0.06%	0.17%	0.15%
Cation exchange capacity (meq/100 g)	10.3	9.7	11.2
Computed percent base saturation			
Percent potassium	5.0	1.3	1.4
Percent magnesium	34.4	16.5	6.3
Percent calcium	49.6	80.6	86.0
Percent hydrogen	0	0	4.5
Percent sodium	11.0	1.6	1.8
Soil structure			
Percent sand	76.4	70.4	24.4
Percent silt	18.4	16.4	34.4
Percent clay	5.2	13.2	41.2

	Dominant minerals (Greatest % to Least %)
X-ray diffraction	
Sharpe	Quartz, feldspar, calcite, illite
Twin Cities	Quartz, feldspar, calcite, illite
Letterkenny	Quartz, illite, feldspar
Dominant clay for all soils:	illite

[a] Concentration in ppm unless otherwise noted.

4.3 Data analysis.

4.3.1 General. Data were generated in two phases. The first was shakedown of the apparatus and investigation of behavior of soils with and without TCE under experimental conditions. This phase required significantly more effort than originally planned because of the nature of the soil/solvent system. Data and observations collected during shakedown were useful in redesigning the experimental program from what was originally planned to what was necessary.

Data generated in the second phase resulted from execution of two factorially designed experiments which were subsets of the original factorial design. Second phase experimental designs reflected observations from shakedown and incorporated experimental procedures refined from the original test plan.

Preliminary data analysis was by means of multi-way Analysis of Variance (ANOVA). Results of the analysis were evaluated at the 5 percent level of significance. The purpose was to find, from second phase data, which of the experimental factors (or combination of factors) contributed most to variations in volatilization kinetics and residual levels.

4.3.2 Volatilization kinetics. The operational effect of interest was volatilization of TCE at the operating temperature. Some amount of TCE was volatilized at each of the three test temperatures. The amounts differed, and review of the chromatograms indicated that the amount was generally finite. Volatilization was completed at the operating temperature by at most 20 minutes. The measure of interest was the time required for 90 percent of that amount of TCE to be volatilized.

Two experimental designs were used. The first maintained a constant soil moisture level (Level 1) and varied the three factors:

(a) Operational temperature.
(b) TCE concentration.
(c) Soil type.

ANOVA results are shown in Table 7. Operating temperature was the statistically significant contributor to variation. The relationship between kinetics and operating temperature is shown in Figure 15.

TABLE 7. ANALYSIS OF VARIANCE FOR VOLATILIZATION KINETICS AT CONSTANT MOISTURE (MOISTURE LEVEL 1) CONDITIONS

Source of variation	Sum of squares	Degrees of freedom	Mean square	Calculated F
Replication	0.4334	1	0.4334	0.0072
A Operating temperature	1,460.435	2	730.2175	12.1703 >3.59*
B TCE concentration	2.816888	1	2.816888	0.0475
C Soil type	81.8684	2	40.9342	0.6903
AB	1.8492	2	0.9246	0.0469
AC	118.9094	4	29.7262	0.4954
BC	265.3115	2	132.6558	2.2109
ABC	694.396	4	173.5990	2.8933 Almost significant
Error	1,019.9923	17	59.9995	
Total	3,258.9376	35		

$F_{0.05}$ (1, 17) = 4.45
$F_{0.05}$ (2, 17) = 3.59
$F_{0.05}$ (4, 17) = 2.96

*Significant at the 5 percent level.

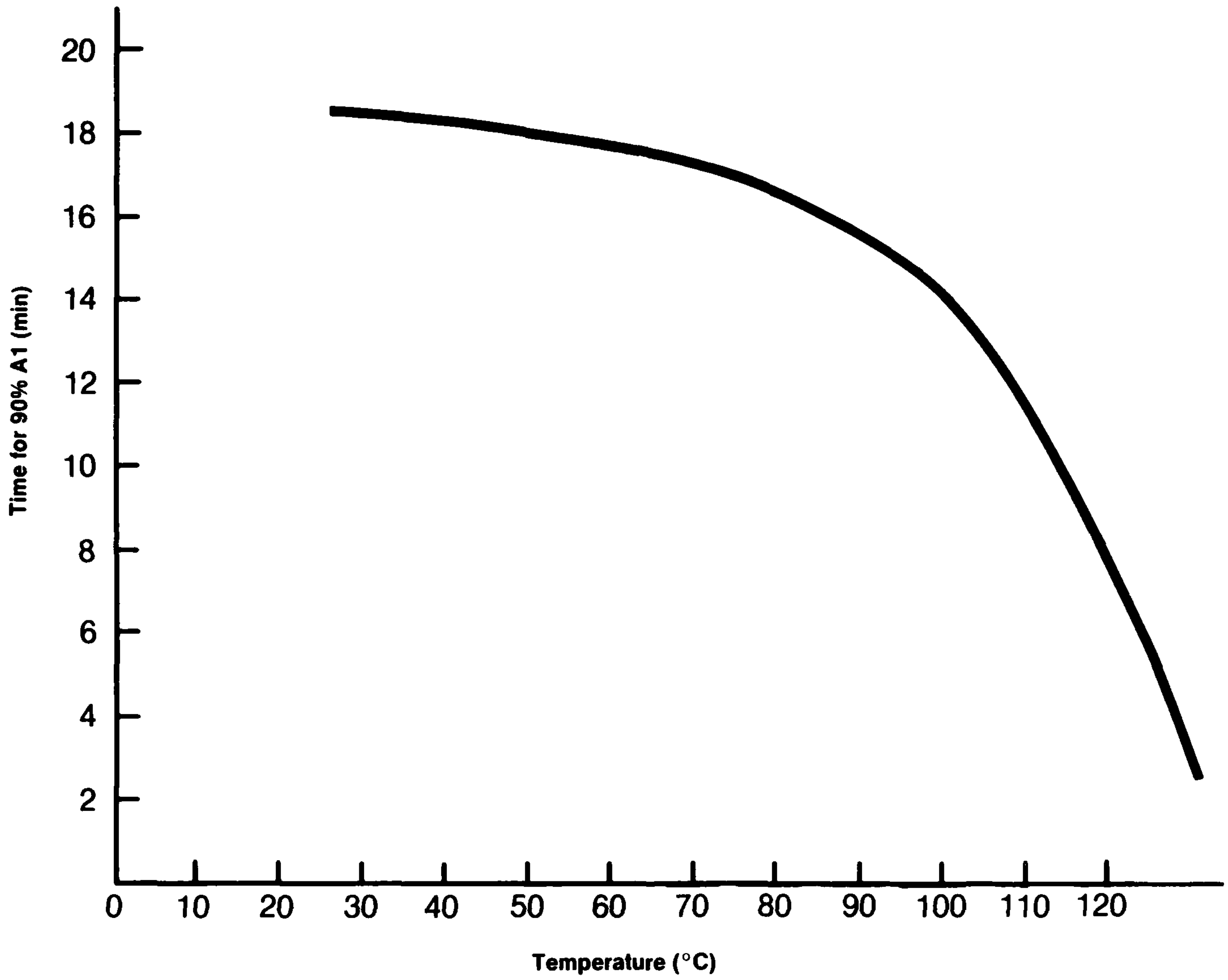


Figure 15. Operating temperature versus average time for 90 percent A1 at constant soil moisture levels.

The second experiment maintained a constant TCE concentration and varied the three factors:

(a) Operational temperature.
(b) Soil moisture.
(c) Soil type.

ANOVA results are shown in Table 8. Significant factors were:

(a) Soil moisture.
(b) Operational temperature.
(c) Interaction between (a) and (b).

Of these, soil moisture was the dominant factor. Figure 16 demonstrates moisture and temperature effects and interactions on 90 percent removal times.

It can be concluded that soil moisture and operating temperature were the two experimental factors which most significantly affected the rate of TCE volatilization.

4.3.3 Residual TCE, percentages. After all the TCE which would volatilize at the operating temperature was collected, soil temperature was ramped to drive off any remaining TCE. Residuals were observed during temperature ramping under certain experimental conditions.

The measurement of interest was the proportion of total TCE volatilized represented by these residuals. Data analyzed were the percentage of residual TCE to total TCE volatilized.

Data were collected from the same two sets of experiments used for volatilization kinetics. The first set of data were for conditions of constant soil moisture and variable operating temperature, TCE concentration, and soil type. ANOVA results are summarized in Table 9. Statistically significant factors were:

(a) Operating temperature.
(b) Soil type.
(c) Interaction between (a) and (b).

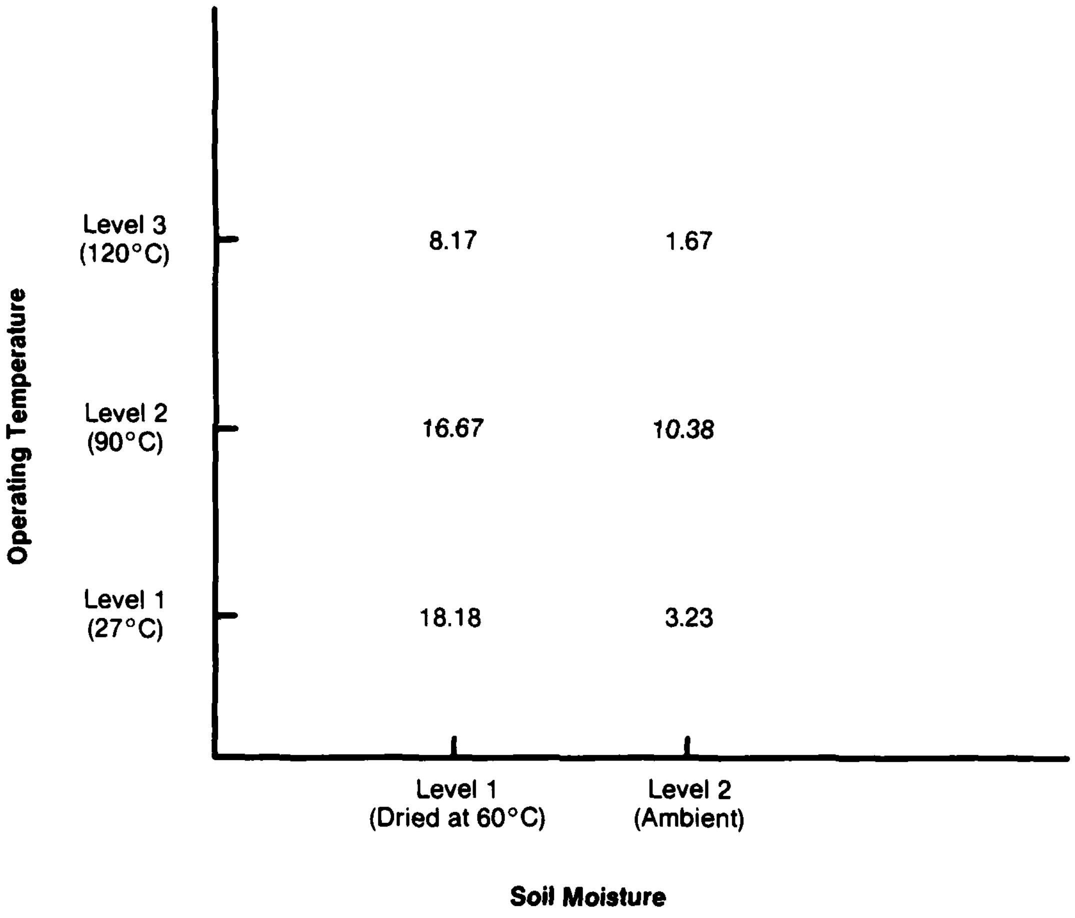
Operating temperature was the dominant factor. Interaction effects were statistically significant at the 5 percent level, but they were marginally significant compared with operating temperature. Figure 17 displays individual and combined significant factor effects on percentage residuals.

TABLE 8. ANALYSIS OF VARIANCE FOR VOLATILIZATION KINETICS AT CONSTANT TCE CONCENTRATIONS

Source of variation	Sum of squares	Degrees of freedom	Mean square	Calculated F
Replication	0.9344	1	0.9344	0.0237
A Soil moisture	1,078.2467	1	1,078.2467	27.3739 >4.45*
B Operating temperature	568.4723	2	284.2362	7.2160 >3.59*
C Soil type	15.7096	2	7.8548	0.1994
AB	368.1472	2	184.0736	4.6732 >3.59*
AC	242.6701	2	121.3351	3.0804
BC	265.8560	4	66.464	1.6874
ABC	171.6655	4	42.9164	1.0895
Error	669.6223	17	39.3895	
Total	3,381.3241	35		

$F_{0.05}$ (1, 17) = 4.45
$F_{0.05}$ (2, 17) = 3.59
$F_{0.05}$ (4, 17) = 2.96

*Significant at the 5 percent level.



Operating Temperature	Soil Moisture: Level 1 (Dried at 60°C)	Soil Moisture: Level 2 (Ambient)
Level 3 (120°C)	8.17	1.67
Level 2 (90°C)	16.67	10.38
Level 1 (27°C)	18.18	3.23

Note: Higher temperatures and increased moisture levels promote higher stripping rate of TCE from soil.

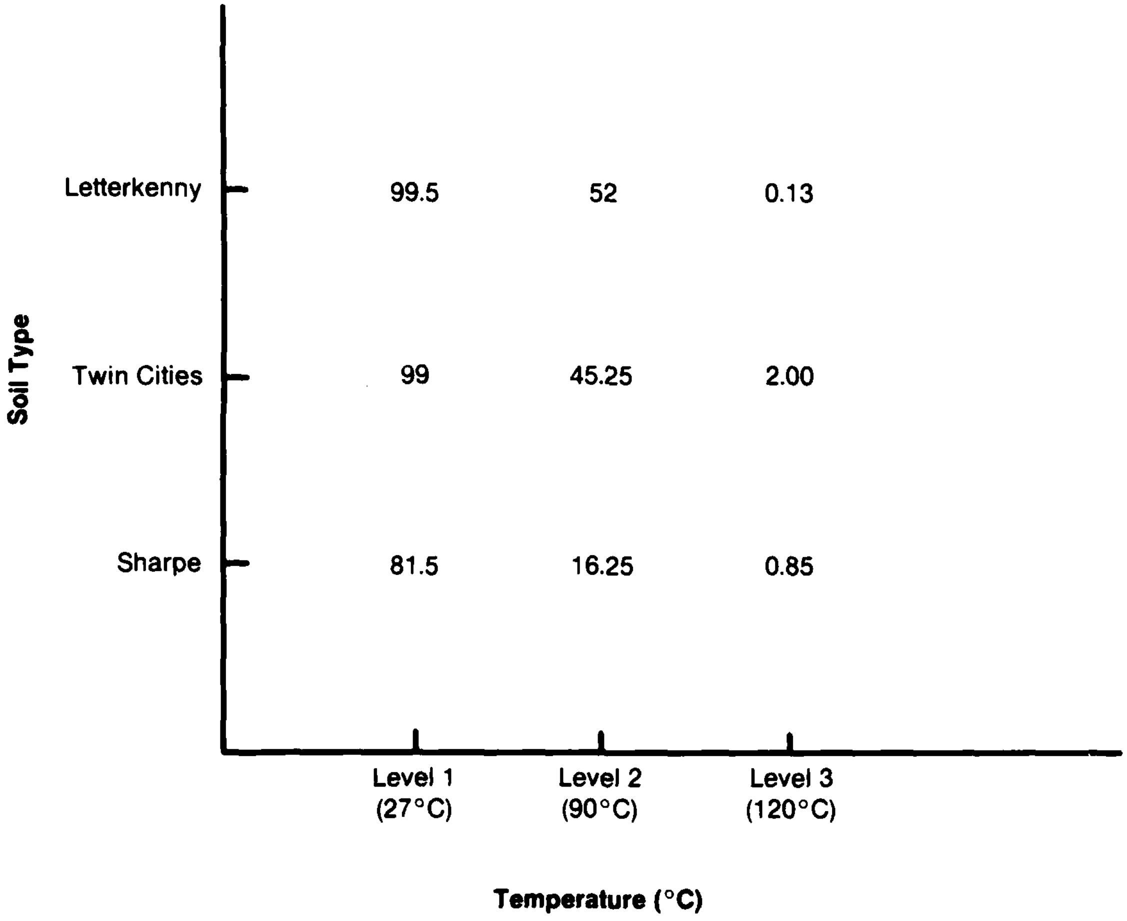
Figure 16. **Average time (minutes) for 90 percent removal (of A1) of TCE at a fixed TCE concentration at specified operating temperatures and soil moisture levels prior to ramping operating temperature to 175°C.**

TABLE 9. ANALYSIS OF VARIANCE FOR PERCENTAGE RESIDUAL TCE, CONSTANT MOISTURE CONDITIONS

Source of variation	Sum of squares	Degrees of freedom	Mean square	Calculated F
Replication	15.2881	1	15.2881	0.134
A Operating temperature	51,938.4829	2	25,969.24	228.34 ≫3.59*
B TCE concentration	182.9707	1	182.9707	1.61
C Soil type	2,281.92	2	1,140.96	10.03 >3.59*
AB	256.8456	2	128.4228	1.13
AC	1,465.8828	4	364.2207	3.20 >2.96*
BC	417.6272	2	208.8136	1.84
ABC	671.2563	4	167.8141	1.48
Error	1,933.3903	17	113.7288	
Total	59,163.6639	35		

$F_{0.05}$ (1, 17) = 4.45
$F_{0.05}$ (2, 17) = 3.59
$F_{0.05}$ (4, 17) = 2.96

*Significant at the 5 percent level.



Soil Type	Level 1 (27°C)	Level 2 (90°C)	Level 3 (120°C)
Letterkenny	99.5	52	0.13
Twin Cities	99	45.25	2.00
Sharpe	81.5	16.25	0.85

Note: Moisture levels - SH: 0.5%; TC: 0.5%; LK: 1.0%.
Percent residual TCE increased with
decreasing operating temperatures.

Figure 17. Percent residual TCE at a fixed moisture level compared to soil type and operating temperature.

The concentration of TCE did not appear to significantly influence either the existence or the relative magnitude of a post-operating temperature residual under constant moisture conditions.

The second set of data were for the factors of soil moisture, operating temperature, and soil type with TCE concentration held constant. ANOVA results are shown in Table 10. These indicated that the statistically significant factors were:

(a) Soil moisture.
(b) Operating temperature.
(c) Interaction between (a) and (b).

Operating temperature was the dominant factor. Figure 18 displays individual and combined significant factor effects on residual percentages. Soil type was not significant under conditions of constant TCE concentration.

These results indicated that operating temperature, soil type, and soil moisture significantly influenced the existence and proportion of TCE residuals which remained after maximum possible volatilization at an operating temperature.

4.3.4 Residual TCE, concentrations. The calculation of residual percentages, although an important engineering parameter, eliminates the physical differences in density and test volumes of the test soils. It was necessary, therefore, to compute residual concentrations since these are the quantities more relevant to regulatory agencies. Individual soil volumes and weights were used which introduced additional variations in the set of experimental results.

Figure 19 presents estimated residual concentrations in ppm for the same two sets of experiments described earlier. Values range from not detected to more than 1,300 ppm.

The data in Figure 19 were subjected to the same type of ANOVA as were the data already described. ANOVA results for constant moisture conditions are presented in Table 11. All factors and their paired interactions were statistically significant at the 5 percent level.

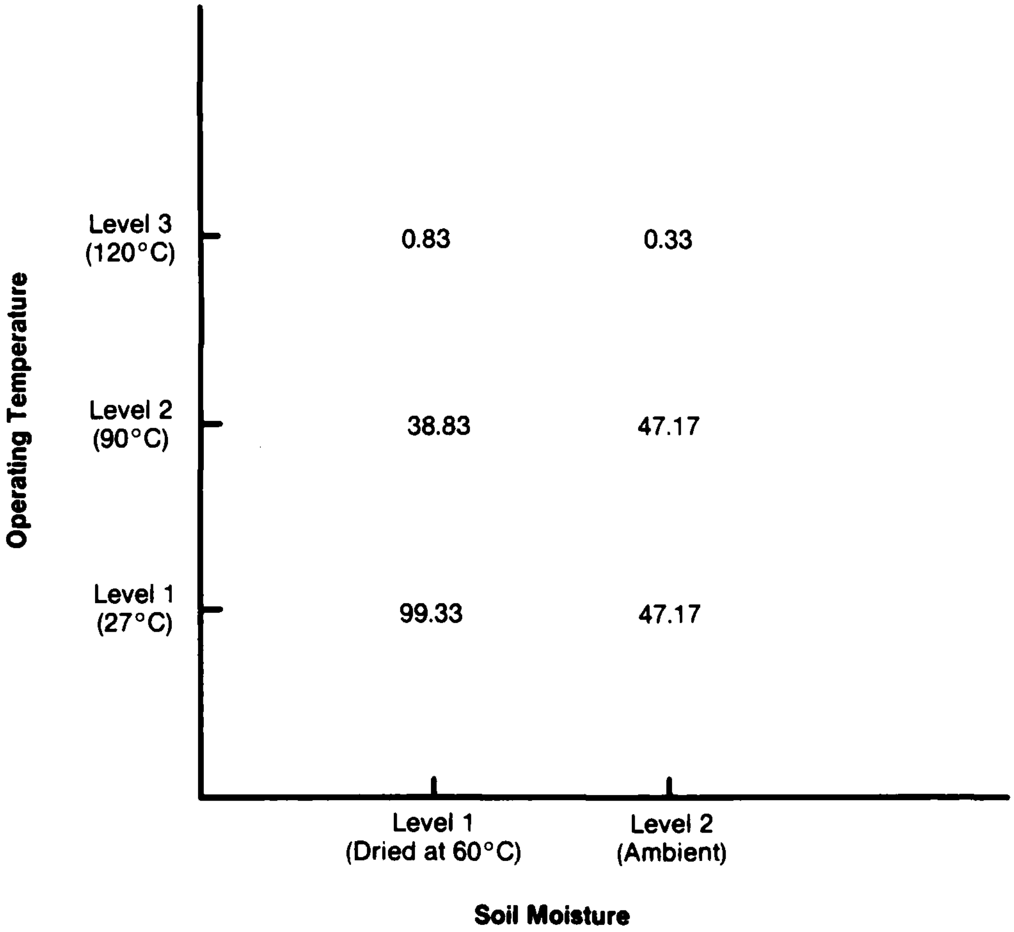
ANOVA results for constant TCE concentration are presented in Table 12. Again, all individual factors were statistically significant. In this case, only the interaction between soil moisture and operating temperature was also significant.

TABLE 10. ANALYSIS OF VARIANCE FOR PERCENTAGE RESIDUAL TCE, CONSTANT TCE CONCENTRATIONS

Source of variation	Sum of squares	Degrees of freedom	Mean square	Calculated F	
Replication	236.2881	1	236.2881	0.688	
A Soil moisture	1,967.9574	1	1,967.9574	5.73	>4.45*
B Oven Temperature	32,042.9885	2	16,021.494	46.67	≫3.59*
C Soil type	1,482.0763	2	741.038	2.16	
AB	6,394.8630	2	3,197.432	9.31	>3.59*
AC	673.5140	2	336.757	0.98	
BC	3,689.6142	4	922.404	2.69	
ABC	2,756.1622	4	689.041	2.01	
Error	5,836.5218	17	343.3248		
Total	55,079.9855	35			

$F_{0.05}$ (1, 17) = 4.45
$F_{0.05}$ (2, 17) = 3.59
$F_{0.05}$ (4, 17) = 2.96

*Significant at the 5 percent level.



Note: TCE removal is increased by increasing moisture levels in soils. Level 2 data resulted from experimental error.

Figure 18. Percent residual TCE at fixed TCE concentration (1 μL) compared to operating temperature and soil moisture level independent of soil type.

		Soil moisture level 1 A_1, lower			Soil moisture level 2 A_2, higher		
		Dryer Temperature 1 B_1	Dryer Temperature 2 B_2	Dryer Temperature 3 B_3	Dryer Temperature 1 B_1	Dryer Temperature 2 B_2	Dryer Temperature 3 B_3
TCE concentration 1	**Soil 1**	1111 204.4 213.8	1211 58.1 48.2	1311 1.8 1.4	2111 56.2 40.0	2211 16.9 3.8	2311 ND[a] ND[a]
	Soil 2	1112 278.1 243.1	1212 131.7 154.7	1312 5.1 5.1	2112 159.9 64.3	2212 37.4 25.7	2312 ND[a] ND[a]
	Soil 3	1113 82.3 253.0 255.7	1213 86.6 145.1	1313 ND[a] 1.2	2113 282.7 139.1	2213 72.6 75.4	2313 ND 16.5
TCE concentration 2	**Soil 1**	1121 890.5 411.5	1221 143 172	1321 9.0 16.0			
	Soil 2	1122 1,244.6 1,348.6	1222 499.4 557.2	1322 75.4 35.3			
	Soil 3	1123 1,305 1,228	1223 825.2 636.5	1323 0.2 24.3			

[a] No TCE detected at this operating condition.

Figure 19. Estimated residual concentrations (ppm) prior to the ramping process.

TABLE 11. ANALYSIS OF VARIANCE FOR PERCENTAGE RESIDUAL TCE, CONSTANT MOISTURE CONDITIONS

Source of variation	Sum of squares	Degrees of freedom	Mean square	Calculated F
Replication	7,321.6545	1	7,321.6545	0.8924
A Operating temperature	2,489,293.351	2	1,244,646.676	151.71>>3.59*
B TCE concentration	1,494,343.255	1	1,494,343.255	182.14>>4.45*
C Soil type	348,568.3177	2	174,284.1589	21.24 >3.59*
AB	980,809.627	2	490,404.8135	59.76 >3.59*
AC	176,736.1173	4	44,184.0293	5.39 >2.96*
BC	275,974.2063	2	137,987.1032	16.82 >3.59*
ABC	82,087.7717	4	20,521.9429	2.50
Error	139,470.6755	17	8,204.1574	
Total	5,994,604.976	35		

$F_{0.05}$ (1, 17) = 4.45
$F_{0.05}$ (2, 17) = 3.59
$F_{0.05}$ (4, 17) = 2.96

*Significant at the 5 percent level.

TABLE 12. ANALYSIS OF VARIANCE FOR TCE RESIDUAL CONCENTRATION, CONSTANT TCE CONCENTRATIONS

Source of variation	Sum of squares	Degrees of freedom	Mean square	Calculated F	
Replication	1,241.3878	1	1,241.3878	1.2599	
A Operating temperature	33,403.6545	1	33,403.6545	33.901	>4.45*
B Moisture content	197,854.3739	2	98,927.1870	100.40	>3.59*
C Soil type	20,238.8123	2	10,119.4061	10.27	>3.59*
AB	20,965.7772	2	10,482.8886	10.64	>3.59*
AC	6,121.8088	2	3,060.9044	3.11	
BC	11,040.6294	4	2,760.1574	2.80	
ABC	5,505.3395	4	1,376.3349	1.40	
Error	16,750.6922	17	985.3348		
Total	313,122.4756	35			

$F_{0.05}$ (1, 17) = 4.45
$F_{0.05}$ (2, 17) = 3.59
$F_{0.05}$ (4, 17) = 2.96

*Significant at the 5 percent level.

5. DISCUSSION

5.1 Volatilization kinetics. Statistically significant factors were:

(a) Constant moisture:
  - Operating temperature.
(b) Constant TCE concentration:
  - Operating temperature.
  - Soil moisture (dominant factor).
  - Interaction between them.

Relationships indicated by Figures 15 and 16 were:

(a) Kinetics is a function of operating temperature.
(b) Kinetics is a function of soil moisture.
(c) Kinetics is a function of a combination of temperature and moisture.

It may be expected that the rate of volatilization of a compound such as TCE would be a function of soil temperature. Figure 15 indicates that there may be a critical temperature in the vicinity of the boiling point of TCE (87°C) above which volatilization rates increase rapidly. This is a nonlinear relationship which most likely involves sorption/desorption thermodynamics.

The significant behavior of soil moisture and its interaction with operating temperature precludes a simple temperature relationship. Increased volatilization rates with increased moisture (within the bounds of moisture levels used in this study), and the interaction of moisture with temperature suggest a volatilization mechanism which involves sorption/desorption with soil particles and solution/desolution with soil moisture. This leads to the conjecture that TCE may follow a model formulated for certain pesticides.

According to this model, the volatilized compound rarely desorbs directly from soil particles. The reason is that in the competition for sorption sites on and within soil particles, TCE and similar low polarity compounds may be subordinate to soil water. That portion of TCE which succeeds in finding soil particle sorption sites may be difficult to dislodge directly. Therefore, the compound is more easily volatilized from either pockets of bulk material or from solution in soil water. Volatilization from bulk material is possible if the material is present far in excess of its solubility in available soil moisture and few sorption sites are available. This is most likely the case for the concentrations of TCE used in this study. Volatilization from soil moisture follows Henry's Law. Material already in solution is simply air stripped according to established mechanisms. Material sorbed in or on soil particles is more easily dissolved in soil moisture than stripped directly. Once in solution, air stripping proceeds.

This model holds until the amount of soil moisture drops below some critical value. It is thought that this critical value represents the moisture level at which the volatile material becomes the dominant sorbed species. It is now necessary to desorb larger amounts of the material directly from soil particles, something which requires significantly more energy than air stripping from solution.

The rate of desorption (volatilization) decreases proportionally.

Data generated in this study was sufficient to indicate statistical significance. This was necessary and sufficient for engineering preparation of pilot studies. They were not sufficient to verify the volatilization model outlined above. The data do fit the model conceptually, and it is recommended that mechanisms analogous to those of the model are operative in this situation.

Temperature and moisture are critical to the rate of volatilization of TCE. It is important that the moisture level of soil being air stripped of TCE not be decreased prior to placement in the volatilization chamber.

5.2 TCE residuals, percentage. The existence of a TCE residual, verified by separate analysis, was a surprise. Formulation of the original Test Plan, Appendix A, was based on the assumption that TCE would be sufficiently volatile to permit essentially complete stripping. Time for completion was anticipated to be the primary dependent variable.

A residual did exist under most of the experimental conditions of this study. Evaluation of residuals was first made on the basis of residual proportion to total TCE volatilized so that direct comparison of data could be made without reference to specific soil properties (e.g., sample weight and soil density). Summary results of statistically significant factors were:

(a) Constant moisture:
  - Operating temperature.
  - Soil type.
  - Interaction between the above.

(b) Constant TCE concentration:
  - Operating temperature.
  - Soil moisture.
  - Interaction between the above.

Operating temperature was the dominant factor in both cases.

Relationships indicated by Figures 17 and 18 were:

(a) Residual fraction decreases as temperature increases.
(b) Residual fraction decreases as soil moisture increases.
(c) Residual fraction inversely proportional to an unspecified interaction between soil type and operating temperature.
(d) Residual fraction inversely proportional to an unspecified interaction between soil moisture and operating temperature.

TCE concentration was not statistically significant to the behavior of residual fractions. This was not surprising since proportions were used rather than absolute values. In such cases, the proportions tend to normalize data and eliminate variations due to absolute values. Proportions permit wide comparability of data when searching for trends, patterns, and related behavior.

A model is not proposed for TCE residuals. It is conjectured that the existence and relative magnitude of a residual may be dependent upon soil parameters such as clay content (related to specific surface area) and organic content (related to sorption of organic compounds in the organic fraction). These are key parameters in modeling transport of materials through soils.

The primary characteristic of the TCE residuals observed in this study is that they existed at stripping temperatures below 120°C for processing times less than 20 minutes.

5.3 TCE residuals, concentration. When sample weights were used to compute absolute values of residual concentration, increased variability was introduced to the residual data because of differences in individual soil densities and variations in experimental sample weights. Under these conditions, all experimental factors and most of their paired interactions were statistically significant. These results followed observations for residual fractions.

Important to this discussion are the residual concentration values. These values ranged from not detected to more than 1,300 ppm. It is not clear if these concentrations were true properties of the soil/solvent system under study or were artifacts of the experimental apparatus and procedures. Residual patterns were reasonably consistent, however, and their existence at temperatures below 120°C have strong implications for design of pilot studies for heated air stripping of contaminated soils. Other implications, such as those for regulatory compliance, should be noted but placed in abeyance since only this set of data are available at present. Verification studies for the existence, magnitude, and conditions of TCE residuals are required. Some verification will come from an in situ pilot study under way at this writing.

5.4 Carrier gas flow rate. The experiment performed was designed with a fixed carrier gas flow through the soil contained in the test cell. This restriction (20 cubic centimeters per minute) was implemented during shakedown since higher carrier gas rates resulted in poor performance of the Hall cell.

In any gas stripping system the carrier gas rate is important to the stripping rate of a volatile compound from another media. Increasing the rate of stripping gas will increase the amount of contaminant stripped (based on mass transfer theory). Future pilot studies must utilize gas flow rate as an experimental parameter to observe the effects on TCE removal rate efficiency.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Volatilization kinetics. Operating temperature (the temperature of the soil being treated) and the level of soil moisture are two factors in determining the rate of TCE volatilization from the three soils under study. Volatilization rates can be increased by almost a factor of 3 when the operating temperature is raised from 27° to 120°C. Volatilization rates can be increased by almost a factor of 8 when soil moisture is raised from a 60°C equilibrium to an ambient equilibrium level.

There is an undefined interaction between temperature and moisture which is also significant.

6.2 TCE residuals, percentage. TCE residuals occurred in this study for all experimental conditions at operating temperatures less than 120°C.

Residual fractions were signifcantly dependent upon all experimental factors except TCE concentration. Increased operating temperature, increased soil moisture, and change from Letterkenny to Sharpe types of soils all decreased residual fractions. Paired interactions between the significant factors were noted to exist but were not definable.

6.3 TCE residuals, concentration. All experimental factors and all paired interactions between them were statistically significant to TCE residual concentration levels.

6.4 Engineering implications.

6.4.1 Assumptions.

(a) The significant factors identified in this study will also be significant factors in a pilot study.
(b) The conclusions from this study are correct and based upon actual phenomena.
(c) Increased carrier gas flow rate will be a significant factor in increased TCE removal rates.
(d) Engineering extrapolations can be made from the data of this study for the purpose of designing subsequent pilot-scale studies or for the purpose of suggesting modifications to study plans for pilot-scale studies in progress.

6.4.2 Implications for ambient temperature volatilization. The obvious and consistent patterns in temperature dependency of both kinetics and residuals implies that significant residuals would remain from attempts to air strip TCE from soils at ambient temperatures greater than 90 percent of original TCE spike with soils at ambient moisture. The kinetics factor must be taken into account. Pilot studies may reveal that ambient temperatures merely prolong the stripping process and the end result would be the same regardless of temperature. This has to be verified.

6.4.3 Implications for thermally induced volatilization. Temperatures above ambient are required to improve stripping kinetics and to minimize residuals. The operating temperature should reach 110 to 120°C for complete stripping of TCE. Covolatilization of water vapor with the TCE may assist in completely scrubbing the TCE residual. This has to be verified.

Machinery for stripping TCE from soil may be of two types. The first is a single chamber device operating at the appropriate temperature throughout. The second is a two-stage device having a low temperature first stage and a high temperature second. A comparative evaluation is required to be able to recommend which generic type may be most applicable.

6.4.4 Options for pilot-scale testing of thermally induced volatilization. Equipment most readily adaptable to pilot testing of thermally induced volatilization comes from the field of commercial drying.

The protocol for pilot testing should be designed to verify the conclusions of this study and to provide answers to engineering questions of optimization.

Machinery employed for pilot testing should have sufficient controls to permit parametric testing of both design and operational parameters. Compromises will be required to avoid the necessity of custom construction. Parameters include feed rate, TCE concentration, operating temperature, soil moisture, feed preparation, agitation rate, and air recycle rate.

Options for equipment include actual pilot-scale machinery and small-scale commercial machinery. A brief survey of the equipment market revealed that both options are conceptually viable. Actual selection will depend upon availability, configuration, cost, and dependency on proprietary designs.

APPENDIX A

TEST PLAN FOR A BENCH-SCALE INVESTIGATION OF LOW TEMPERATURE THERMAL REMOVAL OF TCE FROM SOIL

Contract No. DAAK11-82-C-0017
Task Order 4

INSTALLATION RESTORATION GENERAL ENVIRONMENTAL TECHNOLOGY DEVELOPMENT

Test Plan for a Bench-Scale Investigation of Low Temperature Thermal Removal of TCE from Soil

Walter L. Lambert, Ph.D.

Lawrence J. Bove

Peter J. Marks

ROY F. WESTON, INC.
West Chester, Pennsylvania 19380

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Prepared for:

U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
Aberdeen Proving Ground (Edgewood Area), Maryland 21010

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EXECUTIVE SUMMARY

The purpose of the test is to prove the concept of low temperature (ambient, i.e., 100+ °C) thermal removal of trichloroethylene (TCE) from soils.

The objectives of the bench-scale study are the following:

(a) Identify statistically significant parameters that affect removal rate and residual levels.
(b) Determine the sensitivity of residuals to key operational parameters.
(c) Bracket the values of key design and operational parameters.
(d) Provide a data base for deciding whether to employ pilot- or demonstration-scale testing.

The variables and parameters to be controlled and/or measured are the following:

(a) Independent experimental variables:

- Moisture content of soil at two levels.
- Temperature of the test environment at three levels.
- TCE concentration of the test soil at three levels.
- Flow rate of purge gas (nitrogen flow used to carry TCE from heated soil), fixed by preliminary experiments at one level.
- Soil type (uncontaminated soil from actual installations) fixed at three levels (from three sites).

(b) Dependent experimental variables are the following:

- TCE concentration of purge gas (leaving heated soil sample), continuously sampled and measured.
- TCE concentration of the soil during an experiment, computed by mass balance.
- TCE concentration of the soil, measured immediately upon completion of an experiment.

(c) Parameters to be monitored as part of an experiment are the following:

- Temperature of soil sample at start of experiment.
- Temperature of soil sample during an experiment.
- Temperature of soil sample immediately upon completion of an experiment.
- Temperature of purge gas entering sample container.
- TCE concentration of purge gas before entering sample container.
- Dry weight of soil sample.
- Time.

The test design is a full factorial, as follows:

(2 levels of soil moisture) x (3 temperatures) x (3 TCE concentrations) x (3 soil types) x (3 replications) = 162 experiments

The levels of the experimental variables are as follows:

Variable	Level 1	Level 2	Level 3
Soil moisture	20 percent	40 percent	---
Temperature	25°C	90°C	150°C
TCE concentration in soil	10 mg/kg (dry)	100 mg/kg (dry)	1,000 mg/kg (dry)
Soil type	Location 1	Location 2	Location 3

The test apparatus is a modified Hewlett-Packard Model 5880A gas chromatograph (GC) with a Hall detector. Flow-through sample tubes will be held under isothermal conditions in the GC oven. Dry nitrogen purge gas will flow through the tube and carry off TCE through a programmed sampling valve to a Hall detector. The rate of TCE volatilization will be recorded on an individual grab sample and cumulative basis. A mass balance around the soil sample will provide interim values for TCE residuals. Figure 1 is a diagram of the test apparatus.

Data analysis will be step-wise linear regression and analysis of variance. Models have been identified from the areas of soil volatilization of organic chemicals, commercial drying operations, and dimensional analysis for investigating stripping effectiveness and kinetics.

1. Hydrogen flow control
2,3. Nitrogen flow control
4. Divert valve
5. Thermocouple
6. Sample column
7. Glass wool
8. 1/10 in. SS tubing
9. Forced air oven
10. 6 port 3 cross valve
11. Valve oven
12. Valve driver
13. Hall furnace
14. Hall conductivity cell

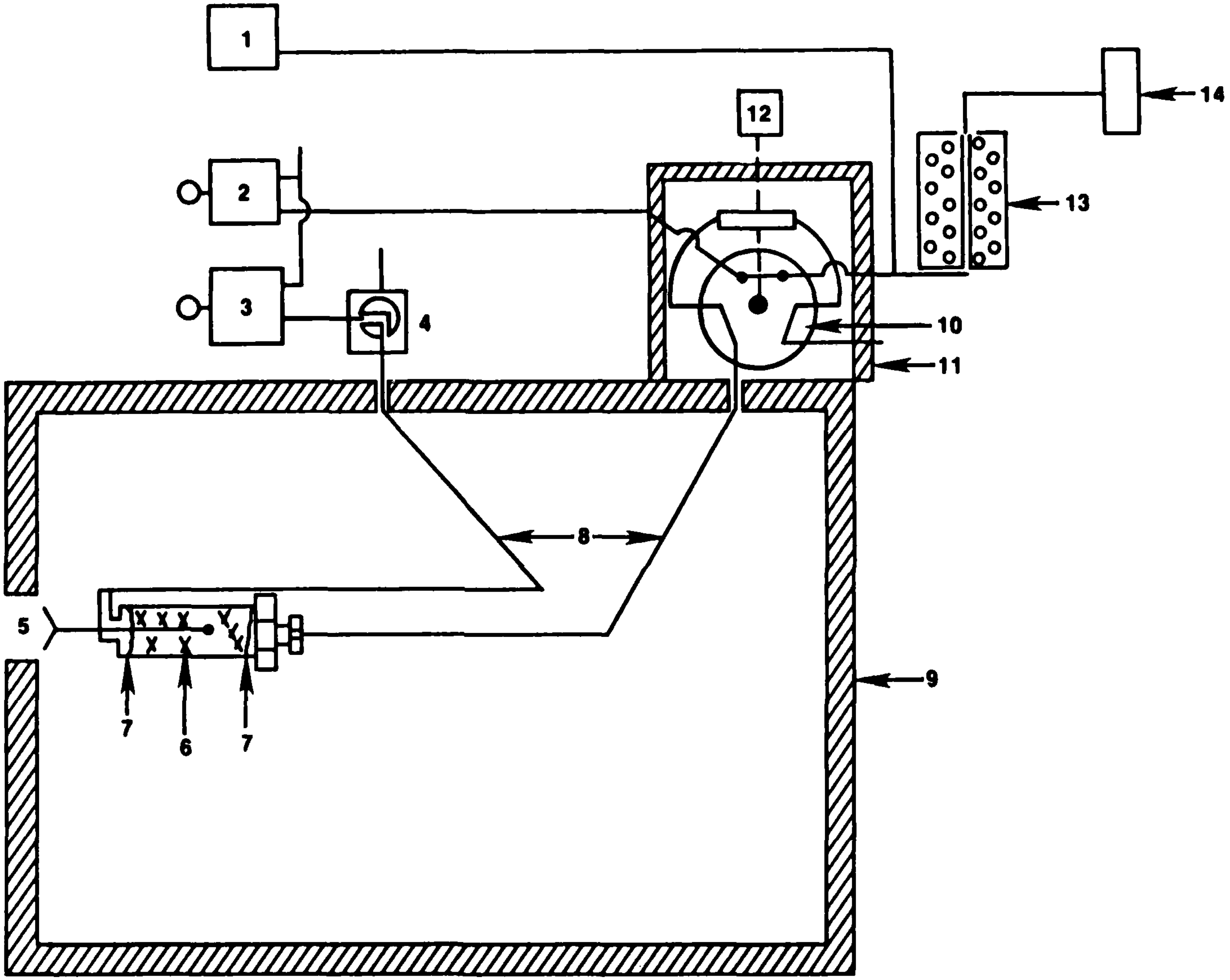


Figure 1. Schematic of the apparatus to measure the volatilization of TCE from soil.

Details concerning the rationale for the selection of experimental variables, test apparatus, and the most likely commercial-scale unit processes are provided in this test plan.

Execution of the plan will involve continual interaction between WESTON and USATHAMA. It is anticipated that a mid-stream decision will be required on the final choice of the third temperature to be used. Data analysis will begin soon after the receipt of initial experimental data. The results of that analysis may indicate that a temperature other than 150°C should be used. This will be presented prior to the start of experiments at the third temperature level.

1. PURPOSE AND OBJECTIVES

1.1 Purpose. Contamination of soils with trichloroethylene (TCE) is an identified concern at several U.S. Army Development and Readiness Command (DARCOM) installations. The purpose of this test plan is to provide detailed guidance and specific procedural information for execution of bench-scale testing of a concept for low temperature removal of TCE from soils.

Low temperature stripping of TCE from aqueous solutions has been demonstrated to be an economical and practical process. However, information concerning low temperature removal from a soil medium is scarce and limited. The objective of this investigation will be to develop design parameters for this process, and to determine the factors that would affect removal efficiency.

The purpose of the investigation is to determine if the concept is feasible.

1.2 Programmatic framework. This test plan is an intermediate product within a general program for the development of pollution abatement technology. Preceding the test plan were extensive efforts in the following areas:

(a) Defining soil contamination problems at selected DARCOM installations.
(b) Identifying technologies that were conceptually feasible and economically attractive in mitigation but that were not necessarily state-of-the-art for such applications.
(c) Assessing those technologies to determine which, if any, were promising candidates for further research and development.

Experimental evaluation of promising technologies is to be conducted in a phased program that includes bench-scale investigations for proof of concept and pilot-scale investigations for verification of concept and for evaluation of engineering design and performance parameters. Each phase of the testing program is governed by detailed test plans of which this document is one.

1.3 Objectives. The primary objective of the investigation is to decide if the concept of low temperature thermal removal of TCE merits pilot-scale testing.

Secondary objectives include the following:

(a) Identification of process sensitive parameters, including an analysis of sensitivity.
(b) Indications of optimum ranges of operational parameters.
(c) Indications of the type of pilot- and full-scale equipment that may be most applicable.
(d) Preliminary (order of magnitude) cost analysis of the concept.
(e) Cost/benefit analysis to deterine applicability of further technology development.

1.4 Criteria for positive test of concept. A positive test of concept indicates that the concept is applicable. The criterion for judging whether the test is positive is a treated soil containing barely detectable trichloroethylene concentrations after treatment.

This criterion is based on anticipated requirements for volume production through commercial equipment. The available equipment itself demands an operating temperature in the range of ambient to 400°F. Economical throughput requires a soil residence time measured in minutes. The absence of a universally acceptable residual level of TCE in soils, and the exploratory testing for potential engineering performance (mass balance on TCE around the test system) require that essentially all of the TCE be removed.

2. PARAMETERS AND TEST CONDITIONS

2.1 Test parameters.

2.1.1 Definitions.

(a) Parameter. This is a measurable property or characteristic that may be quantified as part of bench-scale testing. The word is also used for constants, coefficients, and exponents that describe statistical populations. Both uses of the word will be applied in this test plan.

(b) Experimental variable. This is a parameter that is under investigation. Experimental variables are either dependent or independent. The latter are controlled, and their values are predetermined. The former are uncontrolled, and their values are monitored and measured.

2.1.2 Relevant test parameters. Thirty-seven parameters were identified as having relevance to this study. Of those, 18 were soil characteristics that were fixed by the source and type of soils to be used. The remainder were associated with either experimental or full-scale operation of potentially adaptable commercial equipment. Each of the parameters was considered to be a candidate experimental variable. An analysis of each was conducted, and the results are shown in Table 1.

All of the parameters in the list were either controllable or not. Some had relevance to bench testing, and all had relevance to full-scale operations. All were measurable. If used as an experimental variable, some were judged to be dependent in that they were judged to be products of a commercial operation. Others were judged to be independent because they were either fixed by materials to be used or could be controlled independently of one another.

Experimental variables were identified as parameters meeting the following set of criteria:

(a) Controllable.
(b) Relevant to bench-scale investigations.
(c) Measurable.
(d) Not fixed by preservation method, source of material, or condition of supply, e.g., TCE-free purge gas supplied in that condition in cylinders.

TABLE 1. ANALYSIS OF EXPERIMENTAL VARIABLES

Parameter, characteristics, descriptor, variable, or condition	Controllable?	Relevance to phases of testing				Measurable/ method	As an experimental parameter		Sample type		Test plan classification of parameter		
		Bench	Breadboard	Pilot	Production		Independent	Dependent	Discrete	Continuous	Dependent	Independent	Experimental parameter, but not a variable
1. Moisture content, soil, initial	Yes	X	X	X	X	Yes -- ASA 7-2.2	X		X			X	
2. Moisure content, soil, final	No			X	X	Yes -- ASA 7-2.2		X	X				
3. Moisture content, soil, interim	No			X	X	Yes -- Mass balance calculation - ASA 7-2.2		X	X				
4. Moisture content, purge gas, inflow	Yes -- bench No -- production			X	X	Yes -- fixed-dry	X		X				
5. Moisture content, purge gas, outflow	No -- bench Yes -- production			X	X	Yes -- GC		X	X				
6. Temperature, oven environment	Yes	X	X	X	X	Yes -- thermocouple, direct reading	X			X		X	
7. Temperature, soil sample, initial	Yes	X	X	X	X	Yes -- thermocouple, direct reading, fixed	X		X				X
8. Temperature, soil sample, interim	No			X	X	Yes -- thermocouple, direct reading		X		X			X
9. Temperature, soil sample, final	Yes			X	X	Yes -- thermocouple, direct reading		X	X				X
10. Temperature, purge gas, inflow	Yes	X	X	X	X	Yes -- fixed at oven temperature	X			X			X

TABLE 1. (Continued)

Parameter, characteristics, descriptor, variable, or condition	Controllable?	Relevance to phases of testing				Measurable/method	As an experimental parameter		Sample type		Test plan classification of parameter		
		Bench	Breadboard	Pilot	Production		Independent	Dependent	Discrete	Continuous	Dependent	Independent	Experimental parameter, but not a variable
11. Temperature, purge gas, outflow	Yes			X	X	Yes -- fixed at oven temperature		X		X			
12. TCE concentration, soil, initial	Yes	X	X	X	X	Yes -- method-	X		X			X	
13. TCE concentration, soil, interim	No	X	X			Yes -- computed by mass balance		X	X		X Computed		
14. TCE concentration, soil, final	No	X	X	X	X	Yes -- method-		X	X		X Computed		
15. TCE concentration, purge gas, inflow	Yes			X	X	Yes -- fixed at zero	X		X				X
16. TCE concentration, purge gas, outflow	No	X	X	X	X	Yes -- GC sample method		X	X		X Measured		
17. Weight, soil sample, dry	Yes	X	X	X	X	Yes -- ASA 7-2.2 "fixed"	X		X				X
18. Time of volatilization	No	X	X	X	X	Yes -- elapsed time, GC computer	X			X			X
19. Flow rate, purge gas	Yes	X	X	X	X	Yes -- mass flowmeter, GC	X			X		X	
20. Soil characteristics	Fixed source	X	X	X	X	Yes	X		X			X	

Independent experimental variables for consideration in this study are the following:

(a) Moisture content, soil, initial.
(b) Temperature, oven.
(c) TCE concentration, soil, initial.
(d) Flow rate, purge gas.
(e) Soil characteristics (18 characteristics).

Dependent experimental variables are the following:

(a) TCE concentration, purge gas, outflow (measured), continuous.
(b) TCE concentration, soil, interim (computed).
(c) TCE concentration, soil, final (measured).

Experimental parameters for monitoring are the following:

(a) Temperature, soil sample, initial.
(b) Temperature, soil sample, interim.
(c) Temperature, soil sample, final.
(d) Temperature, purge gas, inflow.
(e) TCE concentration, purge gas, inflow.
(f) Weight, soil sample, dry.
(g) Time.

2.2 Test design.

2.2.1 Discussion, independent variables. The moisture content of the soil to be stripped of TCE is a key parameter for several reasons. First, the various forms of water found in soils are energy sinks. It is anticipated that water will be vaporized jointly with TCE, with energy consumed in the process. On the other hand, the microscopic behavior of TCE toward soil particles, interstitial water, and their interface is unknown. It may be that free water will be required to expedite TCE removal because TCE may be more easily distilled from solution than stripped from dry soil particles. For full-scale operations, it may not be feasible to reduce the moisture content of contaminated soils prior to heating; however, it may be possible to increase the moisture. Therefore, two moisture levels are considered adequate for bench testing. One level will reflect current past experience with actual contaminated soils (12+ percent). The second will be at a higher level to determine the sensitivity of the thermal process and to simulate conditions that may be feasible at full-scale. Both levels need to be controlled. The lower was chosen to be 20 percent, which is a little above ambient to allow control in the laboratory. The second was 40 percent.

Stripping temperature is a second key parameter. Attaining and maintaining temperature in a commercial unit will depend on the heat capacity and initial temperature of the feed material, heat losses of the equipment, and amount of water costripped. Maintaining the stripping temperature is directly related to fuel costs. The objective of a commercial operation will be to operate at the lowest temperature that provides an acceptable product. Bench testing should narrow the range of preferred temperatures as much as possible. Three benchmark temperatures are the following:

(a) Ambient (25°C).
(b) Greater than ambient and less than the boiling point of water ($25^oC > T < 100^oC$).
(c) Greater than the boiling point of water (above 100°C).

The level of TCE in the feed material is an obvious key parameter. It will be interesting to determine if, however, the rate of removal of TCE is a simple function of temperature. If so, operating parameters such as soil residence time may be predicted by knowing the TCE level. Making such a determination requires at least three levels of TCE in the feed soil. Three levels considered adequate for investigating TCE concentration effects are 10, 100, and 1,000 mg TCE/kg dry soil. These concentrations were selected based on WESTON's experience with TCE levels in contaminated soils on DARCOM installations.

The flow rate of the purge gas moving through or over heated soil is a critical operational parameter for removal of water or large quantities of solvents. In those cases, the relative humidity of the purge gas before and during operations influences the rate and amount of water or solvent pickup. A review of the psychometric behavior of benzene, whose physical behavior should approximate that of TCE, indicated that saturation of the purge gas is unlikely at the levels of TCE used in this study. Therefore, it appears that the flow rate of the purge gas can be fixed at a value approximating that which would be found in full-scale equipment.

Eighteen soil characteristics are given for the soil under study. It is anticipated that widely differing soils from three sites will be used.

A soil scientist will collect bulk quantities of each soil at each location. It is important to recognize differences between soil horizons with depth, especially organic content. Collecting a representative sample of site-specific soil will depend on proper sampling and compositing. How each soil is to be collected will depend on an estimate of soil conditions at each site. The specific sampling strategy to be used will be determined after the site assessment.

2.2.2 Data analysis. It is desirable to extract as much information as possible from the minimum number of experimental runs. The method planned for data analysis is step-wise linear regression with two-way analysis of variance.

2.2.3 Experimental design. A full factorial design with three replicates per test case is planned. The number of runs are:

> (2 levels of soil moisture) x (3 drying temperatures) x (3 TCE concentrations) x (3 soil types) x (3 replicates) = 162 runs.

Experimental runs made as part of the factorial design do not include preparatory runs for equipment shakedown and exploratory runs for fixing the flow rate of the purge gas.

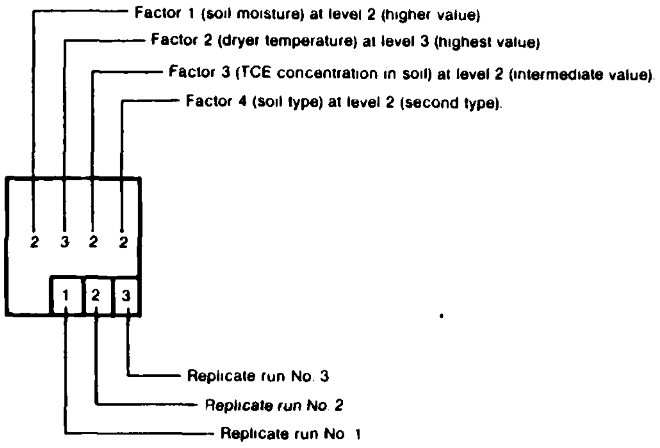
Identification of each run is provided in Figure 2. Each run is identified by a five-digit number. Each digit denotes one of five experimental variables (factors), and the value of the digit denotes the level (value) of that factor.

The values shown in Figure 2 for each level of the experimental factors are tentative. They are based on best estimates at the time of plan preparation. During the shakedown phase of the project, it may be found that levels for some factors may have to be changed. Temperature is an example. The standardized method for TCE headspace analysis uses 100°C as the driving temperature for removing TCE from small soil samples, quantitatively. It may turn out that two of the temperatures originally chosen fit the objectives of the study, but the third may have to be adjusted. If such adjustments are necessary, USATHAMA approval will be solicited prior to making the adjustment.

		Soil moisture level 1			Soil moisture level 2		
		Dryer temp. level 1	Dryer temp. level 2	Dryer temp. level 3	Dryer temp. level 1	Dryer temp. level 2	Dryer temp. level 3
TCE concentration level 1 in soil	Soil type 1	1111 1 2 3	1211 1 2 3	1311 1 2 3	2111 1 2 3	2211 1 2 3	2311 1 2 3
	Soil type 2	1112 1 2 3	1212 1 2 3	1312 1 2 3	2112 1 2 3	2212 1 2 3	2312 1 2 3
	Soil type 3	1113 1 2 3	1213 1 2 3	1313 1 2 3	2113 1 2 3	2213 1 2 3	2313 1 2 3
TCE concentration level 2 in soil	Soil type 1	1121 1 2 3	1221 1 2 3	1321 1 2 3	2121 1 2 3	2221 1 2 3	2321 1 2 3
	Soil type 2	1122 1 2 3	1222 1 2 3	1322 1 2 3	2122 1 2 3	2222 1 2 3	2322 1 2 3
	Soil type 3	1123 1 2 3	1223 1 2 3	1323 1 2 3	2123 1 2 3	2223 1 2 3	2323 1 2 3
TCE concentration level 3 in soil	Soil type 1	1131 1 2 3	1231 1 2 3	1331 1 2 3	2131 1 2 3	2231 1 2 3	2331 1 2 3
	Soil type 2	1132 1 2 3	1232 1 2 3	1332 1 2 3	2132 1 2 3	2232 1 2 3	2332 1 2 3
	Soil type 3	1133 1 2 3	1233 1 2 3	1333 1 2 3	2133 1 2 3	2233 1 2 3	2333 1 2 3

Note. This is a full factorial experimental design in which there are four factors (experimental variables), three of which are at three levels (three values), and one of which is at two levels (two values).

Each block in the design represents one set of experimental conditions. Each condition is to be run in three replicates. An explanation of the diagram blocks is shown below



Variable	Level 1	Level 2	Level 3
Soil moisture	20%	40%	
Dryer temperature	25°C	90°C	150°C
TCE concentration in soil	10 mg/kg *(dry)*	100 mg/kg	1,000 mg/kg
Soil type	Location 1	Location 2	Location 3

Figure 2. **Experimental design for investigating low temperature thermal removal of trichloroethylene from soils.**

3. TEST APPARATUS

3.1 Background. Thought was given to the types of commercial-scale equipment that might be used for volatilization of TCE from soils. A brief review of chemical and metallurgical processing equipment resulted in industrial dryers being the prime candidate for full-scale operations. A brief survey of dryer manufacturers and vendors was completed. It was evident from discussions with vendors that a bench-scale study using a general apparatus could not simulate the engineering performance of a full-scale unit. Therefore, the thrust of the bench study is proof of concept.

Considerations for selection, design, configuration, and operation of bench-scale apparatus included the following:

(a) A soil sample size in the 1-5 gram range. A review of thermal testing equipment available off-the-shelf, including a rather sophisticated differential scanning calorimeter, indicated that instrumentation for thermal analysis of either pure or homogeneous material is available. However, sample sizes are often in the 10 to 200 milligram range. This was considered too small. It was anticipated that variability among soil samples of such size would be unacceptably large, and the resultant masses of TCE evolved would be very small.

(b) Flow-through purge gas. Most of the applicable industrial dryer designs subject the treated material to either extensive tumbling or they force purge gas through the material as it travels on slotted belts and trays. In either case, purge gas passes through the material. It was considered important that this mode of gas travel be incorporated in the test apparatus design.

(c) Temperature control. Isothermal conditions rather than ramped heating of the sample were considered more applicable and meaningful. For proof of concept, temperature control to within a degree Celsius was judged adequate.

(d) Mass balance of TCE. The following three methods for closing the mass balance for TCE around the samples were considered:

- Direct weight loss measurement. This is a technique used in thermal gravimetric analysis (TGA). An analysis of sample size and TCE concentrations indicated that TCE weight losses over time would be so small that considerable experimental error would be introduced. This technique was rejected.

- Residuals measurement. A sampling technique was considered by which treated soil samples could be withdrawn from the heated environment and directly analyzed for TCE. A review of sample handling requirements, the number of samples required, and the sources of experimental error caused this technique to be rejected.
- TCE concentration in the purge gas. GC/Hall cell analysis for TCE appeared to be sufficiently sensitive to permit periodic sampling of the purge gas evolved from the heated soil sample. Frequent sampling with results integrated over the run time promised to provide a time-release curve for TCE. Analysis of duplicate soil samples prior to heating could provide the initial concentration of TCE in the soil. Elevating the oven temperature to approximately 110°C at the conclusion of a test run would drive off any residual TCE in the sample (this is analogous to the headspace method used to measure TCE in soils). This method promised to provide a reasonably accurate mass balance over time and was the method chosen.

(e) A review of candidate bench-scale laboratory equipment was made. It was concluded that all of the requirements for control, sample size, and detection could be satisfied if the test were run using various subassemblies of a standard gas chromatograph.

3.2 Test apparatus. Figure 3 is a diagram of the proposed test apparatus. Major subsystems of a Hewlett-Packard Model 5880A gas chromatograph (GC) will be adapted for use as a simulation system for through-circulation volatilization of TCE from a variety of soils.

The GC oven (Figure 3, item 9) will provide a controlled, isothermal environment. It can also provide ramped temperatures for TCE residuals volatilization, and for drying soil samples at the end of a run.

1. Hydrogen flow control
2,3. Nitrogen flow control
4. Divert valve
5. Thermocouple
6. Sample column
7. Glass wool
8. 1/10 in. SS tubing
9. Forced air oven
10. 6 port 3 cross valve
11. Valve oven
12. Valve driver
13. Hall furnace
14. Hall conductivity cell

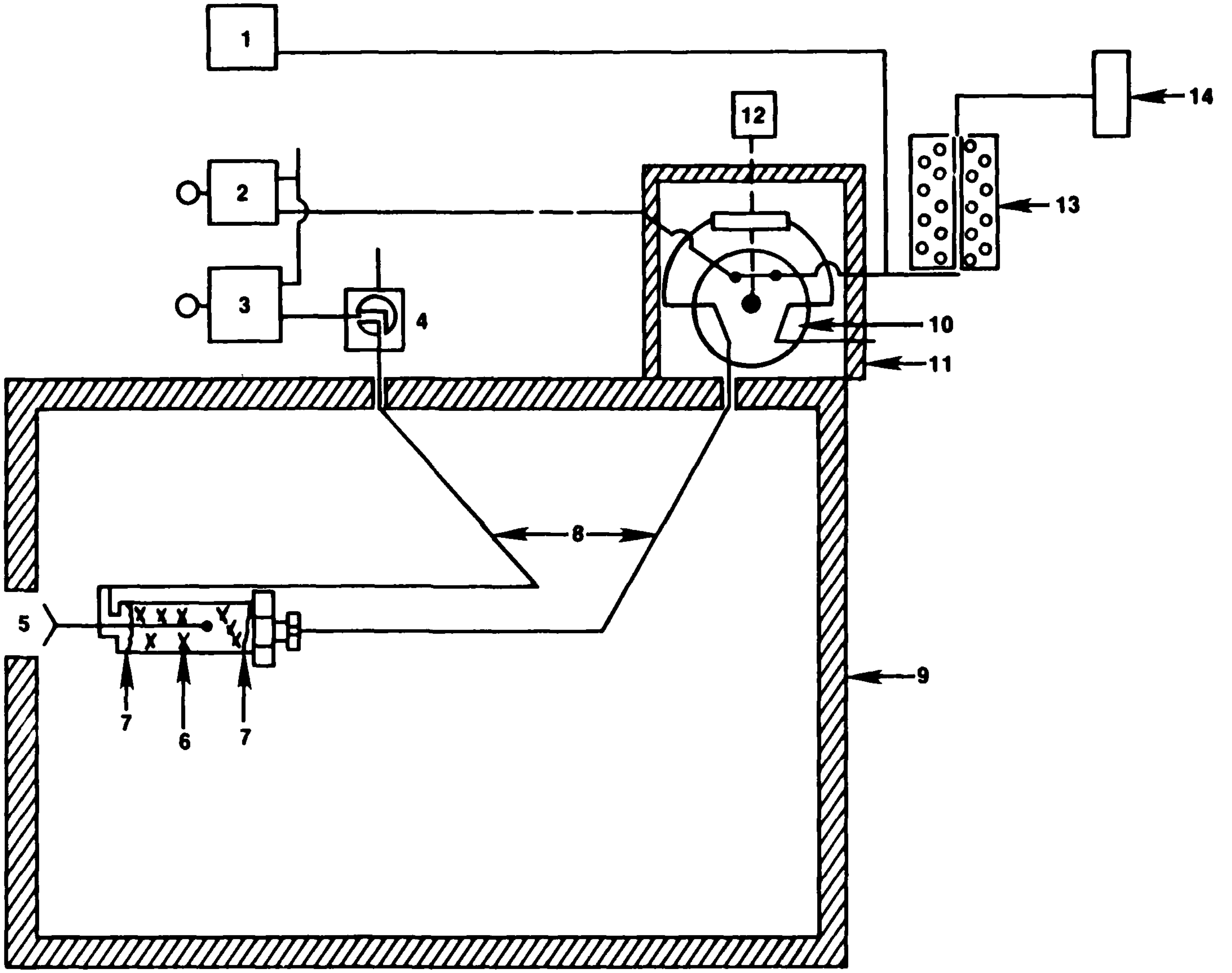


Figure 3. Schematic of the apparatus to measure the volatilization of TCE from soil.

Purge gas will be dry nitrogen (Figure 3, item 3). It will be brought to oven temperature by passing it through a coil of 1/16-inch stainless steel tubing (Figure 3, item 8) prior to entering the sample holding tube. The choice of dry nitrogen for purging was made on a worst-case basis. In a commercial dryer, it would be most economical to operate with unprocessed air that would have a variable relative humidity. Work on the volatilization of pesticides indicated that the rate of volatilization depended in a complex way on diffusion and mass transport of soil moisture. A dry purge gas will maximize the rate of water evaporation, which may provide the slowest rate of TCE volatilization. Nitrogen will not interfere with operation of the Hall cell.

One to five gram samples of spiked soil will be held in glass-wool stoppered tubing (Figure 3, item 6) at oven temperature. The sample tube will be fitted on either end with swageloc fittings for mating to the purge gas tubing. Inside the sample tube, and imbedded in the soil sample, will be a thermocouple (Figure 3, item 5) for recording the temperature of the soil sample during the experiment.

Off-gas carrying TCE and moisture will be valved (Figure 3, item 10) to a Hall furnace (Figure 3, item 13) and a Hall detector (Figure 3, item 14) for quantification of the TCE. The heated valve assembly (Figure 3, items 10, 11, and 12) will provide a series of short duration samples. The series of TCE peaks expected to be generated during a stripping simulation run will provide a TCE mass evolution rate (i.e., flux). Integration of the area under the set of curves will quantify the total mass of TCE evolved.

Temperatures in the oven and of the soil sample will be monitored by thermocouples connected to the GC's real-time clock with printer.

4. SAMPLING AND ANALYSIS PLAN

4.1 Sample preparation and handling.

4.1.1 Soils. Actual soils from three locations will be used. These soils should be free of TCE contamination (to be verified by analysis) but should be representative of the types of soils from their respective sites.

A stockpile of each of the three soils will be prepared from "virgin" material according to ASTM Method D-346-78. This will provide material that passes either a No. 60 (0.25 mm) screen (silts, clays, and loams), or a No. 20 screen (sands). The amount of dry material required in each of the three stockpiles is approximately 10 kg. Table 2 shows the estimates of processed soil required for each type of application to be made. Given 2,600 gm required, the amount to be prepared and stockpiled is:

$$(2{,}600\ \text{gm})\left(\frac{1\ \text{kg}}{1{,}000\ \text{gm}}\right)\underbrace{(1.50)}_{\substack{\text{Loss}\\ \text{factor}}}\ \underbrace{(2.5)}_{\substack{\text{Storage}\\ \text{factor}}} = 9.75 \doteq 10\ \text{kg}.$$

The amount of soil to be collected from each of the three sites is at least:

$$(10\ \text{kg})\underbrace{\left(\frac{1}{0.40}\right)}_{\substack{\text{Fraction}\\ \text{forced}\\ \text{through}\\ \text{No. 60 mesh}}}\left(\frac{2.205\ \text{lb}}{\text{kg}}\right) = 55.1 \doteq 55\ \text{lb}.$$

Since this is a small amount of soil to account for unseen on accidental losses, approximately 200 pounds of uncontaminated, representative soil (dry weight) should be collected per site to provide sufficient material to carry through the entire test plan.

A portion of the clean, prepared soil will be allowed to come to equilibrium with the relative humidity in the laboratory at ambient temperature and pressure. This portion will be used for moisture determination according to ASTM Method D-346-78 ($110^{\circ}C$). This moisture level is denoted W_e and will be used in subsequent data analyses.

TABLE 2. AMOUNT OF SOIL OF EACH TYPE REQUIRED

Application for soil sample	Weight per application	Number of applications	Total weight per type application
1. Equilibrium moisture	10 gm	3	30 gm
2. Headspace verification	10 gm	3	30 gm
3. Shakedown moistures	10 gm	5	50 gm
4. Shakedown headspace	10 gm	5	50 gm
5. Experimental moistures	10 gm	54	540 gm
6. Experimental headspace	10 gm	54	540 gm
7. Characterizations	1,000 gm	1	1,000 gm
8. Drying curves	5 gm	18	90 gm
9. Volatilization curves	5 gm	54	270 gm
Total minimum amount of prepared soil			2,600 gm

A second portion will be subjected to USATHAMA Method 2J, headspace analysis for TCE. This will verify the presence or absence of TCE or analytical interferences in the soil stockpiles. For example, carbonates and sulfates may cause interference if special handling is not used.

A third portion of each of the three soil types will be characterized for the parameters listed in Table 3. The methods to be used are also listed.

The remaining screened clean soil will be stored at 0 to 5°C in appropriate containers as a reserve stockpile. The remaining material will be used for characterization analyses, methodology shakedown, and experimentation.

4.1.2 Bulk samples. Eighteen different bulk TCE spiked soil samples will be prepared. These will reflect the following:

(3 types of soils) x (2 moisture levels)
x (3 TCE levels) = 18.

Bulk samples will be prepared in the following sequence:

(a) Air dry to equilibrium moisture.
(b) Spike with distilled water to bring up to predetermined moisture level.
(c) Mix in Teflon-sealed amber jar on rolling mill.
(d) Add TCE to predetermined level in bottle and seal.
(e) Move immediately to cold room (4 to 6°C).
(f) Mix thoroughly in Teflon-sealed amber jar on rolling mill.
(g) Store at 0°C.

Labels will reflect the factorial design identity of each bulk sample.

4.1.3 Experimental samples, soil. Experimental samples will be approximately 5-gm aliquots from their respective bulk containers. All handling of bulk containers and experimental sample tubes will be done in the cold room.

TABLE 3. CHARACTERIZATION PARAMETERS FOR EACH SOIL TYPE

Parameter	Method	Amount of soil required per test
Soil pH	ASA 60-3 (glass electrode pH meter)[a]	10 gm
Total organic carbon	ASA 90-2 (wet combustion)	2 gm
Total exchangeable bases (base saturation)	ASA 59-2 (residual carbonate method)	120 gm
Sand	ASA 43-3 (filtration/sieving)	100 gm
Silt and clay	ASA 43-3	Same sample
Particle size distribution	Standard sieve analysis	500 gm
Kaolinite	ASA 49-4 (X-ray diffraction)	100 gm
Illite	ASA 49-4	Same sample
Vermiculite	ASA 49-4	Same sample
Montmorillonite	ASA 49-4	Same sample
Chlorite	ASA 49-4	Same sample
Interstratified combinations of 2:1 type components	ASA 49-4	Same sample
Carbonate ($CaCO_3$)	ASA 91	25 gm
Aluminum, total	ASA 67-2	0.1 gm
Cation exchange capacity	ASA 57-3 (sodium saturation)	4 gm
Exchange acidity	ASA 59-2 (residual carbonate)	10 gm
Heat capacity	ASA 25-3 (calorimeter)	5 gm
Bulk density	ASA 30	100 gm
	Total minimum amount of soil for test battery	500 gm

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[a] C.A. Black, Editor-in-Chief, D.D. Evans, J.L. White, L.E. Ensminger, F.E. Clark, and R.C. Dinauer, Methods of Soil Analysis, Part 1: Physical and Mineralogical Properties, Including Statistics of Measurement and Sampling, and Part 2: Chemical and Microbiological Properties, Madison, Wisconsin: American Society of Agronomy, Inc., 1965.

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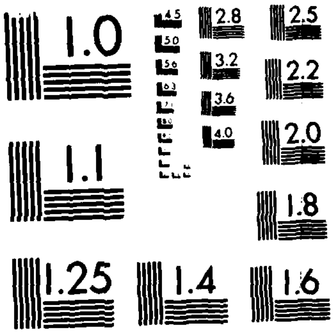

MICROCOPY RESOLUTION TEST CHART
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Experimental samples will be prepared and handled in the following sequence:

(a) Sample tubes, including thermocouple and glass wool, preidentified, are weighed after 24-hour residence in a dessicator at room temperature.

(b) In the cold room, approximately 5 gm of sample are transferred from the bulk container to the sample tube. Glass wool retains the sample, and filling the tube allows the thermocouple to be surrounded by soil. Glass wool is fitted into both ends of the tube, and the end fittings are attached. Both gas ports are capped.

(c) The prepared tube is temporarily stored at 0°C until the GC operator begins a run.

(d) After the run, the oven temperature is ramped up to 110°C for 30 minutes (if that temperature had not been exceeded for at least that long), and any residual TCE is recorded. The tube is then disconnected from the GC and placed in a dessicator, with both gas ports open, overnight.

(e) The tube, with dry soil inside, is reweighed, and the moisture content of the sample is computed. At 20 percent moisture, the amount of water present is, at a minimum, two orders of magnitude greater than the TCE initially present, therefore, any weight loss is attributed to water.

4.1.4 Experimental samples, off-gas. Dry nitrogen is the purge gas to be used for transport of TCE volatilized from experimental soil samples. The flow rate will be between 10 and 100 cu cm per minute, and will be fixed as part of the shakedown protocol.

Purge gas passing through the sample tube moves directly through the Hall furnace and Hall detector for quantitative measurement of HCl conductivity, which is proportional to the TCE carried off. This is a direct adaptation of a standard method for TCE analysis.

Time zero is when the purge gas flow through the sample tube commences.

Since a continuous flow of purge gas is not possible through the detector, a sampling valve is present in the tube exit line so that off-gas samples can be run through the detector at frequent, programmed intervals. Each of these gas samples lasts for a finite period of time (to be determined during shakedown). The mass of the TCE recorded for each gas sample over the sampling time represents a short-duration rate of TCE volatilization. The total mass of TCE or the cumulative mass of TCE volatilized over time is the integral under the curve connecting each of the individual sample values.

4.2 Baseline information requirements and procedures.

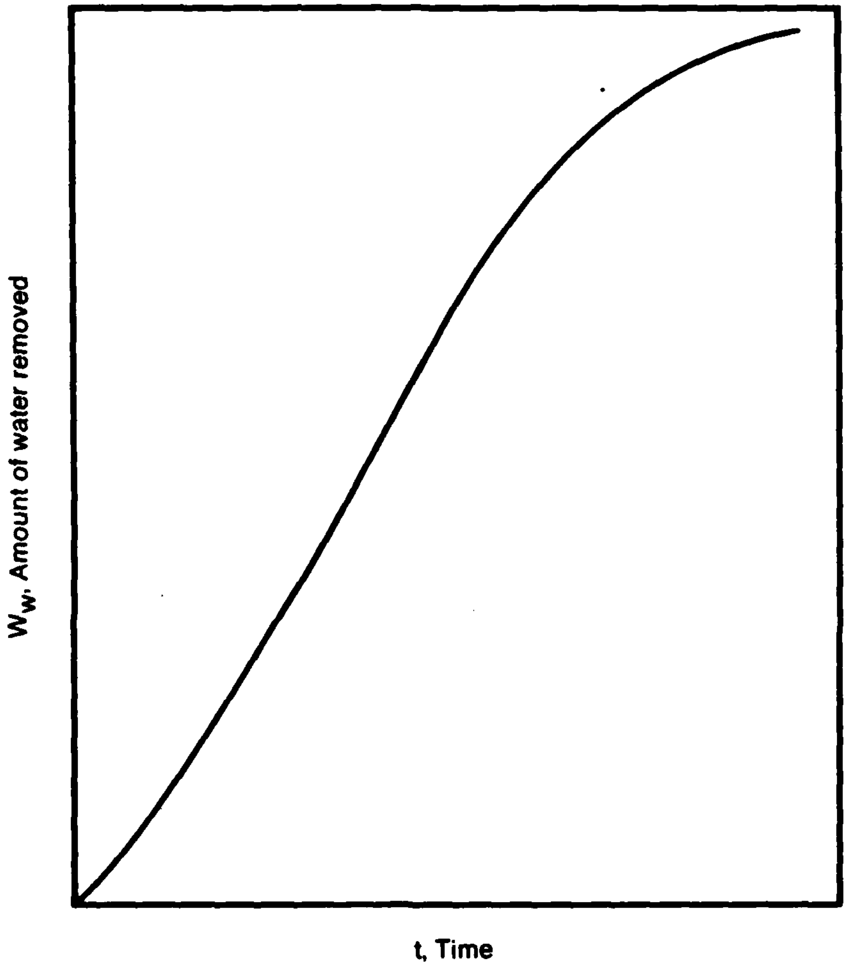
4.2.1 Bulk soil. The characteristics of each of the soils is required. (This list was shown in Table 3.) Each parameter in the list has a bearing on either the rate of volatilization of TCE or on questions concerning full-scale materials handling of TCE-contaminated soils.

The equilibrium moisture content of each soil is required. The value, called W_e, has relevance to theoretical models of water volatilization and may have a bearing on the rate of TCE volatilization.

A drying curve is required for each soil at each moisture being tested. This curve is generated using a technique called thermal gravimetric analysis. The soil is heated at constant temperature. The amount of water driven off is measured by the loss in weight of the soil sample. The number of drying curves needed is:

$$(3 \text{ soil types}) \times (2 \text{ moisture contents}) \times (3 \text{ temperatures}) = 18.$$

The need for this information stems from the unpredictable interaction between water remaining in the soil and the rate of TCE volatilization. An example of one type of drying curve is shown on Figure 4.



Note: This curve is generated at constant temperature gravimetrically. Values of W_w can be picked from the curve as raw data if needed for modelling the TCE volatilization process.

Figure 4. One type of drying curve.

The initial TCE concentration of the bulk material prior to spiking is required. There should be no TCE present in the soil obtained from each of the source sites. However, in the event there is, its concentration is required. At the same time, it will be important to determine if there are substances (i.e., sulfates, carbonates) in each of the soils that interfere with the TCE analytical method to be employed. In such a case, processing or resampling may be required. However, the appropriate course of action will not be clear until the nature of any interference is determined.

4.2.2 Experimental samples, soil and off-gas. The behavior of each of the actual soils to be used in the experimental apparatus is required. Blanks of TCE-free soil and TCE-free purge gas will be run to determine if materials causing interference will appear. This information will be obtained during the shakedown phase of the project and will result from applying exact experimental procedures to the blanks.

4.3 Experimental information requirements and procedures.

4.3.1 Experimental information.

4.3.1.1 TCE volatilized. The mass balance on TCE around an experimental soil sample will depend on accurate analysis of TCE in a duplicate sample immediately prior to the experiment and accurate GC/Hall cell analysis of TCE volatilized with time during an experiment. The method for determining TCE in a duplicate sample prior to experimentation will be USATHAMA Method 2-J. The Hall cell will provide a concentration of TCE captured during periodic sampling of the off-gas from the sample tube over a few seconds. It is anticipated that the trace from the GC will be reduced to a set of curves similar to those on Figure 5. The cumulative TCE volatilized will be the integral over the collection of individual sample curves.

4.3.1.2 Moisture content. A continual check on the actual moisture content of an experimental sample will be made in the course of each experiment by elevating the sample tube (if required) to drying temperature (110°C) at the end of each run. The behavior of water driven from the sample will be derived from drying curves performed previously on duplicate samples.

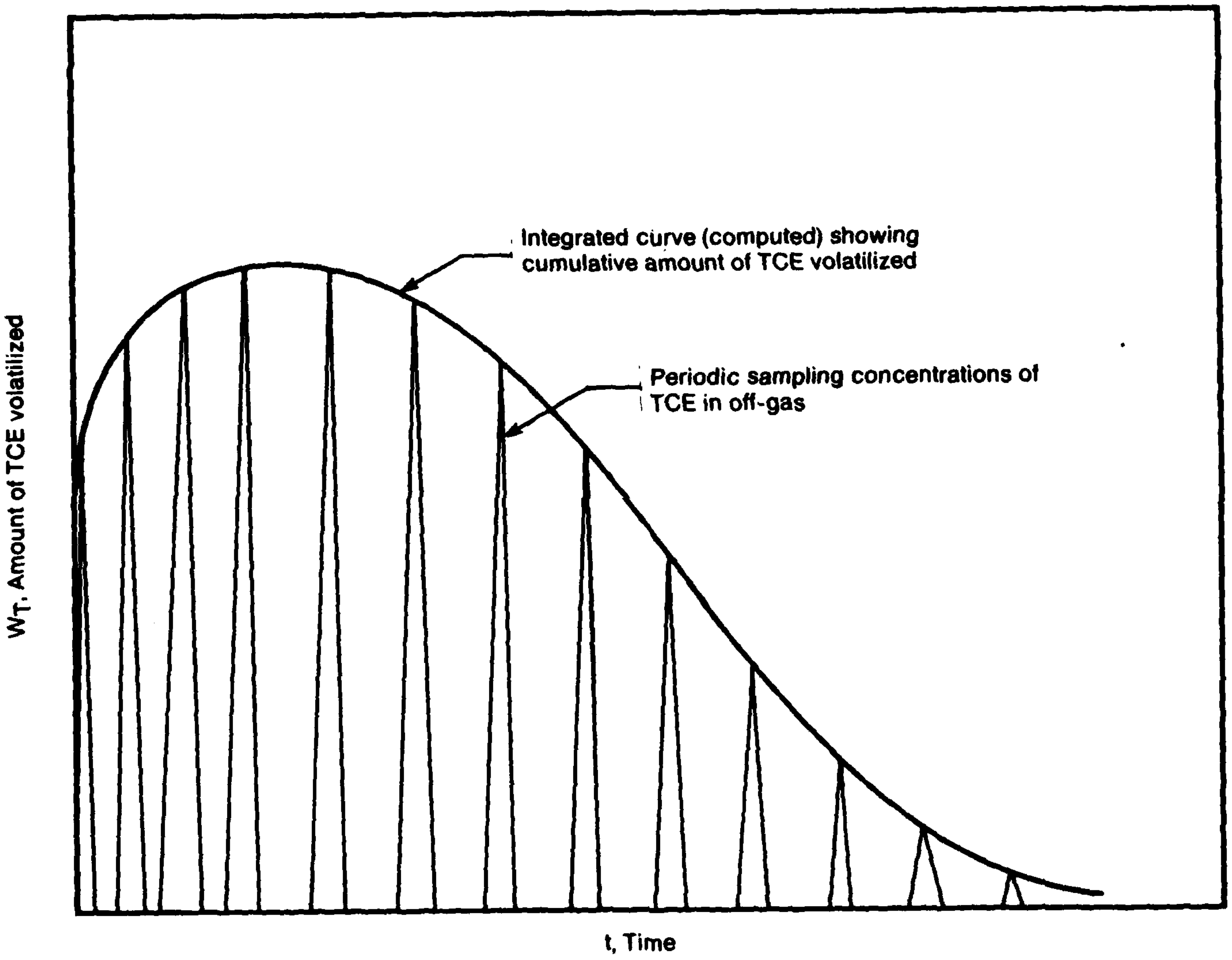


Figure 5. Type of TCE concentration curves anticipated.

4.3.1.3 Time. A real-time clock, which is part of the computerized data acquisition system on the GC, will record time as an overlay on the chromatograph output chart.

4.3.1.4 Temperature, oven. A thermocouple in the oven will continuously monitor oven temperature. A record will be maintained as a written overlay on the chromatograph output chart.

4.3.1.5 Temperature, soil sample. A thermocouple imbedded in the soil sample inside the sample tube will be linked to the GC data acquisition system. Soil temperatures will be overlaid on the chromatograph output chart.

4.3.1.6 Purge gas flow rate. This is a preset value calibrated prior to each experiment.

4.3.2 Experimental protocol. Table 4 shows a simplified protocol that will be followed. Analytical methods have been referenced elsewhere. Data analysis is addressed in more detail in a later section.

TABLE 4. SIMPLIFIED EXPERIMENTAL PROTOCOL

Soil acquisition and preparation	Apparatus preparation	Data or information obtained
1. Coordinate for the collection of 200 pounds of representative, uncontaminated soil from each of the three sites (performed by contractor personnel at each of the sites). These will be nonhazardous materials.	2. Acquire hardware, valves, and other items required for linking the various system components.	
	3. Assemble the experimental apparatus. Perform hydrodynamic testing for system integrity. Execute a shakedown protocol (internal) for determination of purge gas flow rate, sampling frequency of the off-gas, and other operational parameters.	3.[a] Purge gas flow rate. Sampling frequency of off-gas. Sample tube assembly and handling techniques. Temperature ramping for TCE residual and moisture content measurements.
4. Receive raw samples. Process by screening and crushing. Segregate aliquots for characterization and TGA analysis. Air dry bulk quantities in preparation for spiking.		
5. Spike bulk samples with water and TCE. Label according to experimental design. Perform shakedown protocol with experimental apparatus.	6. Complete assembly of three days of sample tubes and thermocouple assemblies.	
	7. Perform shakedown runs on Tektronix graphics terminal with stepwise linear regression routines for use in data analysis. Confirm format and style of input data. Prepare data tape. Design laboratory notebook data pages to permit fast data transcription.	
8. Perform characterization and TGA analyses.		8. Time release rates for water at experimental moisture and temperature levels. Permits calculation of residual water content, W_w, relevant to volatilization kinetics of TCE. Comparative characteristics including total organic content and relative clay content.
	9. Execute experimental design.	9. TCE release rates, moisture content, and TCE mass balance.
	10. Transcribe data onto floppy disk and analyze (with transformations and multiplicative models).	10. Significant and not significant parameters; kinetics model.

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[a] Numbers relate to protocol paragraphs of the same number.

5. DATA ANALYSIS

5.1 Proof of concept. The primary objective of the study is to demonstrate concept feasibility. Therefore, a plot of the type shown on Figure 6 may be sufficient to illustrate TCE volatilization for the test systems used.

A more meaningful graphic, however, would be one that related TCE residual in soil over time to various operational parameters. Figure 6 demonstrates one such plot that may come from this study. TCE residual in soil is related over time to the organic content of the test soil.

Figure 7 is along similar lines. It is anticipated that the rate of TCE volatilization may be directly proportional to drying temperatures for a period of time, and inversely proportional thereafter. This stems from a complex relationship between the partitioning of TCE among soil particles, interstitial water, and air. As the dry nitrogen carries off soil moisture, there is a possibility that TCE will strongly adsorb onto soil particles and be driven off more slowly.

Since there are no established allowable residual levels for TCE in soil, one objective of the data analysis will be to demonstrate how effective thermal removal of the chemical may be under specific conditions. It is anticipated that the lowest residual levels will at some point in time be more than sufficient to meet ambient residual levels.

5.2 Data analysis. This study was purposely designed to maximize the amount of information obtained with the minimum number of experiments. The analytical technique projected for use is stepwise linear regression with two-way analysis of variance. Results from such an analysis should indicate the following:

(a) Significant and relatively insignificant parameters.
(b) Insight into how significant parameters may be related.
(c) Insight into how the rate of TCE volatilization may be enhanced.
(d) In what direction a pilot or full-scale commercial dryer design might be made.

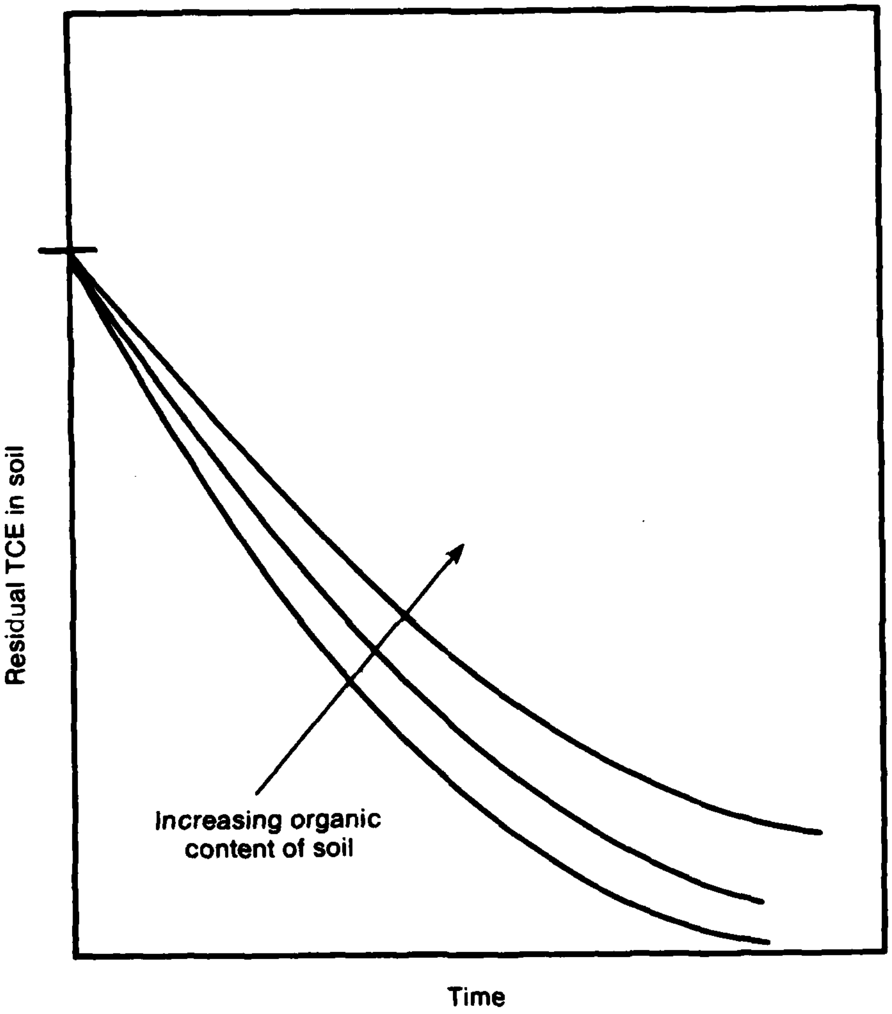

Figure 6. Anticipated relationship between TCE residuals in soil and total organic carbon of the soil.

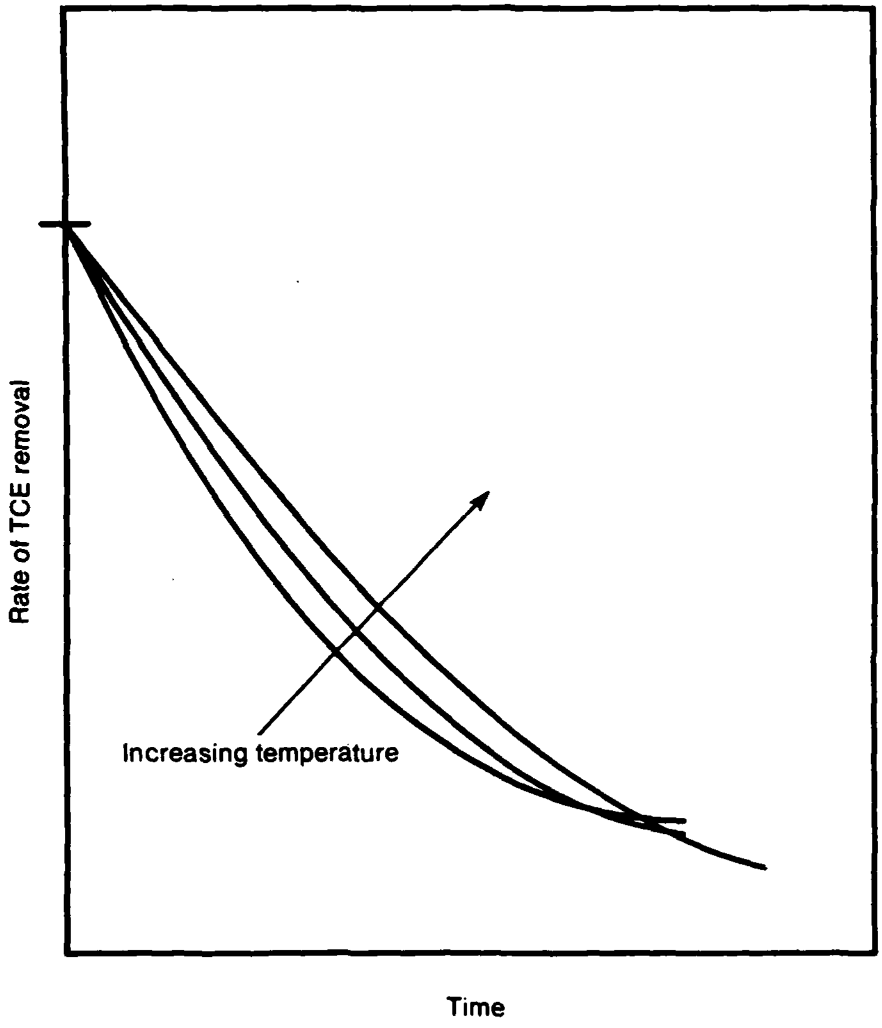

Figure 7. Anticipated relationship between TCE volatilization and drying temperature.

Data analysis will be performed using off-the-shelf software for the Tektronix graphics terminal system. Logarithmic transformations are anticipated to be required to linearize the data according to the various models.

A preliminary (order of magnitude) cost analysis will be made. It will be combined with a cost/benefit assessment of the question of whether to proceed to pilot-scale testing.

6. SCHEDULE

6.1 Project structure.

6.1.1 Work breakdown structure. The work breakdown structure anticipated for this project involves the following five technical tasks:

(a) Task 1 -- Setup and coordination.
(b) Task 2 -- Shakedown.
(c) Task 3 -- Experimentation.
(d) Task 4 -- Data analysis.
(e) Task 5 -- Final report.

6.1.2 Task 1 -- Setup and coordination. The objectives of this task include the following:

(a) Coordination, collection, and shipment of bulk quantities of soils.
(b) Final design and acquisition of hardware for an integrated test apparatus.
(c) Establishment of work areas and records for the project.
(d) Contract administration.

6.1.3 Task 2 -- Shakedown. The objectives of Task 2 include the following:

(a) Full operation of the test apparatus.
(b) Preparation of all bulk samples.
(c) Characterization of all soils.
(d) TGA analysis on all soils.
(e) Finalization of format and style of laboratory notebooks.
(f) Specification of purge gas flow rate.

This task will be conducted within the bounds of a formal protocol for those operations requiring close supervision and timely execution. This protocol will be internal and will not be a contract deliverable. Upon completion of this task, all preparations for experimentation will have been completed.

6.1.4 Task 3 -- Experimentation. This task is the execution of the designed experiment.

6.1.5 Task 4 -- Data analysis. Work will begin on this task during Task 2 and will accelerate upon completion of approximately a third of the experimental design. It may be necessary to change experimental conditions upon completion of two-thirds of the design to accommodate new information or indications that the original parameter values were not optimum. Therefore, partial analysis of experimental data will occur throughout Task 3.

6.1.6 Task 5 -- Final report. This is a contract deliverable and will incorporate a complete record of the project. Both a draft final and a final report will be prepared.

6.2 Project schedule. Figure 8 provides a tentative Gantt chart showing that the anticipated execution time to produce a draft final report is approximately 19 weeks.

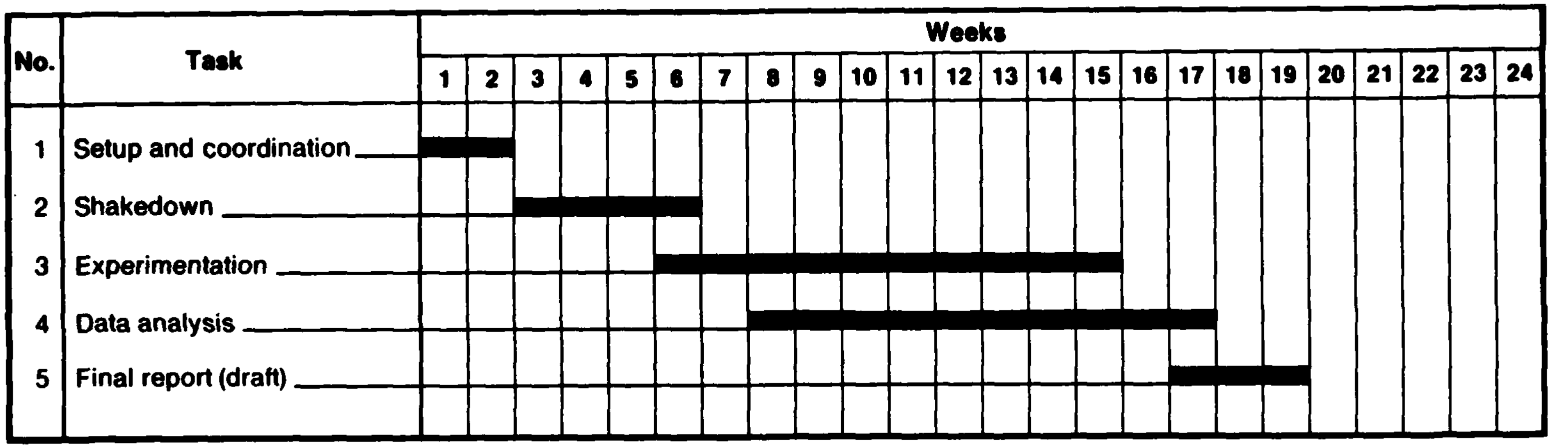

Figure 8. Projected technical schedule.

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