Environmental Technology Verification Report

CONSTELLATION TECHNOLOGY CORPORATION
CT-1128 PORTABLE GAS CHROMATOGRAPH-MASS SPECTROMETER

Prepared by
Battelle

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The Business of Innovation

Under a cooperative agreement with

U.S. Environmental Protection Agency

ETV ETV ETV

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

EPA
U.S. Environmental Protection Agency

Battelle
The Business of Innovation

ETV Joint Verification Statement

TECHNOLOGY TYPE:	**Mobile Mass Spectrometers**
APPLICATION:	**Monitoring volatile organic compounds, pesticides, and chemical agents in water**
TECHNOLOGY NAME:	**CT-1128 Portable Gas Chromatograph–Mass Spectrometer (GC-MS)**
COMPANY:	**Constellation Technology Corporation**
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The U.S. Environmental Protection Agency (EPA) has established the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies. Information and ETV documents are available at www.epa.gov/etv.

ETV works in partnership with recognized standards and testing organizations, with stakeholder groups (consisting of buyers, vendor organizations, and permitters), and with individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The Advanced Monitoring Systems (AMS) Center, one of six technology areas under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. The AMS Center evaluated the performance of the Constellation Technology Corporation's CT-1128 Portable Gas Chromatograph–Mass Spectrometer (GC-MS). This verification statement provides a summary of the test results.

VERIFICATION TEST DESCRIPTION

Many volatile and semivolatile contaminants in water are detected using bench-top mass spectrometers in a traditional laboratory setting. However, the CT-1128 verified in this test was a portable unit designed to be taken outside the laboratory setting for field analysis. This portability offers an advantage to first-responders and other users who need chemical information when time, sampling, and other limitations preclude analysis in a laboratory.

The ability of the CT-1128 to identify and quantify target contaminants was tested in various water matrices. The CT-1128 was evaluated for the following performance parameters:

- Accuracy
- Precision
- Linearity
- Instrument stability
- Potential matrix and interference effects
- Sensitivity
- Field portability
- Operational factors.

Three classes of contaminants were used for testing: volatile organic compounds (benzene, toluene, ethyl benzene, total xylenes [BTEX]), pesticides (2,4-D and dicrotophos), and chemical warfare agents (VX, GB, and GD). The contaminants were selected based on recommendations from the AMS Center stakeholders.

Performance test (PT) samples were prepared in American Society for Testing and Materials (ASTM) Type II water. The target contaminant concentrations were constructed to bracket the concentrations of interest, which were calculated using LD_{50} values assuming a 70-kilogram individual consuming 250 milliliters of the contaminated water. When LD_{50} data were not available or feasible for testing, maximum contaminant levels (MCLs), as defined by EPA National Primary Drinking Water Regulations, were used. Reference measurements were conducted on PT samples only, to confirm the accuracy of sample preparation. EPA methods 524.2 and 515.1 were used for analyzing BTEX and 2,4-D, respectively. Internally developed methods were used for the remainder of the contaminant reference methods since no external methods were available from commercial laboratories at the time of testing.

The PT samples were used to determine the accuracy of the CT-1128; one set of which was used to establish a calibration curve. Subsequent analyses of the PT samples on multiple testing days were then used to calculate the accuracy of the CT-1128 measurements. To measure the potential matrix effects on the CT-1128 in selected real-world applications, it was challenged by analyzing samples fortified with the target contaminant in various matrices including drinking water (DW) samples (which varied in source and treatment), a weakly buffered water sample, a strongly buffered water sample, and a trihalomethanes (THMs)-fortified water sample. The concentration of a mid-level PT sample was used to fortify the matrix samples. This concentration provided a convenient level that was approximate to or below the concentration of interest for the target contaminants.

In addition to the PT, DW, buffered waters, and THMs-fortified water samples, blanks and unfortified matrix samples were analyzed to confirm negative responses in the absence of target contaminants and also to ensure that no sources of contamination were introduced during the analysis.

Experienced GC-MS operators were used for testing since the vendor suggests that a new user obtain training in the use of a GC-MS prior to operating the CT-1128. The vendor identified solid phase microextraction (SPME) as the technique for preparing the water samples for subsequent GC-MS analysis by the CT-1128. It is very important to note that the methodology provided by the vendor was not optimized for any one specific target chemical. The same SPME fiber type and GC column were used throughout the test for all analytes.

QA oversight of verification testing was provided by Battelle and EPA. Battelle QA staff conducted a technical systems audit, a performance evaluation audit, and a data quality audit of 10% of the test data. This verification statement, the full report on which it is based, and the test/QA plan for this verification test are all available at www.epa.gov/etv/centers/center1.html.

TECHNOLOGY DESCRIPTION

The following description of the CT-1128 is based on information provided by the vendor. This technology description was not verified in this test.

The CT-1128 analyzes, on-site, known and unknown chemicals. The CT-1128 is a lightweight, ruggedized, field deployable GC-MS system that can accommodate the applications of traditional laboratory based GC-MS systems. With the appropriate extraction techniques, analysis may be performed on a variety of matrices including DW, which can be prepared using SPME.

The CT-1128 weighs approximately 75 pounds (34 kilograms) and is 15 inches (38.1 cm) by 23 inches (58.4 cm) by 15 inches (38.1 cm). It is contained in a carrying case housing the entire system. The CT-1128 has a range of 1.6 to 800 atomic mass units with unit resolution throughout the mass range. In selected ion mode (SIM), the CT-1128 can scan for 50 groups of masses with 30 masses per group. For identification of chemicals, the CT-1128 is equipped with an automated mass spectral data base searching function that can use a range of commercial mass spectral libraries (e.g., National Institute of Standards and Technology Mass Spectral Library) as well as user-defined libraries. The system is controlled with a laptop computer that uses a program for GC control and MSD Chemstation (Agilent Technologies) for MS control and data analysis.

The CT-1128, which requires ultra-high purity hydrogen or helium (or nitrogen if desired) for the carrier gas, can use either an external gas tank or its on-board hydrogen storage bottle. The metal hydride storage bottle can be charged with hydrogen to provide a source of carrier gas that is convenient for mobile operation. The mass spectrometer can be tuned using an internal calibrant such as perfluorotributylamine (PFTBA) to perform a standard spectra tune or autotune (for maximum sensitivity over the entire scanning range) depending on the user's needs. At the time of testing, the cost of the CT-1128 GC-MS system, with optional SPME stirrer/heater, was $140,000.

VERIFICATION RESULTS

Summary of Accuracy, Precision, Linearity, and Stability

Contaminant	Accuracy	Precision	Linearity	Stability
	Mean Percent Recovery (R)	Mean Relative Standard Deviation (RSD)	Coefficient of Determination of Curve (r^2)	Mean Relative Percent Difference (RPD)
benzene	172%	10%	1.000	27%
toluene	440%	43%	1.000	52%
ethylbenzene	104%	16%	1.000	9%
xylenes (total)	103%	10%	1.000	12%
2,4-D	62%	21%	0.921	35%
dicrotophos	143%	42%	0.999	92%
GB	108%	24%	1.000	48%
GD	75%	14%	1.000	27%
VX	109%	15%	0.959	27%

Benzene *accuracy* was considerably higher than ideal (100%) at 172% recovery (R) because of a change in response several days after establishing the calibration curve. Toluene exhibited significant over-recoveries, with an overall mean R of 440%, though accuracy for ethylbenzene and xylenes (total) was close to 100%. The mean R for 2,4-D and dicrotophos was 62% and 143%, respectively. For GB, the accuracy was close to ideal at 108%. For GD, R was acceptable at 75. The mean R for VX was 109%, though the concentrations tested were significantly higher than the LD_{50} for this agent. *Precision*, as measured by relative standard deviation (RSD) of replicate samples, ranged from 10% for benzene to 43% for toluene.

In regard to *linearity*, the calibration curves of seven of the nine contaminants had coefficients of determination (r^2) of 0.999 or greater. The exceptions were those contaminants for which the provided method lacked sensitivity—2,4-D and VX (r^2 of 0.921 and 0.959, respectively), though for all contaminants, r^2 values were greater than 0.920. Instrument *stability* was evaluated by comparing the results of mid-level PT samples at the beginning and end of the testing day and determining relative percent difference (RPD) of the PT samples (ideal RPD is 0%). Stability results ranged from 9% RPD for ethylbenzene to 92% for dicrotophos. Only two contaminants, ethylbenzene and xylenes (average RPD of 9% and 12%, respectively), had average RPDs less than 20%, while toluene and dicrotophos had RPDs significantly greater than 20% (52% and 92%, respectively).

Summary of Matrix Effects Observed

Contaminant	Matrix Effect[a] from Potential Interferents ✓ = observed						
	DW1	DW2	DW3	DW4	Weakly Buffered Water	Strongly Buffered Water	THMs Spiked Water
benzene					✓	✓	
toluene		✓	✓		✓	✓	
ethylbenzene						✓	
xylenes						✓	
2,4-D	✓	✓	✓	✓		✓	
dicrotophos		✓	✓	✓	✓	✓	
GB			✓			✓	✓
GD	✓		✓	✓		✓	✓
VX	ND	ND	ND	ND	ND	ND	ND

[a] matrix effect defined as recovery ± 30% of average response of daily PT samples fortified at the same concentration
ND = no data; VX matrix testing was not performed due to lack of sensitivity for this contaminant using the vendor-provided method

A *matrix effect* was present with the strong buffer matrix, which gave R values outside the 70% to 130% range for all eight of the target contaminants tested. DW3 also showed matrix effects for five of the eight contaminants, which may be due to its origin as a groundwater sample.

With the exception of VX and 2,4-D (for which the provided methods lacked sensitivity), the *sensitivity* of the CT-1128 was sufficient to detect the target contaminants at the concentrations of interest (i.e., LD_{50} or MCL concentrations).

Results of CT-1128 Sensitivity Testing for Target Contaminants

Contaminant	Concentration of Interest (mg/L)	Sufficient Sensitivity to Detect Conc. of Interest
benzene	0.005	Yes
toluene	1	Yes
ethylbenzene	0.7	Yes
xylenes (total)	10	Yes
2,4-D	0.07	No
dicrotophos	1400	Yes
GB	20	Yes
GD	1.4	Yes
VX	2.1	No

Field portability and operational factors: Because the CT-1128 requires time for thermal equilibration once electrical power and gas have been supplied, it should be kept on standby (under vacuum and thermally equilibrated) as long as possible when time is a critical factor for analyzing field samples. Mobilization in the field is straightforward, and the CT-1128 requires only a source of electrical power for several hours of field deployment when used with its on-board hydrogen canister for a source of carrier gas. Typical extraction and sample run times ranged from 22 minutes to 32 minutes. Average sample throughput during verification testing was 11 samples per 10-hour working day, or approximately one sample per hour. For 100 samples, the total cost for supplies was approximately $914, not including the GC column and standard chemicals.

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

Constellation Technology Corporation
CT-1128 Portable
Gas Chromatograph-Mass Spectrometer

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Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development, has financially supported and collaborated in the extramural program described here. This document has been peer reviewed by the Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation by the EPA for use.

Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six environmental technology centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. Under a cooperative agreement, Battelle has received EPA funding to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

Acknowledgments

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Figures

Tables

List of Abbreviations

AMS	Advanced Monitoring Systems
ASTM	American Society for Testing and Materials
BTEX	benzene, toluene, ethylbenzene, and xylenes
CWA	chemical warfare agent
DW	drinking water
EI	electron impact
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
GC-MS	gas chromatograph-mass spectrometer
kg	kilogram
m	meter
MCL	maximum contaminant level
mg	milligram
μMHO	micromhos
mL	milliliter
NaCl	sodium chloride
R	recovery (percent)
PE	performance evaluation
PFTBA	perfluorotributylamine
ppb	part per billion
ppm	part per million
psi	pounds per square inch
PT	performance test
QA	quality assurance
QC	quality control
QMP	quality management plan
RPD	relative percent difference
RSD	relative standard deviation
SIM	selected ion mode
SPME	solid phase microextraction
THMs	trihalomethanes
TIC	total ion chromatogram
TSA	technical systems audit

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of the Constellation Technology Corporation CT-1128 Portable Gas Chromatograph-Mass Spectrometer (GC-MS). Mobile mass spectrometers were identified as a priority technology verification category through the AMS Center stakeholder process.

Chapter 2
Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This verification report provides results for the verification testing of the CT-1128 Portable GC-MS. Following is a description of CT-1128, based on information provided by the vendor, Constellation Technology Corporation. The information provided below was not verified in this test.

Figure 2-1. Constellation Technology Corporation CT-1128 Portable GC-MS

The CT-1128 (Figure 2-1) analyzes, on-site, known and unknown chemicals. The CT-1128 is a lightweight, ruggedized, field deployable GC-MS system that can accommodate the applications of traditional laboratory based GC-MS systems. With the appropriate extraction techniques, analysis may be performed on a variety of matrices including drinking water (DW), which can be prepared using solid phase microextraction (SPME).

Technical specifications of the CT-1128 are presented in Table 2-1. The CT-1128 weighs approximately 75 pounds (34 kg) and is 15 inches (38.1 cm) by 23 inches (58.4 cm) by 15 inches (38.1 cm). It is contained in a carrying case housing the entire system. The CT-1128 has a range of 1.6 to 800 atomic mass units with unit resolution throughout the mass range. In selected ion mode (SIM), the CT-1128 can scan for 50 groups of masses with 30 masses per group. For identification of chemicals, the CT-1128 is equipped with an automated mass spectral data base searching function that can use a range of commercial mass spectral libraries (e.g., National Institute of Standards and Technology Mass Spectral Library) as well as user-defined libraries.

The system is controlled with a laptop computer that uses a program for GC control and MSD Chemstation (Agilent Technologies) for MS control and data analysis.

The CT-1128, which requires ultra-high purity hydrogen or helium (or nitrogen if desired) for the carrier gas, can use either an external gas tank or its on-board hydrogen storage bottle. The metal hydride storage bottle can be charged with hydrogen to provide a source of carrier gas that is convenient for mobile operation. The mass spectrometer can be tuned using an internal calibrant such as perfluorotributylamine (PFTBA) to perform a standard spectra tune or autotune (for maximum sensitivity over the entire scanning range) depending on the user's needs. At the time of testing, the cost of the CT-1128 GC-MS system, with optional SPME stirrer/heater, was $140,000.

Table 2-1. CT-1128 Technical Specifications (from Constellation Technology Corporation)[a]

INSTRUMENT PARAMETER	SPECIFICATION
Gas Chromatograph	
GC Injection Port	Varian, model CP-1177; direct injection
GC Oven Ramp Speed	Up to 60°C/min to 325°C
GC Oven / Injection Port Temperature Range	Ambient to 325°C, oven with double ramp capability
Carrier Gas Pressure Capacity	< 200 pounds per square inch (psi) at gas inlet, 0-40 psi variable head pressure to control carrier gas flow through column
Carrier Gas Compatibility	Helium, hydrogen, or nitrogen
Carrier Gas Source	Internal hydrogen bottle (~160 operating hours) or external gas tank (He, H_2, N_2 (although N_2 is rarely used))
Injection Mode	Split or splitless
GC Column	Available from a variety of GC column vendors including Quadrex Corp.
Mass Spectrometer	
Quadrupole Mass Spectrometer	Agilent Technologies, model 5973N MSD
Mass Range Capability	1.6 – 800 m/z, 0.1 m/z steps
Mass Resolution	Unit mass resolution throughout mass range
Scan Speed	Up to 10,400 amu per second
Detector Dynamic Range	Total analog/digital converter (ADC) = 10^6
Mass Axis Stability	±0.15 amu over 12 hours
SIM Capability	Up to 50 groups of masses, with 30 masses per group, can be varied throughout a run
SIM Dwell Time	10 – 9,999 msec/mass
Ionization Mode/Energy/Current	EI (electron impact), voltage/current user-selectable (5-240 eV), dual filaments
Ion Source Temperature	Up to 250°C for EI
Quadrupole Temperature	Up to 200°C, independent of ion source
EI SIM Sensitivity	RMS signal/noise ratio at 272.0 m/z > 10:1 for 20 fg octafluoronaphthalene
Software	MSD Chemstation
MS Data Base	National Institute of Standards and Technology/EPA/National Institutes of Health comprehensive library
MS Tuning Capability	Multiple autotune algorithms available, compound-specific autotunes available for PFTBA, BFB, DFTPP, etc
CT-1128 GC-MS System	
Dimensions (L x W x H)	38.1 cm x 58.4 cm x 38.1 cm (15" x 23" x 15")
Weight	~ 34 kg (75 pounds)
Operating Conditions	10-35°C, 5-95% humidity
Power Requirements	99-127 volts, single phase; A/C; 48-66 Hz
Vacuum System	1 Diaphragm rough pump, 2 turbomolecular pumps
Operating System	Windows 2000
Detection Limits	~100 pg hexachlorobenzene; most compounds have detection limits in the picogram range assuming scanning ion mode

(a) these specifications were not verified during testing; analytical conditions used during testing are provided in Chapter 3

Chapter 3
Test Design

Many volatile and semivolatile contaminants in water are detected using bench-top mass spectrometers in a traditional laboratory setting. However, the CT-1128 verified in this test was a portable unit designed to be taken outside the laboratory setting for field analysis. This portability offers an advantage to first-responders and other users who need chemical information when time, sampling, and other limitations preclude analysis in a laboratory.

This verification was conducted from September through December 2005 according to procedures specified in the *Test/QA Plan for Verification of Mobile Mass Spectrometer.* [1] The ability of the CT-1128 to identify and quantify target contaminants was tested in various water matrices. The CT-1128 was evaluated for the following performance parameters:

- Accuracy
- Precision
- Linearity
- Instrument stability
- Potential matrix and interference effects
- Sensitivity
- Field portability
- Operational factors.

The testing was conducted on the contaminants listed in Table 3-1. Three classes of contaminants were tested: volatile organic compounds (benzene, toluene, ethyl benzene, total xylenes (BTEX)), pesticides (2,4-D and dicrotophos), and chemical warfare agents (VX, GB, and GD). The contaminants were selected based on recommendations from the AMS Center stakeholders.

Table 3-1. Target Contaminants and Concentrations of Interest

Contaminant	CAS#[a]	LD_{50} (mg/L)[b]	Maximum Contaminant Level (mg/L)[c]
VX	50782-69-9	2.1	NA
GB (sarin)	107-44-8	20	NA
GD (soman)	96-64-0	1.4	NA
dicrotophos	141-66-2	1,400	NA
2,4-D	94-75-7	NA	0.07
benzene	71-43-2	NA	0.005
toluene	108-88-3	NA	1
ethylbenzene	100-41-4	NA	0.7
xylenes (total)	1330-20-7	NA	10

(a) Chemical Abstracts Number
(b) LD_{50} values assume a 70-kilogram individual consuming 250 milliliters (mL) of the contaminated water
(c) Maximum Contaminant Level (MCL) as defined by EPA National Primary Drinking Water Regulations
NA = Not applicable

3.1 Test Samples

Samples were prepared daily from stock solutions to minimize loss of target contaminants due to hydrolysis. For chemical warfare agent (CWA) testing, a stock solution containing both GB and GD and another containing VX only were prepared in acetone. Stock solutions for the other contaminants, one containing all BTEX compounds and another containing both 2,4-D and dicrotophos, were prepared in methanol to minimize degradation. Each of the test sample types are described in detail in this section.

3.1.1 Performance Test (PT) Samples

The performance test (PT) samples were prepared in American Society for Testing and Materials (ASTM) Type II water. Table 3-2 shows the concentrations of the PT samples that were analyzed for the target contaminants. The target contaminant concentrations were constructed to cover or approximate the concentrations of interest presented in Table 3-1. The concentrations of interest were calculated using LD_{50} values assuming a 70-kilogram individual consuming 250 milliliters (mL) of the contaminated water. When LD_{50} data were not available or feasible for testing, MCL values, as defined by EPA National Primary Drinking Water Regulations, were used. For 2,4-D and VX, the levels of interest in Table 3-1 could not be reached due to the sensitivity of the analytical methods provided by the vendor. For these contaminants, concentrations with adequate instrumental response were determined and used for verification testing. Reference measurements were conducted on PT samples only, to confirm the accuracy of sample preparation. To avoid discrepancies due to contaminant degradation, reference measurements were made as close as possible in time with the measurements made with the CT-1128.

Table 3-2. Performance Test Sample Solution Concentrations for Target Contaminants

Class	Contaminant	PT Sample 1 (mg/L)	PT Sample 2 (mg/L)	PT Sample 3 (mg/L)	PT Sample 4 (mg/L)	PT Sample 5 (mg/L)
CWA	VX	10	15	30	NA	NA
	GB	0.5	1	10	NA	NA
	GD	0.5	1	10	NA	NA
Pesticide	dicrotophos	5	50	500	1,000	NA
	2,4-D	0.5	5	50	75	100
BTEX	benzene	0.01	0.1	1	10	NA
	toluene	0.001	0.01	0.1	1	NA
	ethylbenzene	0.001	0.01	0.1	1	NA
	xylenes (total)	0.001	0.01	0.1	1	NA

NA = Not applicable.

The PT samples were used to determine the accuracy of the CT-1128. One set of these PT samples was used to establish a calibration curve. Subsequent analyses of the PT samples on multiple testing days were then used to calculate the accuracy of the CT-1128 measurements.

Three replicate measurements were made for each PT sample for the accuracy testing, with the exception of 2,4-D and dicrotophos. As shown in Tables 3-1 and 3-2, the tested concentrations were considerably higher and lower than the levels of interest for 2,4-D and dicrotophos, respectively, due to the analytical sensitivity of the CT-1128. Since a great deal of effort was invested in determining the appropriate concentration levels for 2,4-D and dicrotophos, only one replicate of each pesticide PT sample concentration was analyzed in order to analyze the rest of the test samples prior to CWA testing.

3.1.2 Potential Matrix and Interference Effects Samples

To measure the potential matrix effects on the CT-1128 in selected real-world applications, it was challenged by analyzing samples fortified with the target contaminant in various matrices including regional DW samples, a weakly buffered water sample, a strongly buffered water sample, and a trihalomethanes (THMs)-fortified water sample as shown in Table 3-3. The concentration of a mid-level PT sample was used to fortify the matrix samples. This concentration provided a convenient level that was at or below the concentration of interest for most of the target contaminants. As shown in Table 3-3, matrix and interference effects were not evaluated for VX, due to the relatively low sensitivity for this contaminant with the testing methodology.

Table 3-3. Potential Matrix and Interference Spiking Concentrations

Sample Type	Fortified Concentration in Solution (mg/L)					
	Benzene	Toluene, Ethylbenzene, Xylenes	2,4-D	Dicrotophos	GB, GD	VX[a]
DW1[b]	1	0.1	50	500	1	NA
DW2[b]	1	0.1	50	500	1	NA
DW3[b]	1	0.1	50	500	1	NA
DW4[b]	1	0.1	50	500	1	NA
Weakly Buffered Water (442-30)[c]	1	0.1	50	500	1	NA
Strongly Buffered Water (442-3000)[c]	1	0.1	50	500	1	NA
THMs Spiked Water (ASTM Type II Water)[c]	1	0.1	50	500	1	NA

(a) VX testing was limited due to lack of sensitivity for this contaminant using the vendor-provided method.
NA = Not applicable.
(b) See Section 3.1.2.1 for identification of DW sources.
(c) See Section 3.1.2.2 for a description of these samples.

3.1.2.1 Drinking Water Samples

DW samples were collected from four geographically distributed municipal sources to evaluate the performance of the CT-1128 with various sample matrices. These finished DW samples varied in their source, treatment, and disinfection process. All samples underwent either chlorination or chloramination disinfection prior to receipt. Samples were collected from water utility systems with the treatment and source characteristics listed in Table 3-4.

Table 3-4. Treatment and Source Characteristics of Drinking Water Samples

Drinking Water ID	Water Utility	Water Treatment	Source Type
DW1	Columbus, Ohio (OH)	chlorinated filtered	surface
DW2	New York City, New York (NY)	chlorinated unfiltered	surface
DW3	Orlando, Florida (FL)	chlorinated filtered	ground
DW4	Metropolitan Water District of Southern California (CA)	chloraminated filtered	surface

All samples were collected in pre-cleaned high density polyethylene containers. After sample collection, to characterize the DW matrix, an aliquot of each DW sample was sent to a subcontract laboratory to determine the following water quality parameters: concentration of THM, haloacetic acids, total organic halides, pH, conductivity, alkalinity, turbidity, organic carbon, and hardness (see Table 3-5 for results of these analyses).

Table 3-5. Physio-Chemical Characterization of Drinking Water Samples

Parameter	Unit	Method	Sources of Drinking Water Samples			
			Columbus, OH (DW1)	New York City, NY (DW2)	Orlando, FL (DW3)	MWD[b], CA (DW4)
Turbidity	NTU[a]	EPA 180.1[2]	0.1	1.1	0.5	0.1
Dissolved Organic Carbon	mg/L	SM 5310[3]	2.1	1.1	1.6	2.9
Total Organic Carbon	mg/L	SM 5310[3]	2.1	1.6	1.7	2.5
Specific Conductivity	μMHO	SM 2510[3]	572	84	322	807
Alkalinity	mg/L	SM 2320[3]	40	14	142	71
pH		EPA 150.1[4]	7.6	6.9	8.5	8.0
Calcium	mg/L	EPA 200.8[5]	33	5.6	8.8	45
Magnesium	mg/L	EPA 200.8[5]	7.7	1.3	43	20
Hardness	mg/L	EPA 130.2[6]	118	20	143	192
Total Organic Halides	μg/L	SM 5320[3]	220	82	300	170
Trihalomethanes	μg/L/analyte	EPA 524.2[7]	74.9	39.0	56.4	39.2
Haloacetic Acids	μg/L/analyte	EPA 552.2[8]	32.8	39.0	34.6	17.4

(a) NTU = Nephelometric turbidity unit.
(b) MWD = Metropolitan Water District of Southern California

Because free chlorine degrades many of the target contaminants and interferents during storage, the DW samples were immediately dechlorinated with sodium thiosulfate pentahydrate upon arrival at Battelle. The dechlorination of the DW was qualitatively confirmed by adding a diethyl-p-phenylene diamine tablet to an aliquot of the DW. If the water did not turn pink, the dechlorination process was determined to be successful. If the water did turn pink, an additional dechlorinating reagent was added and the dechlorination confirmation procedure was repeated. The bulk DW samples were dechlorinated upon arrival and did not require any additional dechlorination during testing.

3.1.2.2 Weakly Buffered, Strongly Buffered, and Trihalomethanes Matrices

The effect of ionic strength on the response of the CT-1128 was examined. Since natural water salt type and concentration can vary greatly by location, two sample types were fortified at a mid level PT sample concentration in 442 Natural Water™ Standard Solution (Myron L Instruments, Carlsbad, CA). Two 442 solutions, 442-30 and 442-3000, containing 21.8 parts-per-million (ppm) sodium chloride (NaCl) and 2,027 ppm NaCl, respectively, were used for this purpose.

The CT-1128 was also challenged by the presence of potential interferents. THMs are typically observed at low levels in DW as by-products of the disinfection process. Four THMs (chloroform, bromoform, bromodichloromethane, and dibromochloromethane) were spiked into a midlevel PT sample at 80 parts per billion (ppb) total, which is the MCL for total THMs as

defined in EPA's National Primary Drinking Water Regulations.[12] Chloroform, bromoform, bromodichloromethane, and dibromochloromethane were spiked so that their concentrations in solution were 50, 5, 15, and 10 ppb, respectively, to represent typical ratios of THMs in finished DW.

3.1.3 Quality Control Samples

In addition to the PT, DW, buffered water, and THMs-fortified water samples, blanks and unfortified matrix samples were analyzed to confirm negative responses in the absence of target contaminants and also to ensure that no sources of contamination were introduced during the analysis.

3.2 Testing Procedure

3.2.1 Laboratory Testing

Experienced GC-MS operators were used for testing since the vendor suggests that a new user obtain training in the use of a GC-MS prior to operating the CT-1128. All of the operators were trained laboratory staff and were experienced in the proper use and handling of laboratory chemicals. Additionally, analyses of CWAs were handled by staff trained with specific skills necessary for working in a CWA laboratory.

The vendor provided a sample preparation technique as well as analytical methodology for the three groups of contaminants to be analyzed during the verification test: BTEX, pesticides, and CWAs. Ultra-high purity (UHP) helium was used for the carrier gas. The vendor identified SPME as the technique for preparing the water samples for subsequent GC-MS analysis by the CT-1128. SPME is a relatively simple adsorption/desorption technique for extracting volatile and semivolatile chemicals from a liquid sample or headspace. The technique employs the use of a fused silica fiber that is coated with a polymer. The specific SPME fiber should be chosen based on the application of interest. It is very important to note that the methodology provided by the vendor was not optimized for any one specific target chemical. The same SPME fiber type and GC column were used throughout the test for all analytes. The SPME fiber was replaced approximately after every 50 extractions or at the discretion of the operator. Therefore, further optimization of the extraction and separation/detection process may be possible.

The provided methodology specified daily check procedures that were followed each day before the analysis of samples. These procedures included diagnostic checks for system operation (e.g., check of MS vacuum and temperature of heated zones), tuning of the MS, and column/SPME fiber bakeout. The CT-1128 was mass tuned using PFTBA (as the internal calibrant) and the autotune function. It should be noted that the method provided by the vendor originally specified that the operator should perform MS autotune on a daily basis. According to the vendor, their typical users, who are seeking a *qualitative* rather than quantitative result, start up and shut down the CT-1128 on a regular basis as they transport the instrument from site to site. Since the quantity of a particular contaminant may be a critical factor in determining the appropriate corrective action(s), this verification test focused on the *quantitative* abilities of the mobile mass spectrometer. For the verification test, the CT-1128 ran continuously once it was installed in a

particular location. Since the autotune function will change the MS settings, any quantitative data obtained after an autotune may not compare well to such data obtained prior to the autotune. Since the operator intended to obtain one calibration curve and use it to quantify the results of several days of subsequent testing, the vendor suggested performing an autotune only if the CT-1128 had been shut down and restarted after a period of two hours or more. This change in the methodology was requested by the vendor when the Verification Test Coordinator inquired about the variation in instrument response over the course of several days of testing.

Table 3-6 summarizes the instrumental parameters for each of the three methods provided. Testing solutions were prepared daily from stock solutions. To an empty vial, 15 mL of a test water sample and a disposable magnetic stirbar were added before capping and crimping a seal onto the vial. For all of the target contaminants analyzed in the verification test, the vendor provided Supelco SPME fibers that were coated with 100 µm polydimethylsiloxane (Supelco Catalog # 57300-U). The operator inserted the SPME fiber, which is housed in a syringe-type assembly, into the liquid. After exposing the fiber for a specific amount of time, the operator pulled the fiber back into the assembly, and then removed it from the sample. After inserting the assembly into the injector port of the CT-1128, the operator exposed the fiber for desorption and began the analysis. A SPME mixer heater compartment, which is built into the CT-1128 unit, allowed the operator to keep the sample properly mixed and thermally equilibrated.

Table 3-6. CT-1128 Analytical Methods for Target Contaminants

Analytes	Quantitation Ion	SPME Extraction	GC Column	GC Oven Program	MS Scan Range	MS Sampling Rate	Total Run Time
benzene toluene ethylbenzene xylenes (total)	78 m/z 91 m/z 91 m/z 91 m/z	100 µm polydimethylsiloxane (Supelco 57300-U) exposed for 20 minutes at 25°C with mixer speed = 3	007-5MS, Silpheylene Siloxane, 30m x 0.25 mm ID x 0.25 µm film (Quadrex Corporation 007-5MS-30-0.25F)	35°C hold 2 minutes, ramp to 200°C at 10°C/minute, ramp to 300°C at 20°C/minute	35 to 120 m/z	5 (2.2 scans/ second)	23.5 minutes
2,4-D dicrotophos	162 m/z 127 m/z			50°C hold 0.5 minutes, ramp to 300°C at 15°C/minute, hold 5 minutes	35 to 250 m/z	4 (1.75 scans/ second)	22.2 minutes
GB GD VX	99 m/z 126 m/z 114 m/z			50°C hold 0.5 minutes, ramp to 300°C at 15°C/minute, hold 15 minutes	35 to 275 m/z	4 (1.58 scans/ second)	32.2 minutes

Like the choice of SPME fiber, the vendor provided a single GC capillary column (30 m x 0.25 mm ID x 0.25 µm film, type 007-5MS; Quadrex Corporation, Woodbridge, CT) that was to be

used for the target contaminants analyzed during the verification test. The operator exposed the SPME fiber to the sample for a total absorption time of 20 minutes while the mixer speed was set to "3." After removing the SPME assembly from the sample and inserting it into the injector port of the CT-1128, the operator exposed the fiber, and selected the "Start" button in the GC control software (which works in tandem with the MS control software). The operator retracted and removed the SPME fiber after the end of the 10 minute desorption time. After data acquisition, the operator processed the raw data by extracting the appropriate quantitation ion from the total ion chromatogram (TIC) and then integrating the corresponding peak using the Chemstation software. Using Microsoft Excel, the peak area (response) was plotted against expected analyte concentration to generate calibration curves which were used to quantify the subsequent sample analyses. Though a single calibration curve was acquired, a midlevel PT sample was analyzed at the beginning and end of each day of testing to assess stability of the CT-1128 response.

3.2.2 Non-Laboratory Testing

The CT-1128 was deployed into a non-laboratory setting to verify its performance in a relatively uncontrolled environment. Using the operator's manual for guidance, the operator set up the CT-1128 for analysis in a warehouse located on Battelle's Columbus campus. The site had electricity though temperature and humidity were not as controlled as in a laboratory. For the non-laboratory analysis, the operator followed the same procedures used in the laboratory and analyzed BTEX calibration standards and a water sample that was fortified with BTEX (at concentrations unknown to the operator).

3.3 Reference Methods

Laboratory reference methods (Table 3-7) were used to determine the accuracy of sample preparation and demonstrate the stability of the target contaminants in the PT matrix. The reference laboratories were asked to follow the sample preservation/handling and quality control (QC) requirements specified in Chapter 4, in addition to any QC requirements specified in each reference method.

Table 3-7. Reference Methods for Target Contaminants

Contaminant	Reference Method
VX	Battelle Internally Developed Method[a]
GB	HMRC-IV-118-05[9]
GD	HMRC-IV-118-05[9]
dicrotophos	Battelle Internally Developed Method[b]
2,4-D	U.S. EPA 515.1[10]
benzene	U.S. EPA 524.2[7]
toluene	U.S. EPA 524.2[7]
ethylbenzene	U.S. EPA 524.2[7]
xylenes (total)	U.S. EPA 524.2[7]

(a) VX analysis by Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS).
(b) Dicrotophos analysis by GC-MS.
HMRC = Hazardous Materials Research Center

3.3.1 CWA Reference Method

Samples submitted for GB and GD determination were analyzed by Battelle according to procedures outlined in HMRC-IV-118-05. This procedure involves a liquid-liquid extraction of the water sample and subsequent analysis of the extract by GC-MS. The samples containing VX were analyzed directly in water using an internally developed electrospray ionization liquid-chromatography tandem mass spectrometry (LC-MS/MS) method.

3.3.2 Pesticide Reference Method

Samples for 2,4-D determination were analyzed according to EPA Method 515.1 in which chlorinated acids are extracted and derivatized. The derivatives are then determined by GC using an electron capture detector. Samples for dicrotophos determination were analyzed according to an internal Battelle method. This procedure involves solid phase extraction followed by GC-MS analysis. Battelle performed this method when it was learned that the subcontract laboratory that was going to perform EPA Method 8141, as proposed in test/QA plan for this test, [1] no longer offered this analysis.

3.3.3 BTEX Reference Method

Samples submitted to a subcontract laboratory for BTEX determination were analyzed according to EPA 524.2. This "purge and trap" method involves the purging of volatile organic compounds with low water solubility and trapping these compounds onto a sorbent tube. The compounds are then thermally desorbed and determined by GC-MS.

Chapter 4
Quality Assurance Quality Control

QA/QC procedures were performed in accordance with the quality management plan (QMP) for the AMS Center [11] and the test/QA plan for this verification test [1] except as noted in Table 4-1.

Table 4-1. Changes to Test/QA Plan for Verification of Mobile Mass Spectrometers

Change	Further Discussion
Proposed PT sample concentrations, as listed in test/QA plan, [1] were changed after running preliminary solutions to determine analytical sensitivity.	Section 6.8
Three replicate measurements of the PT samples were not made for two analytes: 2,4-D and dicrotophos.	Section 3.1.1
Accuracy was determined using the theoretical concentration of target analyte instead of the concentration of the target analyte determined by the reference measurement.	Section 4.1.1
Research trailer was not available during time of field testing and one PT sample was analyzed (instead of triplicate analysis of a raw water sample).	Section 6.7
The reference methods for VX and dicrotophos were changed.	Section 3.3
Reference samples were submitted for analysis to demonstrate that the PT samples can be prepared accurately. In particular, BTEX and 2,4-D reference methods were most problematic.	Section 4.1.1
Only PT samples were analyzed for VX.	Section 6.1
Relative percent difference (RPD) was used to measure instrument stability instead of percent recovery (R) of PT samples analyzed on each day of testing.	Section 5.5

A summary of the recovery values (R) for the reference measurements is presented in Table 4-2 (a definition of R is included in Section 5.1). R values for benzene, dicrotophos, and the CWAs were all 80% or greater. Sample degradation was suspected as the cause for lower recoveries observed with the other chemicals.

Table 4-2.   Summary of Reference Measurement Percent Recovery (R)

Contaminant	R of Reference Measurements
VX	124%
GB	80%
GD	87%
dicrotophos	99%
2,4-D	64%
benzene	86%
toluene	52%
ethylbenzene	46%
xylenes (total)	52%

Reference analyses for BTEX and 2,4-D did not meet acceptance criteria for all samples. The EPA-specified holding time for laboratories using EPA method 524.2 for BTEX analysis is 14 days. Several of the samples could not be confirmed to have been analyzed within this specified holding time due to discrepancies in the chain of custodies. Also, a number of results were received with low surrogate recoveries. In addition, as shown in Table 4-2, sample recovery was near 50% for all BTEX analytes except benzene which was 86%. Of 11 samples submitted for 2,4-D analysis, 7 samples were analyzed after the recommended 14 day holding time per EPA method 515.1.

Based on these deficiencies in the reference analyses and since test samples were prepared daily, these reference results were not used to determine accuracy of the CT-1128 GC-MS analytical measurement, but rather to confirm that sample preparation was being performed properly. Since sample preparation procedures were standardized and no systematic errors were observed in the reference measurements, the results provide confidence in the sample preparation. There is no impact on the data because it is a common practice to use the theoretical fortified value for comparison.

4.1 Audits

A performance evaluation audit, a technical systems audit, and an audit of data quality were performed for this verification test.

4.1.1 Performance Evaluation Audit

For all contaminants, "blind" samples were submitted to analysts performing the reference measurements. Since the methods are specific to the contaminant, only the concentration of target contaminants was not disclosed when submitting samples for reference measurements.

These performance evaluation (PE) samples were used to assess the accuracy of the reference measurements and were prepared in accordance with the stated detection limits of the reference laboratories. At least one PE sample was submitted per reference method prior to the start of the verification test and once during the verification test. PE samples that were not within ± 20% of the expected result were repeated.

4.1.2 Technical Systems Audit

The Battelle Quality Manager conducted a technical systems audit (TSA) to ensure that the verification test was performed in accordance with the test/QA plan [1] and the AMS Center QMP. [11] As part of the audit, the Battelle Quality Manager reviewed the reference methods, compared actual test procedures to those specified in the test/QA plan, and reviewed data acquisition and handling procedures. Observations and findings from this audit were documented and submitted to the Battelle Verification Test Coordinator for response. No findings were documented that required any significant action. The records concerning the TSA are permanently stored with the Battelle Quality Manager.

4.1.3 Audit of Data Quality

At least 10% of the data acquired during the verification test was audited. Battelle's Quality Manager traced the data from the initial acquisition, through reduction and statistical analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked.

4.2 QA/QC Reporting

Each internal assessment and audit was documented in accordance with Sections 3.3.4 and 3.3.5 of the QMP for the ETV AMS Center. [11] Once the assessment report was prepared, the Battelle Verification Test Coordinator ensured that a response was provided for each adverse finding or potential problem and implemented any necessary follow-up corrective action. The Battelle Quality Manager ensured that follow-up corrective action was taken. The results of the TSA were sent to EPA.

4.3 Data Review

Records generated in the verification test were reviewed before these records were used to calculate, evaluate, or report verification results. Table 4-3 summarizes the types of data recorded. The review was performed by a technical staff member involved in the verification test, but not the staff member who originally generated the record. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed.

Table 4-3. Summary of Data Recording Process

Data to be Recorded	Responsible Party	Where Recorded	How Often Recorded	Disposition of Data
Dates, times, and details of test events, mass spectrometer maintenance, down time, etc.	Battelle	ETV laboratory record books or data recording forms	Start/end of test procedure, and at each change of a test parameter or change of instrument status	Used to organize/check test results; manually incorporated in data spreadsheets as necessary
Mass spectrometer calibration information	Battelle	ETV laboratory record books or electronically	At instrument calibration or recalibration	Incorporated in verification report as necessary
Mass spectrometer readings	Battelle	Recorded electronically by each instrument and then downloaded daily	For each sample	Converted to spreadsheet for statistical analysis and comparisons
Reference method sample preparation	Battelle	Laboratory record books	Throughout sample preparation	Used to demonstrate validity of samples submitted for reference measurements
Reference method procedures, calibrations, QA, etc.	Battelle or subcontract laboratory	Laboratory record books, or data recording forms	Throughout sampling and analysis processes	Retained as documentation of reference method performance
Reference method analysis results	Battelle or subcontract laboratory	Electronically from reference analytical method	Every sample analysis	Converted to spreadsheets for calculations

Chapter 5
Statistical Methods and Reported Parameters

The statistical methods presented in this chapter were used to verify the performance parameters listed in Chapter 3.

5.1 Accuracy

Determination of accuracy of the PT samples was based on the concentration of the prepared standards. A minimum of three concentrations of PT samples was used to establish the calibration curve. All subsequent analyses of the PT samples were used to determine the accuracy of the CT-1128 relative to the prepared concentrations. Ideally, independent reference measurements would be used to confirm the accuracy of the technology. However, as discussed in Chapter 4, the reference laboratory measurements (particularly in the case of BTEX and 2,4-D) were of questionable quality due to analytical holding times that were exceeded and inadequate QC results. Accuracy of the CT-1128 was therefore determined for all target contaminants using the prepared concentrations rather than the reference laboratory concentrations. The subsequent analyses of the PT samples for determination of accuracy included two types: 1) analysis of an additional two replicate sets of PT samples (except for 2,4-D and dicrotophos where, as described in Section 3.1.1, the calibration curve PT samples were not repeated) and 2) daily verifications of the mid-level PT samples. The accuracy of the CT-1128 was assessed as recovery (R), using Equation 1:

$$R = (Y_i \div X_i) \times 100 \tag{1}$$

where Y_i is the concentration of target contaminant i as measured by the CT-1128 and X_i is the prepared concentration of the contaminant i. R values are presented for PT samples. The ideal R value is 100%. The mean, median, maximum, and minimum R values are presented, as well as the standard deviation of the R values.

5.2 Precision

When possible, the relative standard deviation (RSD) of three replicate measurements of the PT samples across three or four concentrations was determined to assess the precision of the CT-

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1128 measurements. Precision was also evaluated on replicate measurements of mid-level PT samples that were used as daily calibration verifications. Lastly, the precision of replicate matrix-fortified samples was calculated. Regardless of the type of sample analyzed, the precision was defined as the RSD of replicate measurements, using Equation 2:

$$RSD = (SD \div \overline{Y_i}) \times 100 \tag{2}$$

where $\overline{Y_i}$ is the average concentration of target contaminant i as measured by the CT-1128, and SD, the standard deviation of the results. Ideal RSD values are near 0%.

5.3 Linearity

Linearity was determined by performing a linear regression analysis of the instrument response for one set of the PT samples versus the theoretical target contaminant concentrations across a minimum of three concentrations. The linear regression analysis used the target contaminant concentration as the independent variable and the response (integrated peak area for the contaminant of interest) from the CT-1128 as the dependent variable. Linearity was expressed in terms of slope, intercept, and coefficient of determination (r^2), in addition to presenting a plot of the data. The ideal value for r^2 is 1.

5.4 Sensitivity

Sensitivity was assessed by the ability of the CT-1128 to measure the target contaminant at or below the concentration of interest. This evaluation did not focus on determining instrumental detection limits since the purpose was to ascertain whether the CT-1128 was sensitive enough to measure the target contaminants at the concentrations of interest in the various water matrices. Serial ten-fold dilutions of the lowest concentration PT sample were performed until no change in instrument response for the target contaminant was observed. It was also noted whether the instrument response changed accordingly (e.g., ten-fold decrease for each ten-fold dilution).

5.5 Instrument Stability

Instrument stability (S) was determined by analyzing a PT sample at the beginning and end of the analytical sequence (usually over the course of a day) to assess the degree of calibration stability. The result of the PT sample at the end of the sequence was compared to that of the PT sample analyzed at the start of the analytical sequence using Equation 3:

$$RPD = \left[\left| (Y_i2 - Y_i1) \right| \div average \left(Y_i1, Y_i2 \right) \right] \times 100 \tag{3}$$

where Y_i2 and Y_i1 are the results for the last and first PT sample, respectively, for target contaminant i. The ideal value for relative percent difference (RPD) is 0%.

5.6 Potential Matrix and Interference Effects

Potential matrix and interference effects were assessed by comparing the response of the various test matrices fortified with the target contaminants to the average response of the PT samples analyzed on the day of testing. In the absence of instrument drift and target contaminant degradation, it was assumed that a matrix or interferent effect was responsible for any change in performance for the mid-level PT sample. The matrix effects were calculated using the percent recovery calculation. R values between 70% and 130% indicated that a matrix effect was not observed, while R values outside of that range were considered to indicate a matrix effect.

5.7 Field Portability

For this verification test, field portability was defined as the ability for a user to operate the CT-1128 in a non-laboratory environment for sample analysis. Observations related to field portability were observed and reported. These considerations included weight and dimensions of unit, impact on user mobility, start-up time, and power requirements.

5.8 Operational Factors

Operational factors such as maintenance needs, data output, consumables used, ease of use, repair requirements, and sample throughput were evaluated based on observations recorded by Battelle staff. A separate laboratory record book was maintained for the CT-1128 and was used to enter daily observations on these factors. Examples of information to be recorded in the record book include the status of diagnostic indicators for the CT-1128, use or replacement of any consumables, the effort or cost associated with maintenance or repair, vendor effort (e.g., time on site) for repair or maintenance, the duration and causes of any instrument down time or data acquisition failure, and operator observations about ease of use of the CT-1128. These observations were summarized to aid in describing CT-1128 performance.

The time required for each sample from the start of sample preparation to reporting of results defined sample time. The number of samples that could be analyzed per unit time defined sample throughput. The sample throughput was noted for laboratory and field portions of testing.

Chapter 6
Test Results

6.1 Accuracy

Accuracy (Tables 6-1a-g), expressed as percent recovery (R), was determined using the equation given in Section 5.1. This calculation was only performed on PT samples since these samples represent the matrix free of any potential interference (ASTM Type II DI water). In all cases, with the exception of toluene, the integrated peak areas of the first replicate set of three or four PT sample concentrations including the blank when possible (all cases except for CWAs where no blanks were analyzed) were used to generate a linearly regressed calibration curve on which quantitation was based. For toluene, the third replicate set was used to generate the curve due to non-linear response of the lower standards on the first two replicates. In addition to presenting the mean R for each PT level (when more than one PT level was tested) the median, maximum, and minimum R are reported along with the standard deviation of the R values in Tables 6-1a-g. For observations of less than three, standard deviation of R was not determined (as indicated by "nd"). Overall statistics that combine all R values across all concentrations are also presented to summarize the accuracy results for each target analyte. Note that the number of observations for the mid-level PT samples (i.e., PT 2 or PT 3) is considerably higher than that of the other concentration levels due to the periodic calibration checks that were performed daily.

Table 6-1a. Accuracy (Percent Recovery) Results – Benzene

Benzene PT Level	Observations	Mean	Median	Maximum	Minimum	SD
PT 1 (0.01 mg/L)	4	168%	126%	305%	115%	91%
PT 2 (0.10 mg/L)	3	116%	115%	124%	109%	7%
PT 3 (1.00 mg/L)	25	189%	135%	399%	81%	111%
PT 4 (10.00 mg/L)	3	94%	91%	103%	87%	8%
benzene ALL	35	172%	125%	399%	81%	103%

For benzene, accuracy is considerably higher than ideal (100%) at 172% overall mean R. This is primarily due to a change in response for benzene observed several days into testing after establishing the calibration curve. It could not be determined whether the change was due to the SPME extraction of benzene or the instrumental response for benzene. The response for a particular analyte may change over the course of several days and may be due to a number of factors including the extraction technique or environmental conditions; in such a case, it is usually left to the operator's discretion whether to reacquire a calibration curve. It is important to note that this procedure was followed throughout testing (i.e., one calibration curve for each analyte was used to quantify results from subsequent testing). The high degree of variability in the benzene response throughout testing using the single curve is reflected by the SD of the R.

Table 6-1b. Accuracy (Percent Recovery) Results – Toluene

Toluene PT Level	Observations	Mean	Median	Maximum	Minimum	SD
PT 1 (0.001 mg/L)	4	299%	251%	533%	160%	162%
PT 2 (0.01 mg/L)	3	261%	94%	599%	91%	292%
PT 3 (0.10 mg/L)	25	508%	611%	770%	67%	237%
PT 4 (1.00 mg/L)	3	243%	126%	489%	114%	213%
toluene ALL	35	440%	489%	770%	67%	248%

Toluene was the least accurate of the BTEX compounds tested, exhibiting significant over-recoveries with an overall mean R of 440%. The third set of replicates was used to generate the calibration curve since it was the most linear of the replicate sets of PT samples. The high degree of variability in the toluene response is reflected by the SD of the R.

Table 6-1c. Accuracy (Percent Recovery) Results – Ethylbenzene

Ethylbenzene PT Level	Observations	Mean	Median	Maximum	Minimum	SD
PT 1 (0.001 mg/L)	4	102%	94%	140%	82%	26%
PT 2 (0.01 mg/L)	3	99%	89%	130%	79%	27%
PT 3 (0.10 mg/L)	25	110%	121%	143%	66%	27%
PT 4 (1.00 mg/L)[a]	3	58%	55%	65%	54%	6%
ethylbenzene ALL	35	104%	102%	143%	54%	29%

(a) PT 4 not used in calibration curve due to suspected detector saturation

The CT-1128 exhibited accuracy for ethylbenzene that was usually in the range of 70-130%, with a mean of 104%, and relatively small standard deviations of the R values. Ethylbenzene demonstrated reduced accuracy at the PT 4 concentration level (1.00 mg/L), which may have

been due to detector saturation. Therefore, PT 4 was not included in the calibration curve for this analyte.

Table 6-1d. Accuracy (Percent Recovery) Results – Xylenes (Total)

Xylenes (total) PT Level	Observations	Mean	Median	Maximum	Minimum	SD
PT 1 (0.001 mg/L)	4	124%	117%	158%	105%	23%
PT 2 (0.01 mg/L)	3	89%	80%	113%	73%	21%
PT 3 (0.10 mg/L)	25	104%	113%	136%	62%	24%
PT 4 (1.00 mg/L)	3	77%	74%	84%	73%	6%
xylenes ALL	35	103%	109%	158%	62%	25%

To produce the total xylenes result, the operator added the response for both m- and p-xylene (which were not resolved from each other) to that of o-xylene to produce a total response. Though the PT 4 sample was excluded from the calibration curve for xylenes as it was in ethylbenzene, accuracy was not affected to the same extent. Total xylenes R was close to ideal, with a mean R value of 103% and a relatively low SD.

Table 6-1e. Accuracy (Percent Recovery) Results – 2,4-D and Dicrotophos

2,4-D PT Level	Observations	Mean	Median	Maximum	Minimum	SD
PT 3 (50.0 mg/L)	8	62%	66%	79%	29%	16%
Dicrotophos PT Level	**Observations**	**Mean**	**Median**	**Maximum**	**Minimum**	**SD**
PT 3 (500.0 mg/L)	8	143%	104%	520%	7%	160%

Since only one replicate of each PT sample was analyzed for 2,4-D and dicrotophos, accuracy was determined using the PT 3 check samples that were analyzed each day of testing. Accuracy for 2,4-D was less than ideal as the method was not sensitive for this contaminant. For dicrotophos, the PT 4 sample was excluded from the calibration curve as it did not give a linear response with respect to the other PT samples. The dicrotophos response showed high variability as reflected in the SD of the R.

Table 6-1f. Accuracy (Percent Recovery) Results – GB and GD

GB PT Level	Observations	Mean	Median	Maximum	Minimum	SD
PT 1 (0.5 mg/L)	5	120%	130%	185%	51%	53%
PT 2 (1.0 mg/L)	18	106%	119%	185%	35%	51%
PT 3 (10.0 mg/L)	4	101%	114%	140%	36%	46%
GB ALL	27	108%	127%	185%	35%	49%
GD PT Level	**Observations**	**Mean**	**Median**	**Maximum**	**Minimum**	**SD**
PT 1 (0.5 mg/L)	5	74%	70%	126%	47%	32%
PT 2 (1.0 mg/L)	18	72%	70%	148%	15%	33%
PT 3 (10.0 mg/L)	4	92%	95%	115%	65%	21%
GD ALL	27	75%	74%	148%	15%	31%

For GB, the mean accuracy (R) was near ideal at 108%. For GD, the mean R was 75%, though the variability was less than that of the GB response (as reflected in SD of R). The spiking

solution used to fortify the water samples with these two CWAs contains several other chemicals which affected the library matching for GB (resulting in a lower quality match for this analyte). As shown in Figures 6-1a and 6-1b, the operator was able to use the background subtracting feature of Chemstation to improve the quality of the library match (and thus, the confidence in the identification) of GB in the sample from a quality of 50 before the background subtraction to a quality of 83 after the background subtraction.
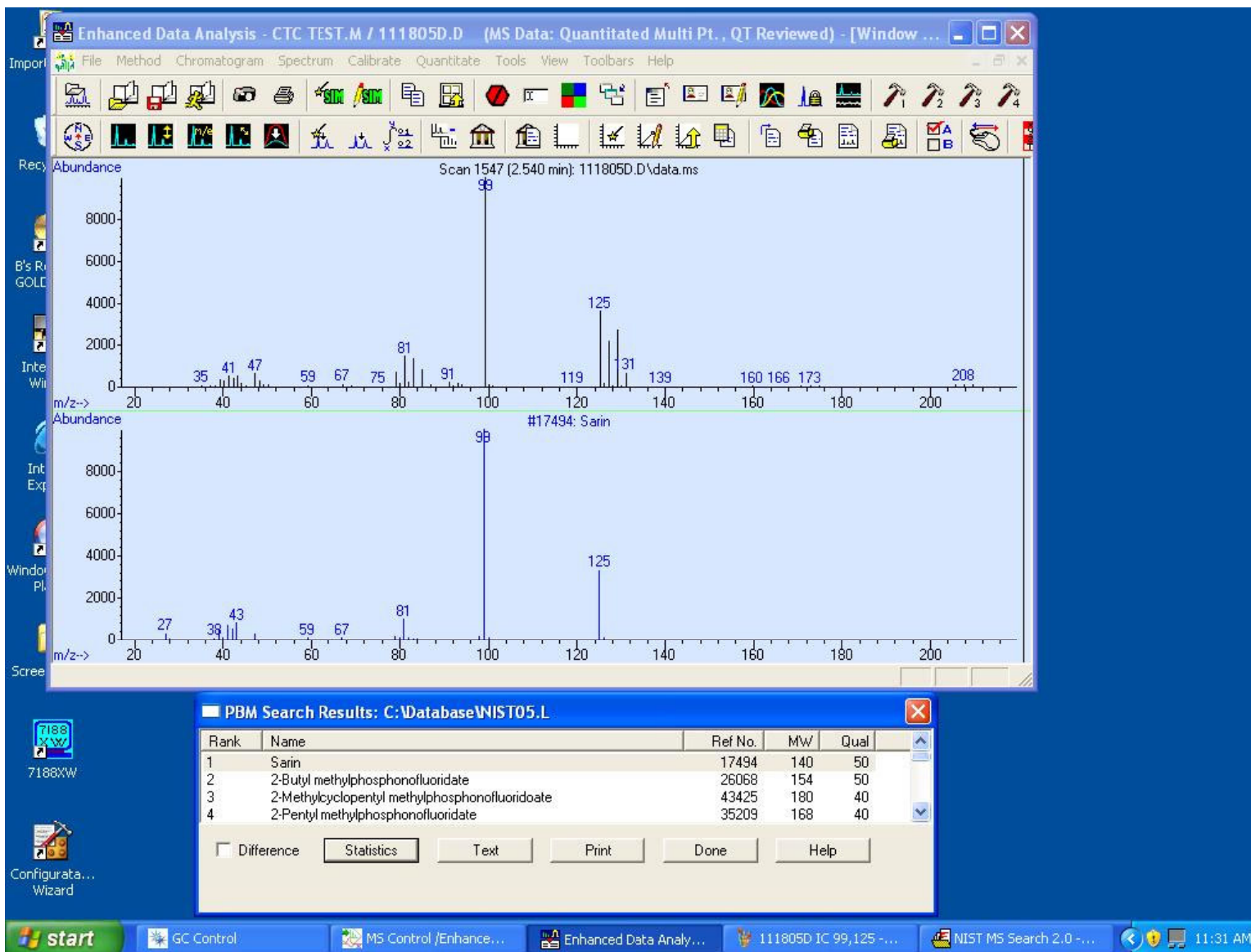

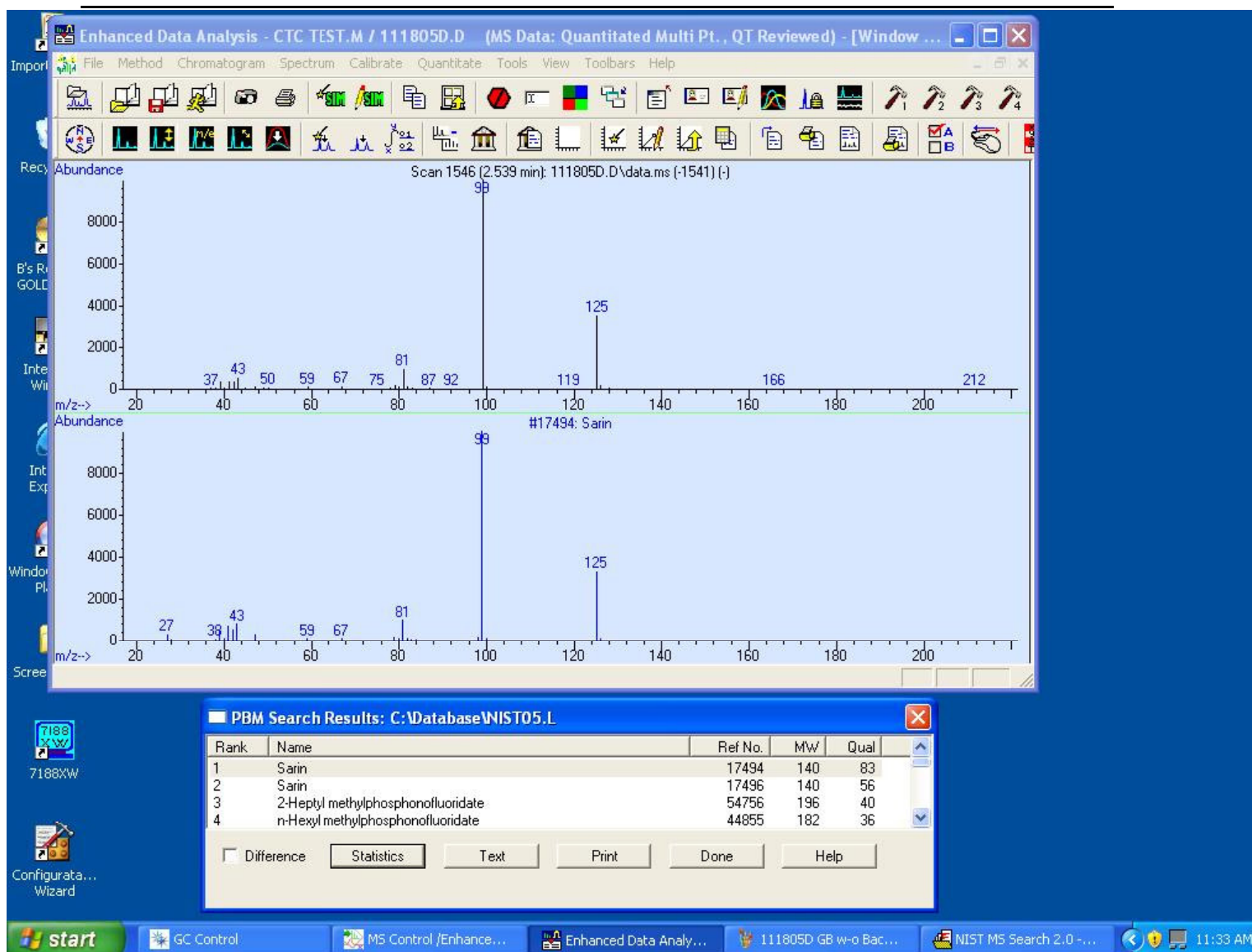**Figure 6-1a.   Library Match for GB without Background Subtraction**

Figure 6-1b.   Library Match for GB with Background Subtraction

Table 6-1g. Accuracy (Percent Recovery) Results – VX

VX PT Level	Observations	Mean	Median	Maximum	Minimum	SD
PT 1 (10.0 mg/L)	2	113%	113%	126%	100%	nd
PT 2 (15.0 mg/L)	2	104%	104%	119%	89%	nd
PT 3 (30.0 mg/L)	2	111%	111%	111%	111%	nd
VX ALL	6	109%	111%	126%	89%	13%

nd = SD of R not calculated for observations less than three

Due to the lack of sensitivity for the originally proposed testing levels for VX, data were limited to three sets of replicates, including the set of replicates from which data were plotted to generate the calibration curves that were used to quantify the subsequently acquired data. Since there were only two replicates, SD was not calculated for each PT sample level (though SD is provided for all PT sample levels combined). Mean recovery for VX was 109%.

6.2 Precision

Precision (Table 6-2), expressed as RSD, was calculated for the three replicate measurements of the PT samples and matrix-fortified samples (except for 2,4-D and dicrotophos, in which cases only matrix-fortified samples were used for the calculation, and VX, in which case no matrix samples were analyzed) by the method listed in Section 5.2. RSD values ranged from 1% to 100% with several trends observed. When compared to benzene and xylenes, where only one sample type showed a RSD greater than 20%, toluene and ethylbenzene, 2,4-D, dicrotophos, GB, and GD had multiple samples types with a RSD greater than 20%. This variable response may be due to either the SPME or the CT-1128 (or contributions from both sources). Additionally, DW3, a groundwater sample, exhibited a RSD greater than 20% for six of the eight analytes tested.

Table 6-2. Summary of RSD of the Various Sample Types[a]

Sample Type	Benzene	Toluene	Ethylbenzene	Xylenes	2,4-D	Dicrotophos	GB	GD	VX
PT 1	4%	*198%*	12%	6%	NA	NA	*26%*	*26%*	*22%*
PT 2	4%	1%	11%	13%	NA	NA	*48%*	*32%*	15%
PT 3	5%	*61%*	6%	8%	NA	NA	*48%*	*24%*	7%
PT 4	7%	12%	1%	2%	NA	NA	NA	NA	NA
DW1	3%	6%	*36%*	7%	*36%*	*30%*	10%	4%	NA
DW2	7%	7%	*44%*	14%	17%	19%	4%	2%	NA
DW3	*50%*	*66%*	*52%*	3%	*25%*	*68%*	*23%*	18%	NA
DW4	13%	14%	3%	14%	15%	*77%*	20%	13%	NA
Weakly Buffered Water (442-30)	9%	*100%*	11%	13%	9%	*24%*	9%	1%	NA
Strongly Buffered Water (442-3000)	3%	3%	4%	5%	*32%*	*58%*	*27%*	14%	NA
THMs Spiked Water (ASTM Type II Water)	5%	3%	0%	*30%*	16%	17%	*21%*	7%	NA

NA = Not applicable.
(a) Entries in bold italics indicate RSD > 20%.

6.3 Linearity

For all target contaminants, a minimum of three PT samples were used to generate a calibration curve as described in Section 5.3. The curves (Figures 6-2a-i) were constructed from the same set of replicates if multiple replicates were analyzed (e.g., the first set of PT sample replicates was used to generate the calibration curve for benzene calibration). When a blank sample was analyzed as part of the calibration curve, the blank response was included in the construction of the corresponding calibration curve. It should be noted that not every concentration level of PT samples was used to construct the curves. For some (ethylbenzene, xylenes, and dicrotophos), the highest PT sample level was removed to yield better calibration curves. Table 6-3 summarizes the calibration curve results. Calibration for seven of the nine analytes yielded curves with coefficient of determination, r^2, of 0.999 or greater. The notable exceptions are those analytes for which the provided method lacked sensitivity, 2,4-D and VX (r^2 of 0.921 and 0.959, respectively), though all of the r^2 values were greater than 0.920. The number of days for which the calibration curve was used to quantitate data is also indicated in Table 6-3.

Table 6-3. Summary of Calibration Curve Data

Contaminant	Number of Points in Curve	Range (mg/L)	r^2	Number of Days Curve was Used
benzene	5	0 to 10	1.000	8
toluene	5	0 to 1	1.000	8
ethylbenzene	4	0 to 0.1 (1 not linear)	1.000	8
xylenes	4	0 to 0.1 (1 not linear)	1.000	8
2,4-D	5	0 to 100	0.921	5
dicrotophos	4	0 to 500 (1000 not linear)	0.999	5
GB	3	0.5 to 10	1.000	9
GD	3	0.5 to 10	1.000	9
VX	3	10 to 30	0.959	1

CT-1128 9-13 Calibration Benzene SPME   n = 5
$r^2 = 1.000$

$y = 578244x - 1098$

X-axis: Expected Concentration (mg/L)
Y-axis: CT-1128 Response (Peak Area)
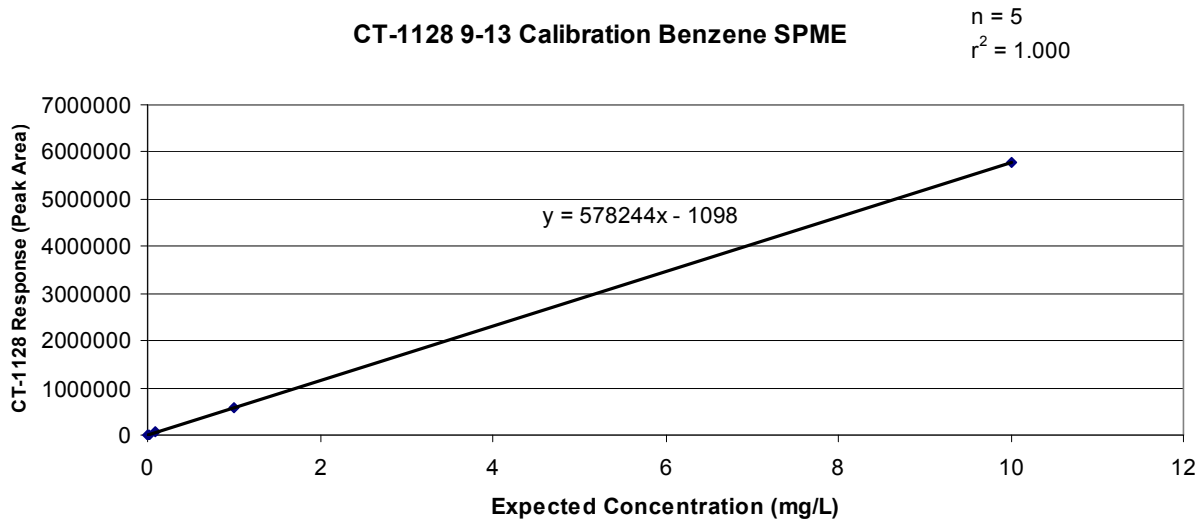
Figure 6-2a. Calibration Curve for Benzene

CT-1128 9-13 Calibration Toluene SPME   n = 5
$r^2 = 1.000$

$y = 1471470x + 3319$

X-axis: Expected Concentration (mg/L)
Y-axis: CT-1128 Response (Peak Area)
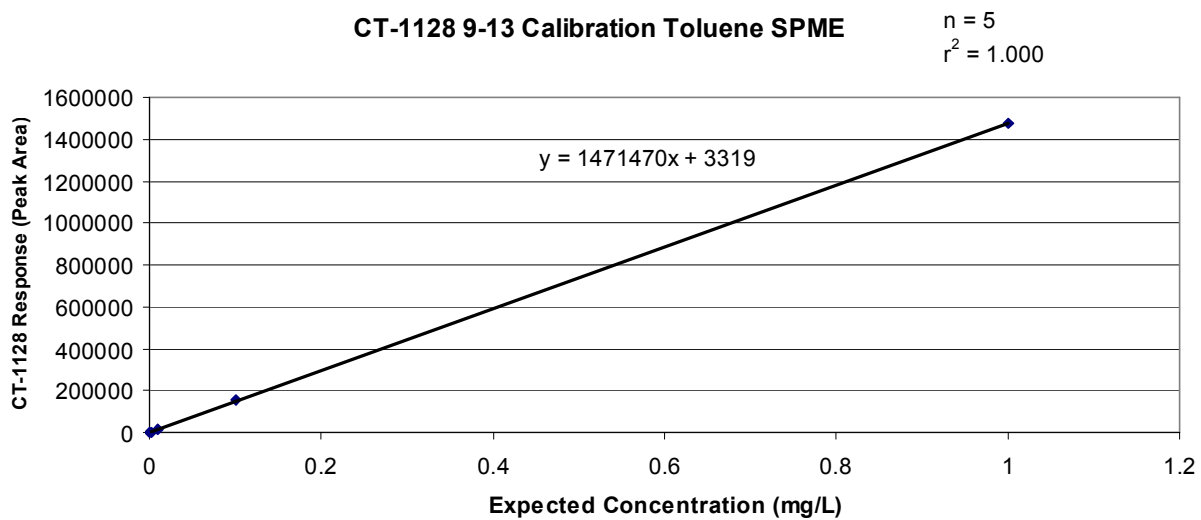
Figure 6-2b.   Calibration Curve for Toluene

CT-1128 9-13 Calibration Ethylbenzene SPME n = 4
r^2 = 1.000

y = 22080249x - 1631
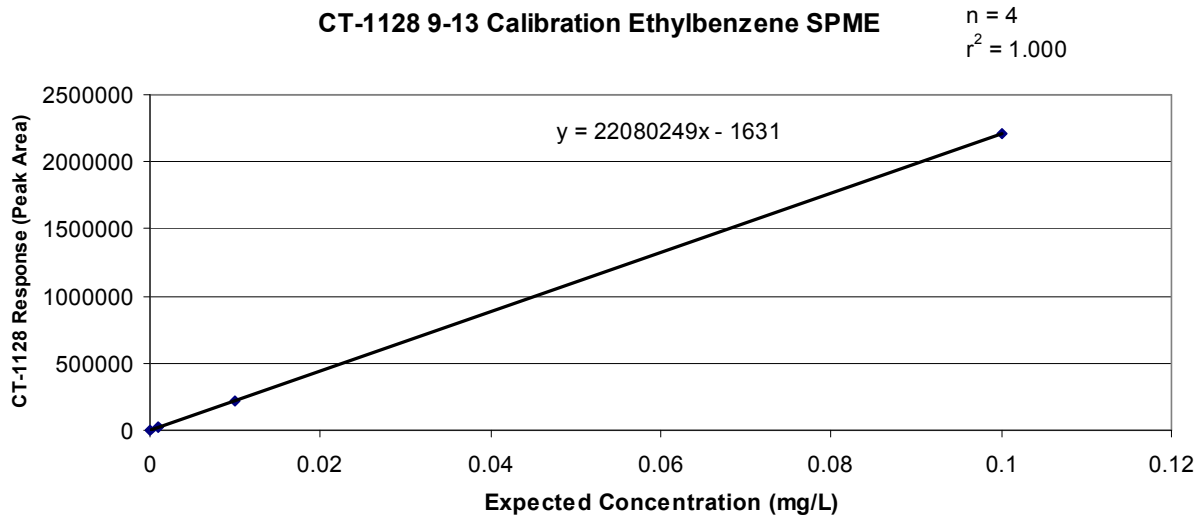
Figure 6-2c. Calibration Curve for Ethylbenzene

CT-1128 9-13 Calibration Xylenes SPME n = 4
r^2 = 1.000

y = 22238885x - 8173
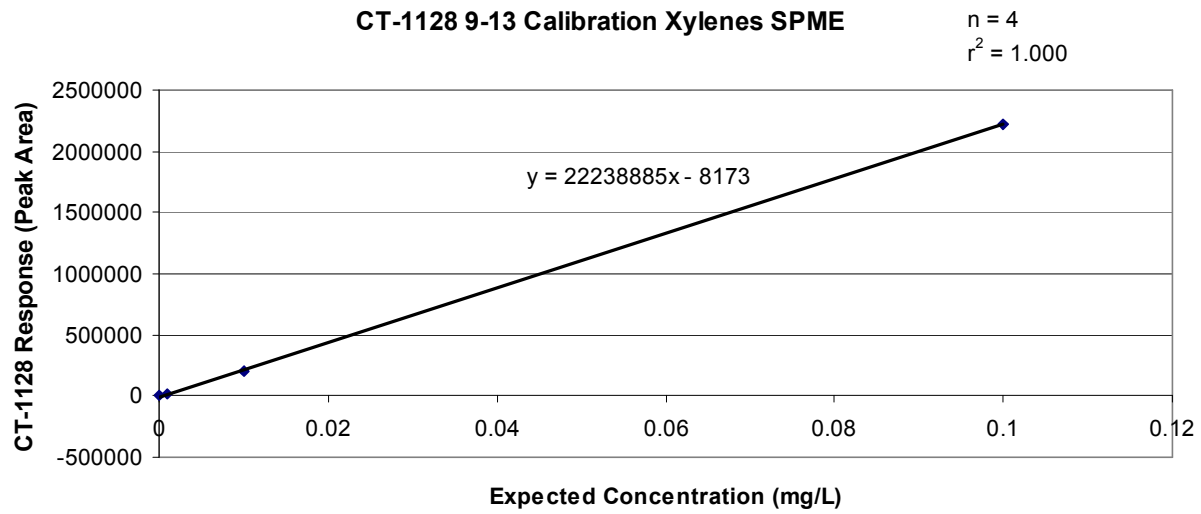
Figure 6-2d. Calibration Curve for Xylenes (Total)

CT-1128 9-29 Calibration 2,4-D SPME

n = 5
$r^2 = 0.921$

$y = 6552x - 27045$
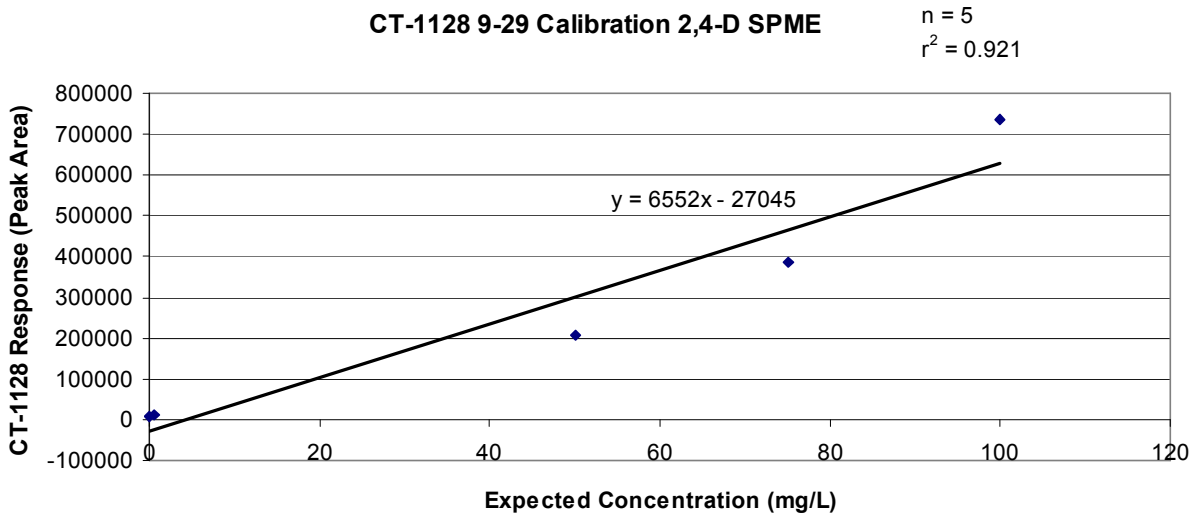
Figure 6-2e.   Calibration Curve for 2,4-D

CT-1128 9-29 Calibration Dicrotophos SPME

n = 4
$r^2 = 0.999$

$y = 1799x + 4308$
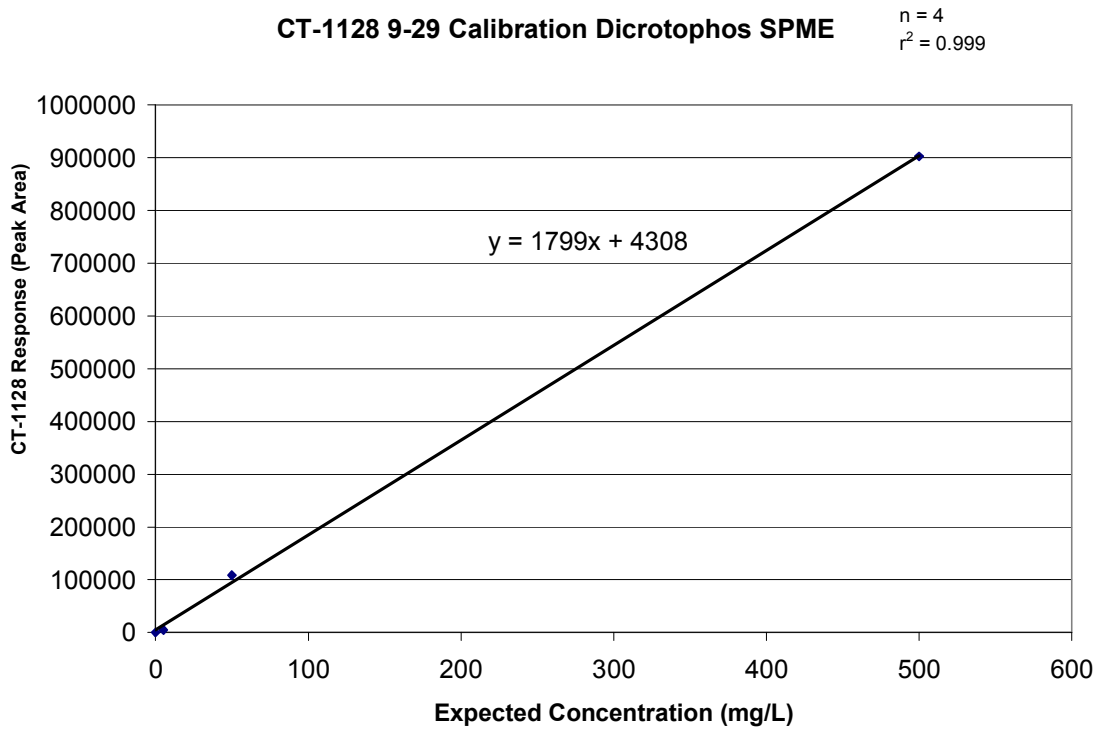
Figure 6-2f.   Calibration Curve for Dicrotophos

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CT-1128 11-01 Calibration GB SPME   n = 3 $r^2 = 1.000$

$y = 8710x - 1015$
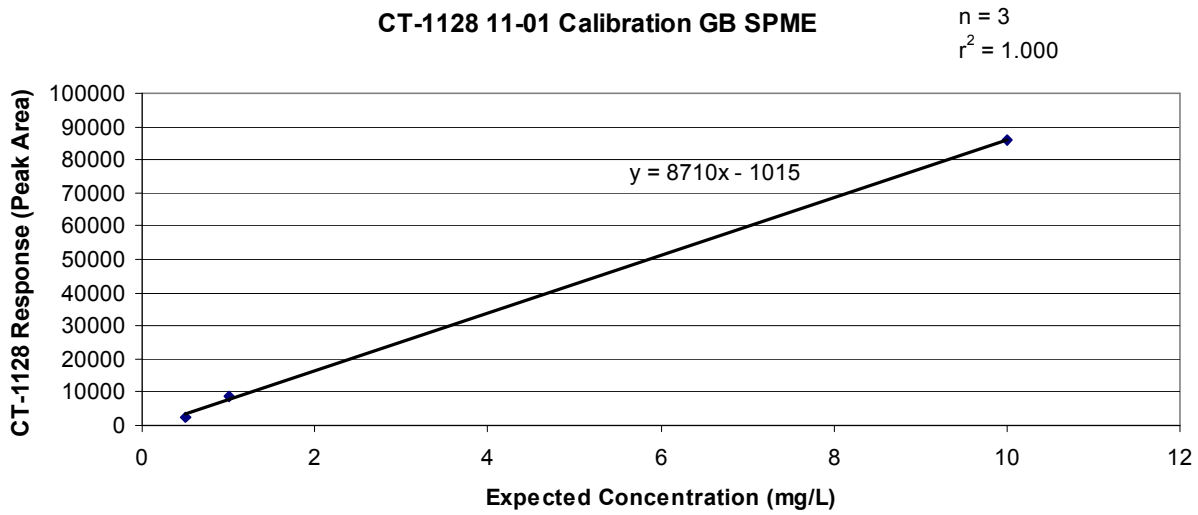
Figure 6-2g.   Calibration Curve for GB

CT-1128 11-01 Calibration GD SPME   n = 3 $r^2 = 1.000$

$y = 69391x + 12827$

Figure 6-2h.   Calibration Curve for GD

Figure 6-2i.   Calibration Curve for VX

6.4 Sensitivity

Sensitivity, as defined in Section 5.4, is the ability to determine the target contaminant at the concentration of interest in the various water matrices. Results of the sensitivity evaluation are shown in Table 6-4. For VX and 2,4-D, the conce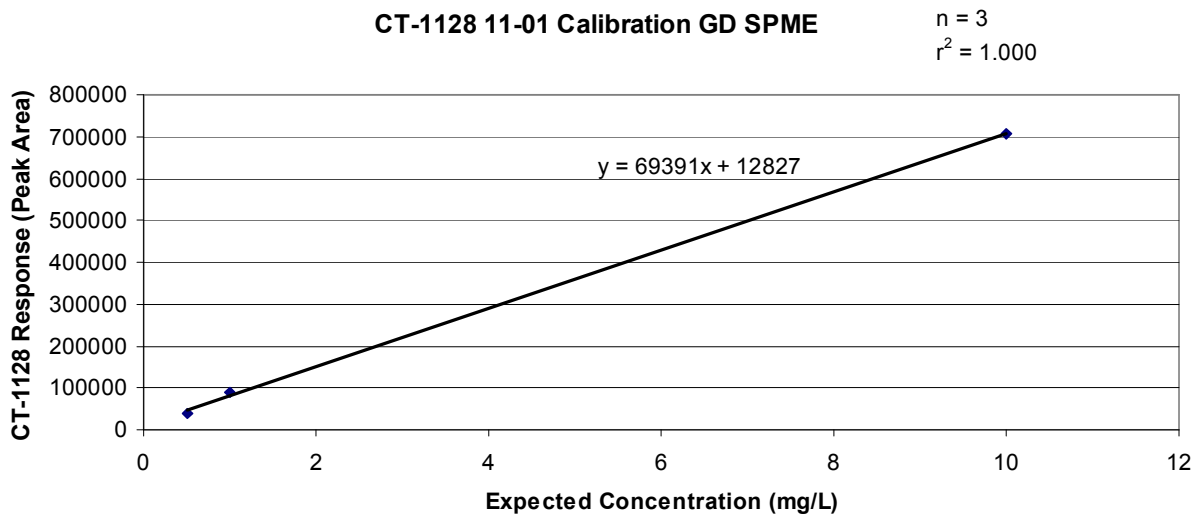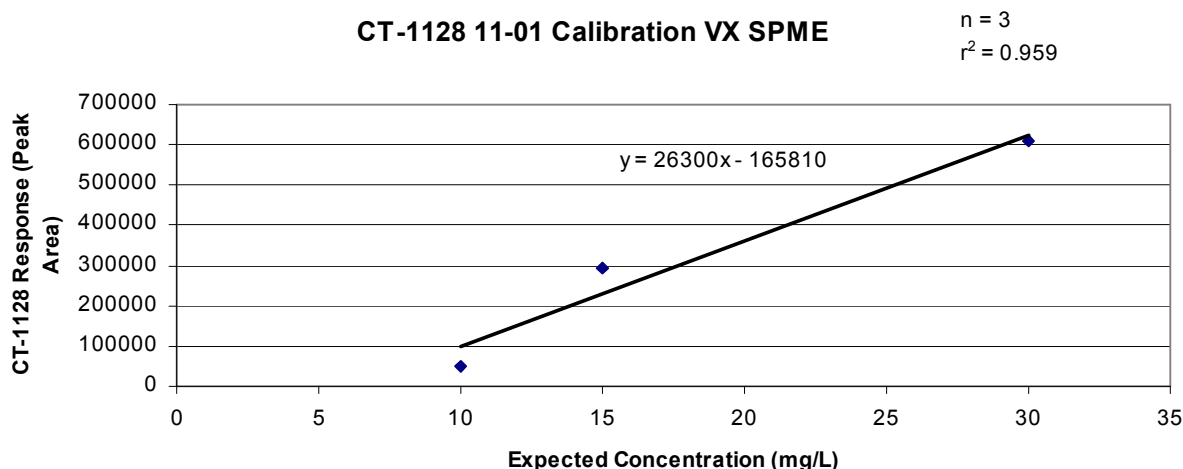ntrations of interest were not achieved due to lack of sensitivity using the provided method. With the exception of benzene, all other contaminants were spiked lower than the concentration of interest in the various matrices (see Table 3-3). For benzene, determining whether the CT-1128 was sensitive enough to detect the concentration of interest was determined using dilutions of the lowest PT sample. Serial ten-fold dilutions of PT 1 were performed for each contaminant, and the dilutions were made and tested until the instrument response did not change by the approximate corresponding dilution factor. For many of the target contaminants, the response at these levels, while low, may be sufficient for a qualitative result or identification.

Table 6-4.   Sensitivity of CT-1128

Contaminant	Concentration of Interest (mg/L)[a]	Sufficient Sensitivity to Detect Conc. of Interest
benzene	0.005	Yes
toluene	1	Yes
ethylbenzene	0.7	Yes
xylenes	10	Yes
2,4-D	0.07	No
dicrotophos	1400	Yes
GB	20	Yes
GD	1.4	Yes
VX	2.1	No

(a) See Table 3-1 for Target Contaminants and Concentrations of Interest.

6.5 Instrument Stability

Stability (Table 6-5), determined by the method described in Section 5.5, was based on the first and last PT sample of a testing day, expressed as an RPD of the two. The ideal RPD is zero with those results greater than 20% flagged (those results listed in bold italics). In addition to presenting the mean percent recovery for each PT level, median, maximum, minimum, and standard deviation of RPD were reported. Though the verification test involved acquiring a single calibration which was used for the duration of testing (the number of days over which stability was tested is indicated in Table 6-5), it is recommended that an operator acquire a new calibration curve when the response has changed. This frequency will depend on the operator's need for accuracy and precision. Alternatively, the operator may use the average response of standards analyzed throughout an analytical run to normalize the sample results for instrumental drift. This approach was used by the operator in determining potential matrix effects and interferents. For example: PT 3 samples for benzene, expected to be 1.0 mg/L gave 3.8, 3.9, and 3.7 mg/L for an average response of 3.8 mg/L throughout the testing day when THMs fortified water samples were analyzed. When determining the R of benzene in the matrix, the operator normalized the THMs-matrix response, which was 3.9, 3.9, and 4.2 for an average response of 4.01 mg/L to the PT 3 response, giving average R as 106%.

Table 6-5. Results of Stability Testing for CT-1128

Contaminant	PT Level (mg/L)	Number of Days	Stability (RPD)[a]				
			Mean	Median	Maximum	Minimum	SD
benzene	1.00	8	*27%*	10%	*100%*	1%	*39%*
toluene	0.10	8	*52%*	14%	*133%*	3%	*61%*
ethylbenzene	0.10	8	9%	10%	17%	0%	5%
xylenes	0.10	8	12%	10%	*33%*	*1%*	10%
2,4-D	50.0	4	*35%*	23%	*83%*	*10%*	*33%*
dicrotophos	500	4	*92%*	*81%*	*195%*	*11%*	*80%*
GB	1.00	7	*48%*	*50%*	*83%*	7%	*31%*
GD	1.00	7	*27%*	*33%*	*63%*	3%	*22%*

(a) The ideal RPD is zero with those results greater than 20% flagged (those results listed in bold italics)

The average RPD ranged from that for ethylbenzene (average RPD of 9% with a SD of 5%) to that for dicrotophos (average RPD of 92% with a SD of 80%). Only two analytes, ethylbenzene and xylenes (average RPD of 9% and 12%, respectively) had average RPD less than 20%, while results for toluene and dicrotophos were much greater than 20% (average RPD of 52% and 92%, respectively).

6.6 Potential Matrix and Interference Effects

The ability of the CT-1128 to detect the target contaminants was challenged by analysis of fortified samples in different matrices. The results are shown in Table 6-6. To determine percent recovery (R) of the fortified samples, the average response of the PT samples throughout the day of testing was used. A matrix effect was defined as recoveries outside of the range of 70% to 130% R value. A trend was observed with the strongly buffered water matrix (442-3000) which gave R outside of that range, indicating that a matrix effect may be present. This result

may be due to an enhancement of the SPME efficiency, which has been observed with the extraction of analytes in high salt matrices. Results for 2,4-D may be due to sensitivity issues. For dicrotophos, all but two of the sample types exhibited matrix effects which may also be due to a less than optimal method for the contaminant. DW3 also showed matrix effects for five of the eight contaminants tested which may be due to the fact that it is the sole groundwater sample of the four regional DWs. Potential matrix and interference effects were not tested for VX due to the lack of sensitivity for this contaminant using the provided method.

Table 6-6. Results of Potential Matrix and Interference Effects

Contaminant	Matrix Effects Observed[a]						
	DW1	DW2	DW3	DW4	Weakly Buffer ed Water (442-30)	Strongly Buffered Water (442-3000)	THMs Spiked Water
benzene	120%	82%	88%	108%	*58%*	*218%*	106%
toluene	107%	*193%*	*180%*	95%	*39%*	*158%*	99%
ethylbenzene	96%	102%	88%	109%	94%	*139%*	101%
xylenes	102%	129%	115%	99%	99%	*135%*	87%
2,4-D	*17%*	*30%*	*22%*	*13%*	90%	*16%*	110%
dicrotophos	103%	*142%*	*349%*	*143%*	*162%*	*236%*	121%
GB	80%	123%	*63%*	79%	91%	*38%*	*140%*
GD	*159%*	92%	*61%*	*133%*	90%	*66%*	*134%*
VX	ND	ND	ND	ND	ND	ND	ND

(a) bold italic font indicates values outside 70-130% range of average response of daily PT samples
ND = no data; VX matrix testing was not performed due to lack of sensitivity for this contaminant using the vendor provided method

6.7 Field Portability

The CT-1128 was removed from the laboratory to be installed and operated within a warehouse facility. To begin the move, the CT-1128 was shut down after a day of laboratory analysis. The heating zones were cooled and the turbo pumps were subsequently allowed to spin down. After venting the instrument, the instrument was packed into the hard transport case for mobilization into the field. This aspect of transportability was straightforward. The CT-1128 unit weighs approximately 70 pounds so it is possible to load the unit into a specially designed hard case using two people. The hard case held the CT-1128 securely and protected the instrument during mobilization. The packed CT-1128 (which, with its hard case, weighed approximately 225 pounds (102 kg) and measured 36" (91.4 cm) x 36" (91.4 cm) x 39" (99.1 cm)) was loaded onto the back of a pickup truck.

Battelle has a warehouse facility in Columbus, Ohio that is located along the banks of the Olentangy River. This location was selected for its proximity to the river, as a possible scenario could involve analyzing grab water samples from the river using the CT-1128. To shield the instrument from the rain, the truck was moved inside the warehouse (Figure 6-3). The instrument was powered and supplied with UHP helium from a gas tank (alternatively, the CT-1128's internal metal hydride storage bottle may be charged to supply hydrogen as the carrier gas but this was not tested during this verification test). After establishing the gas flow, the source and quad temperatures were heated. The system was packed and transported at 8:00 A.M. and by 9:30 A.M., the CT-1128 was installed and under vacuum, though it was necessary to wait for the instrument to reach thermal equilibrium prior to performing the autotune procedure. Though a dialog box in the MSD Chemstation software tells the operator to wait for two hours, the vendor claims that the instrument may be operated to obtain data well before this time (this was not verified as part of the test). At approximately 11:30 A.M., an autotune was performed, followed by an air and water check. It was at this time that the results of the check indicated an air leak. After spending a significant amount of time leak checking the system, a stress fracture in the helium gas line was discovered and replaced. After replacing the gas line, several air and water checks were performed and showed the N_2 and O_2 peaks to be gradually decreasing. After obtaining a satisfactory air and water check (abundance of H_2O, N_2, and O_2 should all be less than 10% of the internal calibrant PFTBA), the instrument was left on standby (as the workday had come to an end). This type of effort highlights the advantage of operating the CT-1128 in a mobile laboratory environment (e.g., van with source of electrical power) so that downtime associated with re-establishing vacuum and tuning, which can be several hours, may be minimized dramatically, allowing the operator to analyze field samples sooner.

Figure 6-3. Use and Installation of CT-1128 Outside of the Laboratory

On the following day, the operator tuned the MS and performed a four-point calibration for BTEX analytes. A separate individual prepared the standards and provided a water sample fortified with BTEX at concentrations unknown to the operator. The operator analyzed the sample and determined concentrations of the BTEX analytes based on the acquired calibration curve. The results are presented in Table 6-7. The recoveries were comparable to what was observed in the laboratory with recoveries for benzene, ethylbenzene, and xylenes at 108%, 135%, and 121% respectively. However, the accuracy for toluene was low,

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which is opposite to the behavior observed in the laboratory testing (during which a mean recovery of 440% was observed – see Table 6-1b). This may be due to a non-optimal method for this contaminant. Overall, in terms of analytical performance, no major differences were observed due to field deployment.

Table 6-7.   Field Portability Results

Contaminant	PT Conc. Level (mg/L)				Linearity	Conc. of Blind Sample (mg/L)	Accuracy (R of Blind Sample)
	PT 1	PT 2	PT 3	PT 4	r^2		
benzene	0.01	0.10	1.00	10.0	1.000	1.00	108
toluene	0.001	0.01	0.10	1.00	0.996	0.10	*23*
ethylbenzene	0.001	0.01	0.10	1.00	0.998	0.10	135
xylenes	0.001	0.01	0.10	1.00	1.000	0.10	121

Since the CT-1128 requires approximately two hours to equilibrate once electrical power and gas have been supplied, it is recommended that the instrument be kept on standby as long as possible when time for analyzing field samples is a critical factor. Mobilization into the field is straightforward and is due in large part to the "button up" design of the CT-1128 and its transport-ready case. When the on-board metal hydride canister is used to supply carrier gas, the CT-1128 requires only a source of electrical power for several hours of field deployment. The advantage of on-site analysis of chemicals makes the CT-1128 a powerful tool for the identification and analysis of chemicals that have been traditionally analyzed by a fixed-laboratory GC-MS system.

6.8 Operational Factors

In general, GC-MS systems are sophisticated analytical instruments that require proper method development and an experienced operator to yield optimal results. The verification test was conducted using experienced GC-MS operators running the analytical methods provided by the vendor. It is important to note that these methods were not explicitly confirmed by the vendor using the levels proposed prior to the verification test. For all analytes, the PT sample starting concentrations had to be determined experimentally in order to determine appropriate levels (as opposed to the levels listed in test/QA plan for this test [1]). In the case of CWAs, this was not possible due to the restrictions on the use and availability of these chemicals. The methods provided for this verification test were not optimized or modified for sensitivity and therefore may not represent the most optimal performance of the CT-1128 for a particular target contaminant. It is also important to note that the results of the verification test reflect the performance of the SPME sample preparation as well as the analysis by the CT-1128. Operator experience with SPME will therefore be beneficial to using the technique in tandem with the CT-1128.

Though a recurring GC oven temperature error was observed during testing, the CT-1128 did not require any extensive maintenance during the verification test. The operator replaced the injection port septum each day as recommended by the vendor. On several occasions, leaks were suspected. Detection and remedial actions can take significant time. During the field test, detecting a small leak that seemed to contribute to a large amount of air and water took several hours. After a suspect copper gas line for the external helium gas cylinder was replaced, it took additional time to remove the water that had been introduced from the humid environment. It was noted that the SPME use resulted in great wear and tear on the septum, often resulting in a cored septum which could serve as a leak. It is therefore advisable to replace the septum at the *end* of each testing day. Such situations coupled with daily preparation and sample run times, which ranged from 22 minutes to 32 minutes, can have a significant impact on sample throughput. Typically, the daily procedures recommended for operation lasted approximately one hour. These activities, performed on a system that has reached thermal equilibrium, include a bakeout procedure, daily mass tuning, and an air/water check. If the system is not at equilibrium such as when it has been first deployed in the field, it is necessary to allow for two hours for thermal equilibration after achieving vacuum. Though it is possible to sequence the analytical steps to maximize sample throughput (e.g., exposing the SPME to absorb analytes for the next sample while the GC oven temperature is ramping down), average sample throughput during verification testing was 11 samples per each ten hour working day, translating to approximately one sample per hour. Operational costs for the verification test included UHP helium, SPME vials, crimp seals, SPME fibers, and disposable stir bars. For 100 samples, the total cost for these supplies was approximately $914. The GC column and standard chemicals were not included in this cost.

During the verification test, the operator occasionally observed errors for the column temperature readback. The problem seemed to be intermittent and erratic (alternating from low to correct to high reading). Inconsistent retention times supported that the problem was not merely a faulty readback, but actual variation in the GC oven temperature. Based on the technical support provided by the vendor, a faulty thermocouple was suspected. In addition to providing troubleshooting support, the vendor provided application support for target contaminants.

Chapter 7
Performance Summary

As shown in Table 7-1, benzene accuracy was considerably higher than ideal (100%) at 172% because of a change in response several days after establishing the calibration curve. Toluene (which had the lowest accuracy of the BTEX chemicals) exhibited significant over-recoveries, with an overall mean R of 440%, though accuracy for ethylbenzene and xylenes (total) was close to 100%. The mean R for 2,4-D and dicrotophos was 62% and 143%, respectively. For GB, the accuracy was close to ideal at 108%. For GD, the R was acceptable at 75%. The mean R for VX was 109%, though the concentrations tested were significantly higher than the LD_{50} for this CWA.

Table 7-1. Summary of Accuracy, Precision, Linearity, and Stability

Contaminant	Accuracy	Precision	Linearity	Stability
	Mean R	**Mean RSD**	**r^2 of curve**	**Mean RPD**
benzene	172%	10%	1.000	27%
toluene	440%	43%	1.000	52%
ethylbenzene	104%	16%	1.000	9%
xylenes (total)	103%	10%	1.000	12%
2,4-D	62%	21%	0.921	35%
dicrotophos	143%	42%	0.999	92%
GB	108%	24%	1.000	48%
GD	75%	14%	1.000	27%
VX	109%	15%	0.959	27%

Table 7-1 also shows that across all sample matrices, precision, as measured by RSD of replicates, ranged from 10% RSD for benzene to 43% RSD for toluene.

The calibration curves of seven of the nine contaminants had coefficients of determination (r^2) of 0.999 or greater. The exceptions were those contaminants for which the provided methods lacked sensitivity—2,4-D and VX (r^2 of 0.921 and 0.959, respectively), though for all contaminants, r^2 values were greater than 0.920.

Instrument stability, in terms of the mean RPD of prepared sample replicates, ranged from 9% average RPD for ethylbenzene (with a SD of 5%) to 92% for dicrotophos (with a SD of 80%).

Only two contaminants, ethylbenzene and xylenes (average RPD of 9% and 12%, respectively), had average RPDs less than 20%, while toluene and dicrotophos had RPDs significantly greater than 20% (52% and 92%, respectively). Table 7-2 summarizes the results of testing for matrix effects on the analyses performed on the CT-1128.

Table 7-2. Summary of Matrix Effects Observed

Contaminant	Matrix Effect[a] from Potential Interferents ✓ = observed						
	DW1	DW2	DW3	DW4	Weakly Buffered Water	Strongly Buffered Water	THMs Spiked Water
benzene					✓	✓	
toluene		✓	✓		✓	✓	
ethylbenzene						✓	
xylenes						✓	
2,4-D	✓	✓	✓	✓		✓	
dicrotophos		✓	✓	✓	✓	✓	
GB			✓			✓	✓
GD	✓		✓	✓		✓	✓
VX	ND	ND	ND	ND	ND	ND	ND

(a) matrix effect defined as recovery outside range of 70-130% of average response of daily PT samples
ND = no data; VX matrix testing was not performed due to lack of sensitivity for this contaminant using the vendor provided method

Table 7-2 shows that a matrix effect was present with the strong buffer matrix, which gave Rs outside the 70% to 130% range for all eight target contaminants tested. DW3 also showed matrix effects for five of the eight contaminants, which may be due to its origin as a groundwater sample. VX was not tested for potential matrix and interference effects because of the lack of sensitivity of the provided method. Table 7-3 shows the results of sensitivity testing of the CT-1128.

Table 7-3. Results of CT-1128 Sensitivity Testing for Target Contaminants

Contaminant	Concentration of Interest (mg/L)	Sufficient Sensitivity to Detect Conc. of Interest
benzene	0.005	Yes
toluene	1	Yes
ethylbenzene	0.7	Yes
xylenes	10	Yes
2,4-D	0.07	No
dicrotophos	1400	Yes
GB	20	Yes
GD	1.4	Yes
VX	2.1	No

Table 7-2 shows that with the exception of VX and 2,4-D (for which the provided methods lacked sensitivity), the sensitivity of the CT-1128 was sufficient to detect the target contaminants at the concentrations of interest, i.e., at LD_{50} or MCL concentrations.

Because the CT-1128 requires approximately two hours to equilibrate once electrical power and gas have been supplied, it should be kept on standby (under vacuum and thermally equilibrated) as long as possible when time is a critical factor for analyzing field samples. Mobilization in the field is straightforward, and the CT-1128 requires only a source of electrical power for several hours of field deployment when used with its on-board hydrogen canister for a source of carrier gas. During the non-laboratory testing, the coefficients of determination (r^2) achieved in the field for benzene, toluene, ethylbenzene, and xylenes were 1.000, 0.996, 0.998, and 1.000, respectively, and the recoveries of a blind test water sample were 108%, 23%, 135%, and 121%, respectively.

The CT-1128 did not require extensive maintenance during the verification test. On several occasions, leaks were suspected, and detection and remediation took a significant amount of time (as it typically does with any GC-MS system). Typical extraction and sample run times ranged from 22 minutes to 32 minutes. The daily procedures recommended for operation during verification testing (e.g., mass tuning, air/water check, and SPME fiber/GC column bakeout) lasted approximately one hour. Average sample throughput during verification testing was 11 samples per 10-hour working day, or approximately one sample per hour. For 100 samples, the total cost for supplies was approximately $914, not including the GC column and standard chemicals. At the time of testing, the cost of the CT-1128 GC-MS system, with optional SPME stirrer/heater, was $140,000.

It is important to note that the results of the verification test reflect the performance of the SPME sample preparation as well as the analytical results generated by the CT-1128. The methods provided for this verification test were not optimized or modified for sensitivity by the vendor prior to use in the verification test and therefore may not represent the most optimal performance of the CT-1128 for a particular target contaminant. Operator experience with SPME would therefore be beneficial to using the technique in conjunction with the CT-1128.

Chapter 8
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