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Phase II Fort Ord Landfill Demonstration Task 8 - Refinement of In-line Instrumental Analytical Tools to Evaluate their Operational Utility and Regulatory Acceptance

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Phase II Fort Ord Landfill Demonstration

Task 8 – Refinement of In-line Instrumental Analytical Tools to Evaluate their Operational Utility and Regulatory Acceptance

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TABLE OF CONTENTS

EXECUTIVE SUMMARY viii
Introduction viii
Site Descriptions ix
On-Line Analytical System Installations x
ASAP Theory of Operation x
GC Operation and Data Management xi
Prospects for future Development xi
Conclusions xiii
RECOMMENDATIONS xiv

1.0 INTRODUCTION 15
2.0 SITE DESCRIPTIONS 16
2.1 Fort Ord Operating Unit 2 Groundwater Treatment System 16
2.2 Ford Ord Operating Unit 1 Integrated Chemical and Flow Monitoring System 18
3.0 ON-LINE ANALYTICAL SYSTEM INSTALLATIONS 18
3.1 Previous Applications of Automated VOC Monitoring Systems 18
3.2 Chemical Analysis System Installation at OU 2 GTS 19
3.3 Chemical Analysis System Installation at OU 1 ICFMS 20
4.0 ASAP THEORY OF OPERATION 21
4.1 ASAP Overview 21
4.2 Sample acquisition 21
4.2 Sample processing 22
5.0 GC OPERATION AND DATA MANAGEMENT 23
5.1 GC Overview 23
5.2 Instrument Control and Data Archiving 24
5.3 LabVIEW Application for Chromatography analysis 24
5.4 Quantitation and Reporting 25
6.0 OLAS PERFORMANCE 26
6.1 Compound Identification and Sensitivity 26
6.2 OLAS Operation at OU 1 27
7.0 PROSPECTS FOR FURTHER DEVELOPMENT 27
7.1 Software Integration for real-time operations 27
7.2 Data and Control Integration With Site-Wide SCADA 28
7.3 Data Communications For Integration of Remote Sites 28
8.0 CONCLUSIONS 29
8.1 Software and Hardware development for improved acceptance of OLAS 29
8.2 Installation and testing of chemical On Line Analysis System 29

9.0 RECOMMENDATIONS 30
9.1 Continued Operation of Integrated System at OU 1 30
9.2 Refocus operation on intentive operation of ASAP/OLAS systems for long-term performance evaluation with improved software, hardware 30
9.3 Networking improvements to allow remote access to improve maintenance and troubleshooting 30
9.4 Data Integration with SCADA Development 30

References 31

LIST OF TABLES iv
LIST OF FIGURES iv
ABBREVIATIONS AND ACRONYMS vi
ACKNOWLEDGMENTS vii

LIST OF TABLES

Table 5-1. Compound coverage by different EPA methods for volatile organic compounds in groundwater and wastewater
Table 5-2. Compounds provided in representative commercial standard blends
Table 6-1. Representative retention times and method detection limits for compounds in a commercial standard blend with two columns and the PID/DELCD combination detector.
Table 6-2. Analytes of interest at Fort Ord, OU 1.

LIST OF FIGURES

Figure 2-1. Schematic layout of the Operable Unit 2 Groundwater Treatment System (OU 2-GTS), and initial location of sampling points.
Figure 2-2. Schematic layout of the Operable Unit 2 Groundwater Treatment System (OU 2-GTS),after removal of UV polishing units, and addition of second pair of large-scale GAC cannisters.
Figure 2-3. Fort Ord Operable Unit 1, Fire Drill Area (OU 1-FDA).

Figure 3-1. Water sampling and analytical system components comprising ASAP1.

Figure 4-1. Main components of the Automated Sampling and Analysis Platform (ASAP1).
Figure 4-2. Liquid flow of the ASAP1 during sample acquisition.
Figure 4-3. Liquid and gas flows of the ASAP1 during sample acquisition and and VOC stripping: idling state between samples.
Figure 4-4. Liquid and gas flows of the ASAP1 during sample acquisition and and VOC stripping: loop filling.
Figure 4-5. Liquid and gas flows of the ASAP1 during sample acquisition and and VOC stripping: sample stripping.
Figure 4-6. Liquid and gas flows of the ASAP1 during sample acquisition and and VOC stripping: valve purging.
Figure 4-7. Liquid and gas flows of the ASAP1 during sample acquisition and and VOC stripping: trap 'dry' purge.
Figure 4-8. Liquid and gas flows of the ASAP1 during sample acquisition and and VOC stripping: trap heating.
Figure 4-9. Liquid and gas flows of the ASAP1 during sample acquisition and and VOC stripping: trap desorb for GC injection.
Figure 4-10. Components of the Automated Sampling and Analysis platform (ASAP, A+RT, Milpitas, CA) equipped with additional switching valve and loop for internal standard, surrogate injection.

Figure 5-1. Typical chromatogram of Contract Laboratory Program Volatiles Target Compound mixture (CLP-150, Ultra Scientific).
Figure 5-2. Main GC control user interface panels. Central plots show PID and DELCD plots from an effluent sample of OU 1-GTS GAC cannister TKB, with low levels of residual VOCs.
Figure 5-3. Example LabVIEW "Virtual Instrument" Diagram, showing code for "PID/DELCD GC.VI" (Figure 5-1).
Figure 5-4. Chromatogram analysis starts with opening of a standard file generally named with a date and standard set identifier (e.g.: 100401s104.std, for standard set #104, run on 10/04/01).
Figure 5-5. The Standard Editor allows viewing and modification of currently defined standard files.
Figure 5-6. The Standard Editor also contains a module for addition or deletion of components, in the event that a new standard blend can more easily created by modiying and renaming an existing one, rather than creating a lengthy list from scratch.
Figure 5-7. Calibration coefficients for standard blend components are calculated after first processing analyses of different loop volumes from the two standard syringes, and saving the peak area data to a "Cal " file.
Figure 5-8. Representative standard regressions from chromatograms of Ultra Scientific Contract Laboratory Program Volatiles Target Compounds mixture (CLP-150), run with the ASAP/OLAS equipment at the OU 1 ICMFS.
Figure 5-9. Representative chromatogram from a sample of groundwater from MW-OU1-20-A at the OU 1-ICMFS.

Figure 6-1. Example OLAS chromatograms, during evaluation of trap materials, column types, and different commercial standards.
Figure 6-2. Stability of chemical standard analyses with the ASAP/OLAS at the Fort Ord OU 1 ICFMS. Repeated samples from one filling of Syringe A using loop 2 (~70 ng per component of CLP-150 Contract Laboratory Program Volatiles Target Compounds mixture; Ultra Scientific, Inc.)
Figure 6-3. Typical chromatogram from Fort Ord well MW-OU1-O4-A, and trends of analyte concentrations measured during On-Line Analysis System test period
Figure 6-4. Typical chromatogram from Fort Ord well MW-OU1-O5-A, and trends of analyte concentrations measured during On-Line Analysis System test period
Figure 6-5. Typical chromatogram from Fort Ord well MW-OU1-O7-A, and trends of analyte concentrations measured during On-Line Analysis System test period
Figure 6-6. Typical chromatogram from Fort Ord well MW-OU1-19-A, and trends of analyte concentrations measured during On-Line Analysis System test period
Figure 6-7. Typical chromatogram from Fort Ord well MW-OU1-20-A, and trends of analyte concentrations measured during On-Line Analysis System test period
Figure 6-8. Typical chromatogram from Fort Ord well MW-OU1-36-A, and trends of analyte concentrations measured during On-Line Analysis System test period
Figure 6-9. Typical chromatogram from Fort Ord well MW-OU1-37-A, and trends of analyte concentrations measured during On-Line Analysis System test period

Figure 6-10. Typical chromatogram from Fort Ord well MW-OU1-38-A, and trends of analyte concentrations measured during On-Line Analysis System test period
Figure 6-11. Typical chromatogram from Fort Ord well MW-OU1-39-A, and trends of analyte concentrations measured during On-Line Analysis System test period
Figure 6-12. Typical chromatogram from Fort Ord well MW-OU1-40-A, and trends of analyte concentrations measured during On-Line Analysis System test period

ABBREVIATIONS AND ACRONYMS

ASAP	Analytical Sampling and Analysis Platform
DAQ	Data Acquisition (system)
DC	Direct Current
EPA	Environmental Protection Agency
EW	Extraction Well
GAC	Granular Activated Carbon
GC	Gas Chromatograph
GC/MS	Gas Chromatography/Mass Spectrometry
GPM	Gallons Per Minute (also gpm).
GTS	Groundwater Treatment System
HLA	Harding Lawson Associates (now Harding ESE)
ICFMS	Integrated Chemical and Flow Monitoring System
MCL	Maximum Contamination Limit
MDL	Method Detection Limit
MW	Monitoring Well
ND	Non-Detect
OLAS	On-Line Analytical System
OU	Operable Unit
OU 2-GTS	Operable Unit 2 Groundwater Treatment System
ppb	Part Per Billion
PQL	Practical Quantitation Limit
ROD	Record of Decision
RT	Retention Time

VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound

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EXECUTIVE SUMMARY

Introduction

The overall objective of this project is the continued development, installation, and testing of continuous water sampling and analysis technologies for application to on-site monitoring of groundwater treatment systems and remediation sites. In a previous project, an on-line analytical system (OLAS) for multistream water sampling was installed at the Fort Ord Operable Unit 2 Groundwater Treatment System, with the objective of developing a simplified analytical method for detection of Compounds of Concern at that plant, and continuous sampling of up to twelve locations in the treatment system, from raw influent waters to treated effluent.

Earlier implementations of the water sampling and processing system (Analytical Sampling and Analysis Platform, A^{+}RT, Milpitas, CA) depended on off-line integrators that produced paper plots of chromatograms, and sent summary tables to a host computer for archiving. We developed a basic LabVIEW (National Instruments, Inc., Austin, TX) based gas chromatography control and data acquisition system that was the foundation for further development and integration with the ASAP system. Advantages of this integration include electronic archiving of all raw chromatographic data, and a flexible programming environment to support development of improved ASAP operation and automated reporting. The initial goals of integrating the preexisting LabVIEW chromatography control system with the ASAP, and demonstration of a simplified, site-specific analytical method were successfully achieved.

However, although the principal objective of this system was assembly of an analytical system that would allow plant operators an up-to-the-minute view of the plant's performance, several obstacles remained. Data reduction with the base LabVIEW system was limited to peak detection and simple tabular output, patterned after commercial chromatography integrators, with compound retention times and peak areas. Preparation of calibration curves, method detection limit estimates and trend plotting were performed with spreadsheets and statistics software. Moreover, the analytical method developed was very limited in compound coverage, and unable to closely mirror the standard analytical methods promulgated by the EPA.

To address these deficiencies, during this award the original equipment was operated at the OU 2-GTS to further evaluate the use of columns, commercial standard blends and other components to broaden the compound coverage of the chromatography system. A second-generation ASAP was designed and built to replace the original system at the OU 2-GTS, and include provision for introduction of internal standard compounds and surrogates into each sample analyzed. An enhanced, LabVIEW based chromatogram analysis application was written, that manages and archives chemical standards information, and provides a basis for NIST traceability for all analyses. Within this same package, all compound calibration response curves are managed, and different report formats were incorporated, that simplify trend analysis. Test results focus on operation of the original system at the OU 1 Integrated Chemical and Flow Monitoring System, at the OU 1 Fire Drill Area remediation site.

Site Descriptions

Earlier implementations of the ASAP at research sites focusing on *in situ* studies of bioremediation and other remedial technologies are reviewed. The two sites at Fort Ord where the original ASAP1/OLAS system was deployed and tested were the OU 2 Groundwater Treatment System (OU 2-GTS), and the OU 1-Fire Drill Area Integrated Chemical and Flow Monitoring System (OU 1/ICFMS).

The OU 2-GTS is a large scale water treatment system that targets removal of eleven compounds of concern from groundwater extracted from beneath a closed landfill. In its original configuration, water from a series of extraction wells converged on the plant in two manifolds. The water was blended, and scrubbed by passage through two 20,000 lb canisters of granulated activated charcoal (GAC). A valve station permitted either of the GAC tanks to be in the upstream or downstream positions; as breakthrough is detected from the upstream tank, a carbon change-out is ordered, and once the carbon from the upstream tank (with the highest contaminant load) is replaced, the other tank becomes the upstream tank, and the newly replaced carbon is in the downstream position. One objective of on-line analysis is the more efficient management of this process, to prolong intervals between carbon change-out without risking contaminant breakthrough.

In a previous project, a network of stainless steel sampling lines were installed at this plant to monitor the influent manifolds, blended inlet to the GAC tanks, and at effluent points following each stage of treatment. During this award, a major overhaul of the plant was performed, adding two additional GAC tanks to treat a new water manifold. As construction proceeded, defects in the original GAC tank foundations were discovered, that forced dismantling of the preexisting treatment system and sampling network. The treatment system has been reconstructed, and new sampling lines installed to relevant points that will monitor all influent manifolds, stream blending points, and effluents from all GAC tanks; however, at this writing, the replacement ASAP2/OLAS instrument package has not been installed at the site.

The second site, where the original OU 2 ASAP1/OLAS has now been moved, is the Operable Unit 1 Fire Drill Area Integrated Chemical and Flow Monitoring System (OU 1-FDA/ICFMS). This is located near the origin of a VOC plume generated by fire fighting training excercises that took place near the former Fritzche Air Field. At this location a continuously operating integrated field facility for monitoring water flow, depth, and VOC concentrations was designed and installed on the scale of an entire remediation site. The low-flow pumping and analysis system uses 2,300 feet of buried PVC pipe to connect 10 wells over 1000 feet apart; dedicated micropurging bladder pumps deliver water continously through 4,800 feet of stainless steel tubing to a centralized analytical equipment station housing the OLAS. In addition to VOC analysis, *in situ* permeable flow sensors (HydroTechnics) measure groundwater flow velocity and direction, and pressure transducers to measure water depth. The facility has been in almost continuous operation for over a year. A detailed description of this site has been submitted as a separate report for this project (Oldenburg et al., 2001).

On-Line Analytical System Installations

Recently, instrumentation that provides conventional compound separation and high sensitivity detection in an on-line configuration has been deployed for continuous, in-field monitoring of groundwater remediation experiments. These analytical systems have the capacity to convert the sampling of water wells from a highly labor intensive and slow process, into a much higher-frequency data acquisition application. These installations took advantage of a novel flow-through sample selection and processing system, the Analytical Sampling and Analysis Platform (ASAP, A^{+}RT, Milpitas, CA, Figure 3-1). This automated device uses sample selection and flow switching valves and a unique thin-film stripping cell to process water samples and analytical standards for purge-and-trap VOC analysis under relatively unattended computer program control for prolonged periods. The earlier studies were small scale experiments that intensively sampled relatively small aquifer zones up to only a few tens of meters in diameter. We elected to evaluate this continuous analytical system in a groundwater treatment plant application, and in a second *in situ* monitoring application on the scale of an entire remediation site, to evaluate the practicality of installation and operation of automated long-term VOC monitoring coupled with ultra-low flow continuous sample pumping, also known as micropurging. Each of the two applications used the same analytical hardware, with slight modifications. The first unit, tested both at OU 2 and OU 1, is referred to as ASAP1; while the second unit, assembled for the OU 2-GTS, is referred to as ASAP2. ASAP1 is designed to sample from up to twelve locations, and flush one of twelve VOA vials with sample water prior to an on-line analysis for VOCs with the associated capillary column gas chromatograph; the VOA vial rack was incorporated to support off-line analysis of materials such as conservative tracers, that can't be analyzed by GC. ASAP2 was designed with only a single off-line VOA sample vial, but incorporates an injection system to permit incorporation of internal standards and surrogate compounds into each analysis, to more closely align the ASAP/OLAS operation with conventional laboratory analytical methods. ASAP1 is now located at the OU 1/ICFMS, and ASAP2 awaits installation at the OU 2-GTS.

ASAP Theory of Operation

The ASAP utilizes multiport selector valves and switching valves to manage high-precision water sample acquisition, VOC stripping, volatiles trapping, and injection into the GC. The basic ASAP is comprised of separate rack-mounted modules that manage each part of the process: a sampling manifold that holds valves that select from one of the incoming sample lines, a liquid processing module that includes sample loops of several fixed volumes mounted on a selection valve, a unique thin-film sample stripping cell, and peristaltic pumps that provide water streams that move samples and standards, and finally a gas trapping module, that contains the embedded processor that operates the ASAP, gas switching valves, and the trap and its associated heaters, temperature sensors and controllers. Our units each have these three units in common, with a fourth in each that offers a specific optional capability. In ASAP1 the fourth module supported a manifold of twelve standard 40 ml VOA vials that could be flushed with sample waters prior to on-line analysis. In the second-generation ASAP2, this module was replaced by a unit supporting an additional six-port switching valve and a loop to deliver

a fixed volume of internal standard and surrogate compound mixture for enhanced sample-by-sample quality control. The description of ASAP operation presented references ASAP1, although nearly all the steps are common to both units.

GC Operation and Data Management

In both the OU 2 and OU 1 installations a capillary gas chromatograph was used, and outfitted with a combination photoionization/dry elecrtrolytic conductivity detector. Three column setups designed for use with EPA volatiles methods were evaluated for separation of commercially available standards and site samples. Two single-columns were evaluated (J&W Scientific DB-624, and Restek RtX 502.2), and a combination DB-624/DB-VRX (J&W Scientific) column was evaluated to determine whether 1,2-dichloroethane and benzene (that co-elute from many single columns) could be separated (Rood, 1999). Compound identification was achieved by comparison of chromatograms with vendor-supplied plots, and injection of single compounds, as necessary.

Commercial vendors have started to produce prepackaged standard blends that cover many routine analyses. These have the great benefit of savings of labor, and traceability to NIST standards. We soon realized that the initial strategy of developing a simplified, custom analytical method for the needs of single sites would leave the system vulnerable to misidentifying compounds, or missing minor components. We examined standard methods supported by capillary GC and PID/DELCD detection, to move the methods supported by the ASAP/OLAS into a closer match with standard laboratory procedures. Target compounds for five relevant EPA methods are given. The EPA 8021B has the best coverage of compounds with respect to the known compounds of concern at Fort Ord, and is a PID/ELCD, capillary column GC procedure. It does not have quite the extensive compound coverage of the GC/MS methods, such as the EPA 8260B, but appears to be the most useful approach for both the OU 2-GTS and the OU 1-FDA/ICFMS.

Software was developed to manage analytical standards and automate chromatography data reduction. Good Laboratory Practices such as locked standard files and incorporation of chromatography system configurations in standard descriptor files was incorporated to bring the integrated software system into congruence with common commercial laboratory procedures. A detailed summary of operator actions during operation of the application is presented.

Prospects for Future Development

The software components for GC control and chromatogram acquisition are separate modules from the Chromatogram Analyzer suite of tools. These can be integrated to support automated trend file generation and live displays for operators, although some additional methods validation and software integration work still remains for this to offer both reliability and adequate alarms for conditions indicating drift from specified performance.

Drift in detector response and compound retention time remains an issue. Detectors can be expected to decline in sensitivity with use, and strategies for routine maintenance

must be enforced. Identifying the appropriate point to perform these maintenance operations is an important issue; observations of the primary chlorocarbon detector used in this project and its response to maintenance are discussed.

In this work, we relied on the use of "external standards," the approach that was used in all earlier implementations of ASAP based systems. A more robust approach used in conventional laboratories is the use of "internal standards," in which a known, fixed amount of a compound related to target analytes, but separable from them in the GC, is introduced into each sample and standard, along with surrogate compounds not found in real samples. The analysis of the internal standards takes place in both samples and standard runs, but the *ratio* of detector response to sample analyte and internal standard is used in forming a regression against target analyte concentration. In this way any losses of internal standard are expected to mirror losses of targets, yet their ratio is preserved throughout; the use of surrogate compounds also enhances the operator's ability to detect shifts in compound retention time or other performance characteristics The ASAP2 unit was designed and assembled with an additional loop for injection of internal standards and surrogates with this enhancement in mind.

The Fort Ord environmental restoration program is currently implementing a supervisory control and data acquisition (SCADA) system to link operations of several groundwater remediation systems. The ASAP/OLAS instrumentation has great potential for integration with this site-wide effort, owing to the use of LabVIEW, that supports flexible communications with SCADA systems.

The lack of broad-band communications at the Fort Ord sites while evaluating the systems described became a significant handicap. During development of an automated vapor analysis system that formed the foundation of the GC control system of the ASAP/OLAS, we relied heavily on ethernet communications at the Lawrence Livermore National Laboratory to communicate with analytical systems sremote from the main Laboratory site and regularly used screen-sharing software to view the remote system screens, transfer data, and support technicians during troubleshooting or maintenance.

Unfortunately this has not been possible at the Fort Ord OLAS sites. Telephone infrastructure at the site is dated, and is unsuitable for data communications. However, both cable and digital subscriber line (DSL) installations are taking place, and there are conventional ethernet installations in parts of the base. We have monitored the growth in industry acceptance of new wireless networking standards, especially IEEE-802.11b wireless ethernet operating in the 2.4 to 2.6 GHz frequency bands. With the use of readily available directional antennas and repeaters, analytical stations such as the ASAP/OLAS could be efficiently linked to site wide communications backbones and greatly facilitate reliable and sustained operation of the on-line hardware.

Conclusions

An automated water sampling and analysis system was developed and tested at two sites at Fort Ord. The analytical equipment successfully supports relatively unattended operation for extended periods, and has demonstrated stability, sensitivity and precision comparable to formal analytical laboratory instruments over at least the time scale of weeks. Moreover, since samples are transported through a highly inert, all-metal sampling system, they apparently arrive at the analytical hardware in a relatively undisturbed state, as analytes not detected with manual sampling and formal laboratory analysis were frequently detected during testing at OU 1, and other compounds, although previously found at the site, were detected in wells where they had not been previously observed. Although during testing data acquisition and subsequent quantitation and reporting were separate processes, these can be integrated in the future to provide integration, and instantaneous updates of contaminant distributions.

Software was developed to manage analytical standards and automate chromatography data reduction. Good Laboratory Practices such as locked standard file types and incorporation of chromatography system configurations was incorporated to bring the integrated software system into congruence with common commercial laboratory procedures.

A second generation ASAP/OLAS sampler that provides optional introduction of internal standards and surrogates for improved analytical reliability was designed and built. Owing to construction delays associated with the rebuilding of the OU 2 groundwater treatment plant, this system has not been installed at that plant.

RECOMMENDATIONS

1) We recommend that the ASAP1/OLAS system should be operated at the OU 1-FDA/ICFMS site to support experiments to better characterize the impact of groundwater pumping patterns and treated water disposal. We further recommend installation of the ASAP2/OLAS at OU 2 as soon as construction at the site allows, so that potentially enhanced capabilities of this unit can be evaluated during routine operation.

2) We recommend that since site installation construction at the OU 1-FDA/ICFMS and OU 2-GTS sites is essentially complete, and analytical software has been initially validated, that the focus of operations should shift to intensive operation of the analytical hardware to improve long-term performance. This will require more attention to regular maintenance using techniques discovered in this project. We recommend that alternate operators already assigned to tasks at the two sites (GTS operators, etc.) receive training in ASAP/OLAS routine maintenance operations (cleaning and filling standard syringes, maintenance of peristaltic pumps, inspection of standard recoveries, etc.), to assist in keeping the analytical hardware in the best working condition.
3) We strongly recommend installation of wireless networking, to allow remote data collection, viewing of operator interfaces, and facilitate troubleshooting and maintenance operations. If this cannot be readily accomplished, we recommend an

alternative manual transfer of data (email, file uploads to an FTP site, etc.) by facility staff, so that system operation can be more regularly reviewed.

4) We recommend integration of data streams from the ASAP/OLAS stations with the SCADA plans at the site. While further software development may be required, this is a realistic proposal supported by the use of LabVIEW by the analytical stations, and related products from the same vendor for the site SCADA system. A detailed review of data types supported by the ASAP/OLAS systems in their present configuration, and areas of prioritized data needs of the SCADA implementation should take place as soon as possible, so that a systematic strategy for implementing and testing software extensions can be developed.

1.0 INTRODUCTION

The overall objective of this project is the continued development, installation, and testing of continuous water sampling and analysis technologies for application to on-site monitoring of groundwater treatment systems and remediation sites. In a previous project, an on-line analytical system (OLAS) for multistream water sampling was installed at the Fort Ord Operable Unit 2 Groundwater Treatment System, with the objective of 1) developing a simplified analytical method for detection of Compounds of Concern at that plant, 2) continuous sampling of up to twelve locations in the treatment system, from raw influent waters to treated effluent, using a semi-custom, multi-stream water sampling and flow-through purge and trap system with gas chromatographic (GC) analysis of VOCs, and 3) integrating operation of the sampling and gas chromatography systems with a LabVIEW based GC data acquisition previously developed at LLNL. These objectives were all achieved.

Earlier implementations of the water sampling and processing system (Analytical Sampling and Analysis Platform, A^{+}RT, Milpitas, CA) depended on off-line integrators that produced paper plots of chromatograms, and sent summary tables to a host computer for archiving. We had developed a basic LabVIEW (National Instruments, Inc., Austin, TX) based gas chromatography control and data acquisition system that appeared to be a suitable foundation for further development and integration with the ASAP system. Advantages of this integration would include electronic archiving of all raw chromatographic data, and a flexible programming environment to support development of improved ASAP operation and automated reporting. The initial goals of integrating the preexisting LabVIEW chromatogrphy control system with the ASAP, and demonstration of a simplified, site-specific analytical method were successfully achieved.

However, although the principal objective of this system was assembly of an analytical system that would allow plant operators an up-to-the-minute view of the plant's performanced, several obstacles remained. Data reduction with the base LabVIEW system was limited to peak detection and simple tabular output, patterned after commercial chromatograhy integrators, with compound retention times, and peak areas. Preparation of calibration curves, method detection limit estimates and trend plots was performed with spreadsheets and plotting software. Moreover, the analytical method developed was very limited in compound coverage, and unable to closely mirror the standard analytical methods promulgated by the EPA.

To address these deficiencies, during this award the following additional objectives were set out: 1) the original equipment was operated at the OU 2-GTS and at the OU 1 ICFMS to further evaluate the use of columns, commercial standard blends and other components to broaden the compound coverage of the chromatography system and characterize detector performance; 2) a second-generation ASAP was designed and built to replace the original system at the OU

2-GTS, that includes provision for introduction of internal standard compounds and surrogates into each sample analyzed; 3) an enhanced, LabVIEW based chromatogram analysis application was written, that manages and archives chemical standards information, and provides a basis for NIST traceability for all analyses. Within this same package, all compound calibration response curves are managed, and different report formats were incorporated, that simplify trend analysis.

The installation and testing plan at the outset of the project was to replace the original sampling system with the second generation ASAP at the OU 2-GTS, and add additional sampling lines to the existing network of sampling points installed in the earlier project. The original unit would then move to a second site at Fort Ord, the Integrated Chemical and Flow Monitoring System demonstration site at the Operable Unit 1 Fire Drill Area (OU 1-FDA/ICFMS; Task 7 of this overall project). The latter move was accomplished, and testing data from the OU 1 site, using the original ASAP/OLAS equipment and the enhanced LabVIEW chromatography analysis software are presented in this report. Unfortunately, during planned treatment system expansion at the OU 2-GTS, structural problems with the foundations supporting the original large-scale granular activated carbon (GAC) tanks, that were the basis of the treatment, were discovered. This forced dismantling of both the original treatment system and removal of all sampling lines. Despite the resulting construction delays, the portable building housing the analytical hardware has been re-installed within the OU 2 GTS main building, and new sampling lines have been installed; at this writing the second generation ASAP/OLAS has not yet been installed at this site, as electrical connections are not yet available. In order to continue progress toward the goal of improving acceptability of the analytical systems, the author, representatives from the environmental restoration program, and managers of this project agreed to a shift in focus to software development and preparation of detailed descriptions of the integrated ASAP/OLAS hardware and software, to provide guidance materials for future operators and regulatory review.

This report summarizes our work from the the beginning of the project in early 1999 to the present in the following sections: (1) Site Descriptions; (2) a review of previous On-Line Analytical System Installations, with brief descriptions of the two sites at Fort Ord where this equipment has been implemented; (3) ASAP Theory of Operation; (4) GC Operation and Data Management; (5) OLAS Performance; and (6) Prospects for Future Development, followed by conclusions and general recommendations.

2.0 SITE DESCRIPTIONS

2.1 Fort Ord Operating Unit 2 Groundwater Treatment System

The Fort Ord Operating Unit 2 Groundwater Treatment System is located near the northern boundary of the former Army post, and was originally designed to received contaminated groundwater from two sets of extraction wells removing contaminated water, primarily from the A aquifer beneath a closed landfill. One

set of wells eight wells were located immediately downgradient from the landfill site (EW-OU2--07-A, -08-A, -09-A, -10-A, -11-A, -12-A, -13-A, and –02-180 in the "180 foot aquifer"); their waters were joined in a manifold designated East-Influent at the GTS (E-In, Figure 1-1). A second set of wells much closer to the treatment system (EW-OU2-01A, -02-A, -03-A, -04-A, -05-A, -06-A, and –02-180) provided down-gradient hydraulic control. Their joined effluent was designated West-Influent (W-In, Figure 2-1).

The OU 2-GTS is a large scale water treatment system that targets removal of eleven compounds of concern from groundwater extracted from beneath a closed landfill. In its original configuration, water from a series of extraction wells converged on the plant in two manifolds as described above. The water was blended, and scrubbed by passage through two 20,000 lb canisters of granulated activated charcoal (GAC). A valve station permitted either of the GAC tanks to be in the upstream or downstream positions; as breakthrough is detected from the upstream tank, a carbon change-out is ordered, and once the carbon from the upstream tank (with the highest contaminant load) is replaced, the other tank becomes the upstream tank, and the newly replaced carbon is in the downstream position. One objective of on-line analysis is the more efficient management of this process, to prolong intervals between carbon change-out without risking contaminant breakthrough.

Exiting from the GAC, water was split into four parallel streams that passed through ultraviolet-peroxide polishing reactors (Solarchem, Inc., UV1 through UV4, Figure 2-1), that were to be operated if contaminant breakthrough was anticipated. The four streams were rejoined, forming a common effluent line. Effluent water passed into two large surge tanks prior to pumping into injection wells west of the OU 2 plume, in the 180 foot aquifer.

Manual sampling was performed weekly at several points in the system: the joined inlet to the GAC vessels (GAC-In), the effluent from each tank (TKA and TKB), the joined inlet to the UV polishers (UV-In), their respective effluents (UV1, UV2, UV3, and UV4), and at the common effluent (Eff), for nine sampling locations.

During initial installation of sampling plumbing in the previous project, we added 'Ts' and additional sampling petcocks to allow manual sampling as well as continuous feed to the ASAP at all of these locations, and added points prior to the joined inlet to the GAC vessels, at the incoming water manifolds, E-In and W-In, for a total of eleven sampling locations.

During the current award, the facility has been substantially rebuilt. The first change that impacted the OLAS was removal of the ultraviolet polishing system. This reduced the total number of sampling points, and made the UV inlet point redundant with the ultimate effluent. The more substantial modification of the plant was addition of a second pair of GAC canisters to treat a new manifold of wells from further south east of the existing extraction wells, producing one additional influent monitoring point (SE-In for Southeast Influent), and tank effluent points (Figure 2-2). Since the waters from these new tanks will rejoin

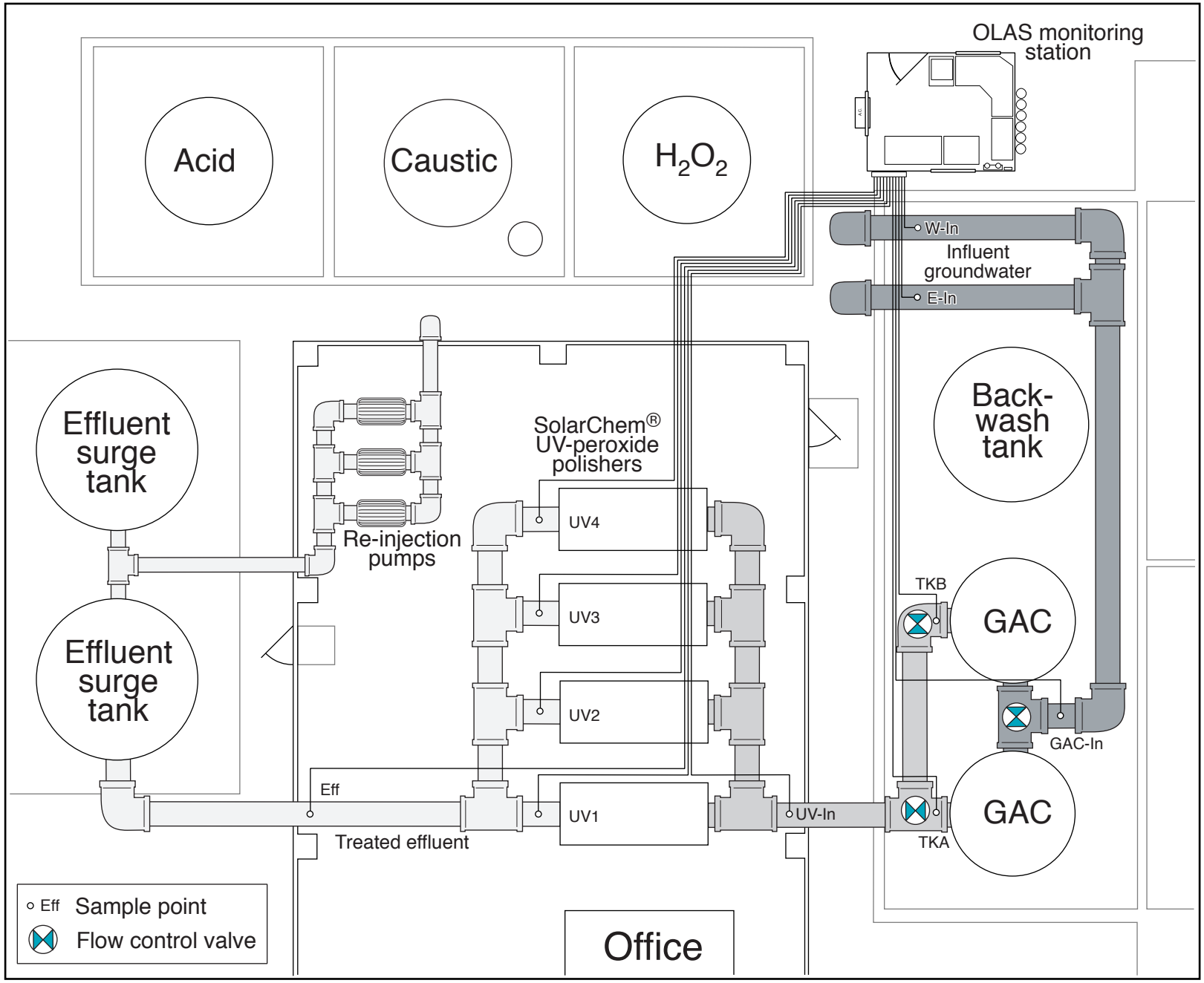

Figure 2-1. Schematic layout of the Operable Unit 2 Groundwater Treatment System (OU 2-GTS), and initial location of sampling points.

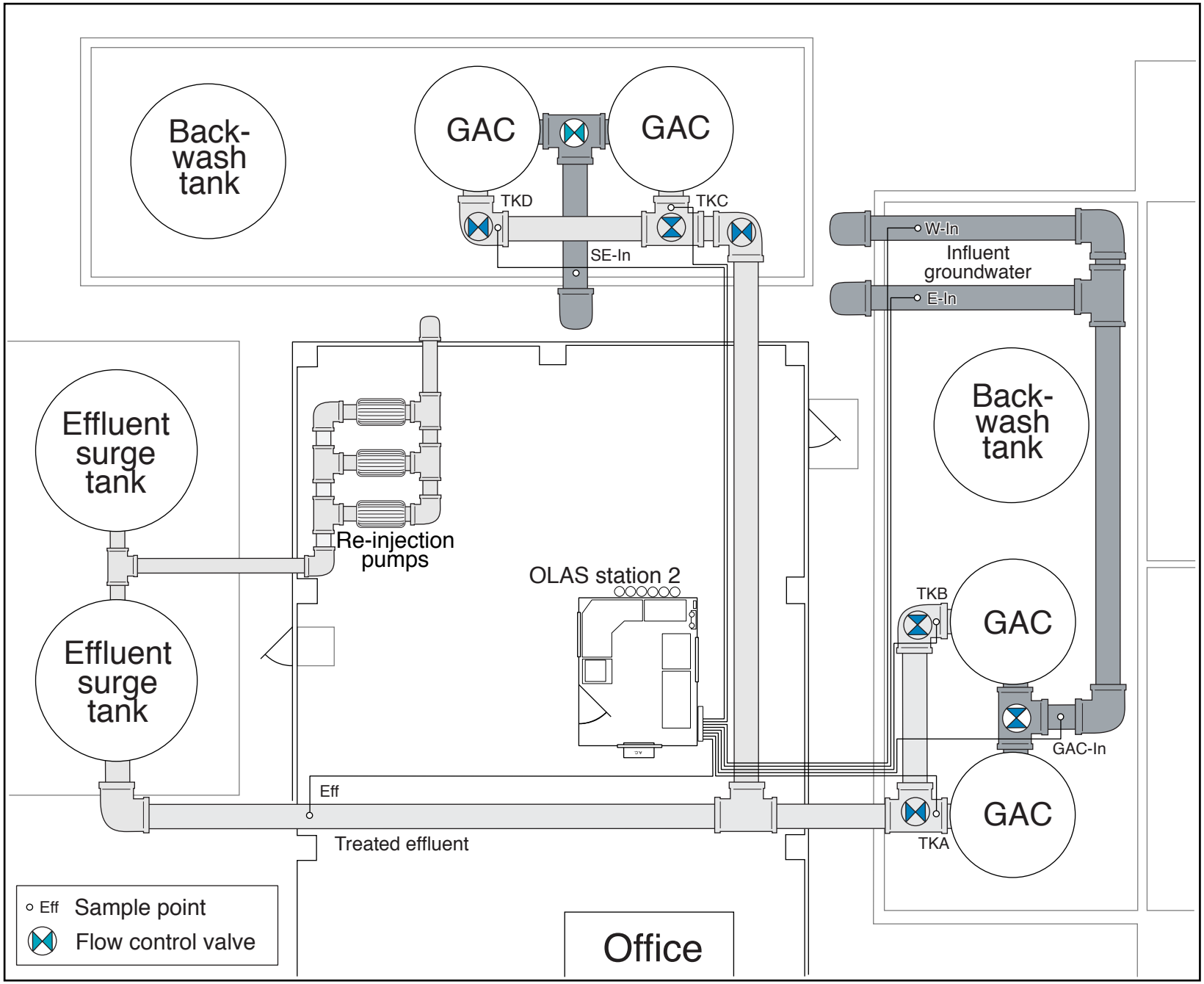

Figure 2-2. Schematic layout of the Operable Unit 2 Groundwater Treatment System (OU 2-GTS),after removal of UV polishing units, and addition of second pair of large-scale GAC cannisters; system capacity increased from ~750 gpm to ~1,000 gpm. Note loss of UV-In and four post-UV sampling points, addition of points to monitor new influent line, effluent from each new GAC cannister. The latter, new tanks also have intermediate sampling ports sampling within the carbon beds at three depths. At this time these are not routed to the OLAS station, but could be added at a later date.

effluent from the reinstalled original system, a single overall effluent still reflects the integrated system outflow.

Removal of the UV polishing system released space inside the plant building that has allowed relocation of the OLAS portable building (Figure 2-2). At this writing reconnection of sample lines to the locations shown in Figure 2-2 has been completed, and plans are underway for reinstallation of the analytical equipment.

2.2 Ford Ord Operating Unit 1 Integrated Chemical and Flow Monitoring System

The second site, where the original OU 2 OLAS has now been moved, is the Operable Unit 1 Fire Drill Area Integrated Chemical and Flow Monitoring System (OU 1-FDA/ICFMS). This is located near the origin of a VOC plume generated by fire fighting training excercises that took place near the former Fritzche Air Field (Figure 2-3).

At this site a continuously operating integrated field facility for monitoring water flow, depth, and VOC concentrations was designed and installed on the scale of an entire remediation site. The low-flow pumping and analysis system uses 2,300 feet of buried PVC pipe to connect 10 wells over 1000 feet apart; dedicated micropurging bladder pumps deliver water continously through 4,800 feet of stainless steel tubing to a centralized analytical equipment station housing the OLAS. In addition to VOC analysis, *in situ* permeable flow sensors (HydroTechnics) measure groundwater flow velocity and direction, and pressure transducers to measure water depth. The facility has been in almost continuous operation for over a year. A detailed description of this site has been submitted as a separate report for this project (Oldenburg et al., 2001).

3.0 ON-LINE ANALYTICAL SYSTEM INSTALLATIONS

3.1 Previous Applications of Automated VOC Monitoring Systems

Automated datalogging and application of multiple types of sensors has become common in numerous industries, giving system operators both a more detailed understanding of the variables under their control, and improved response to operational changes. The net effect is reduced operational costs and avoid untoward failures and downtime (Johnson, 1997). Generally, substitution of automated sampling and application of sensors improves both the quality of data (through reduction of human errors and bias) and frequency of data collection, so short-term systematic perturbations can be detected that otherwise might be interpreted as random sampling noise. Realization of the value of automated data collection has extended into the environmental remediation disciplines, but despite extensive effort by several agencies to develop chemical sensors that could substitute for conventional sampling and laboratory analysis, sensors that offer low cost of operation, long-term *in situ* stability, sensitivity in the realm of

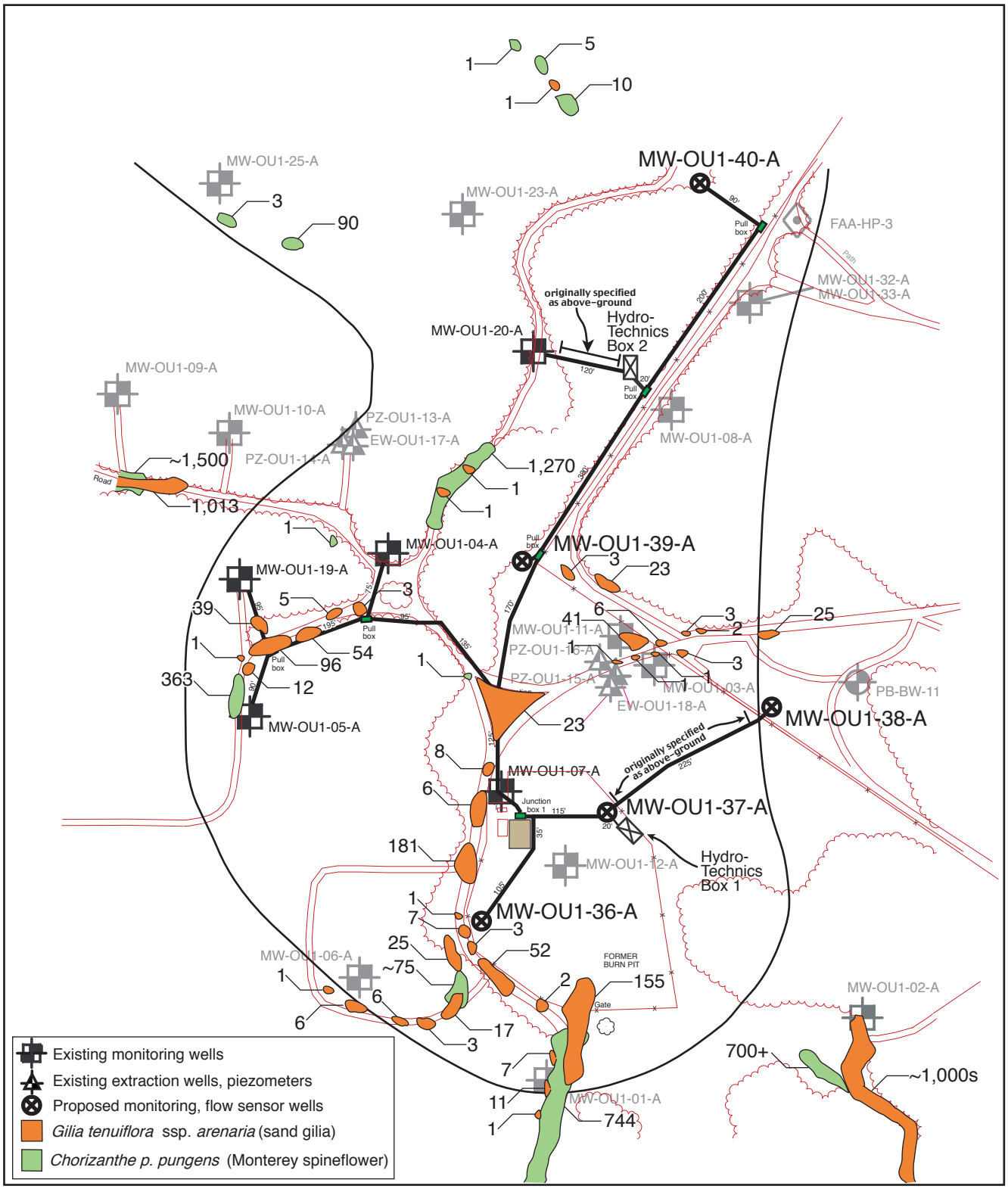

Figure 2-3. Fort Ord Operable Unit 1, Fire Drill Area (OU 1-FDA). The ASAP/OLAS instrumentation originally deployed at the OU 2 GTS was operated at the OU 1 Integrated Chemical and Flow Monitoring System (ICFMS) when the OU 2 GTS was dismantled for expansion in the winter of 2001. This map shows the distribution of new flow monitoring and groundwater sampling wells, and preexisting groundwater monitoring wells that contributed samples to the monitoring station. Colored contours show distributions of rare plant resources at the site.

low parts per billion, and selectivity to the numerous compounds usually found in contaminated groundwater have yet to be developed.

Recently, instrumentation that provides conventional compound separation and high sensitivity detection in an on-line configuration has been deployed for continuous, in-field monitoring of groundwater remediation experiments. These analytical systems have the capacity to convert the sampling of water wells from a highly labor intensive and slow process, into a much higher-frequency data acquisition application. Examples include detailed studies of *in situ* bioremediation processes (Hopkins et al., 1993a, 1993b; Hopkins and McCarty, 1995; McCarty et al., 1998; Roberts et al., 1990; Semprini et al., 1992), and evaluation of pulsed pumping in pump-and-treat remediation (MacKay et al., 2000). These installations took advantage of a novel flow-through sample selection and processing system, the Analytical Sampling and Analysis Platform (ASAP, A^{+}RT, Milpitas, CA, Figure 3-1). This automated device uses sample selection and flow switching valves and a unique thin-film stripping cell to process water samples and analytical standards for purge-and-trap VOC analysis under relatively unattended computer program control for prolonged periods.

The previous studies cited above have been small scale experiments that have intensively sampled relatively small aquifer zones up to only a few tens of meters in diameter. We elected to evaluate this continuous analytical system in a groundwater treatment plant application, and in a second *in situ* monotoring application on the scale of an entire remediation site, to evaluate the practicality of installation and operation of automated long-term VOC monitoring coupled with ultra-low flow continuous sample pumping, also known as micropurging. Each of the two applications used the same analytical hardware, with slight modifications as described below.

3.2 Chemical Analysis System Installation at OU 2 GTS

The ASAP water sampler and gas chromatograph were housed in an 8x10 ft. portable building as a field laboratory. As with other installations of this equipment, the building was equipped with air conditioners and heating to maintain a relatively constant temperature of 23 C. All 1/4 in (0.635 cm) stainless steel sample lines from the treatment system sampling points were mounted on Unistrut® frameworking, which supported them until they were fed into the building and to the ASAP. Each line was filtered with a 40 μm mesh filter, followed by a 15 μm sintered stainless steel filter (Cajon, Inc.). Following an isolation petcock, each sample line was directly attached to the primary sample selection valve of the ASAP. Gases for the chromatography system were mounted in a small enclosure adjacent to the building, and routed through in-line purifying filters prior to the analytical equipment. Waste water from sample flushing, and VOA-free rinse water from the ASAP were collected in a sump and pumped into the system backwash tank (used for backwashing for fines removal following GAC change-out), using a pneumatic sampling pump (Solo pumps, QED Environmental, Inc.). A small refrigerator was required for chemical standards.

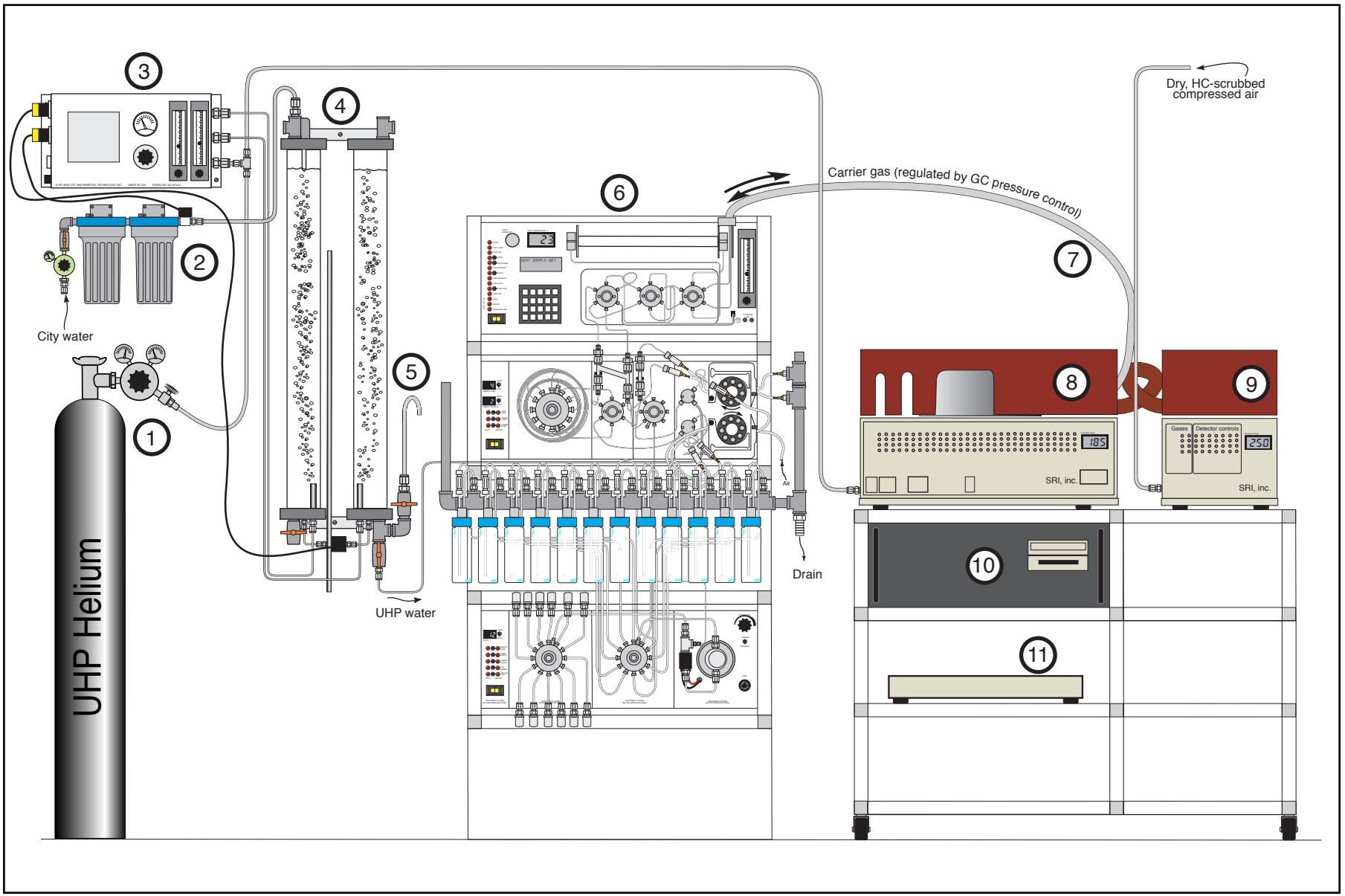

Figure 3-1. Water sampling and analytical system components comprising ASAP1: 1) Ultra-high (UHP) purity helium, 2) carbon-impregnated water filters, 3) controller for UHP water sparger, 4) countercurrent He sparger, 5) UHP water tap for syringe washing and standard dilution, 6) Analytical Sampling and Analysis Platform (ASAP, AR+T, Inc.) sample selector and flow-through purge-and-trap subsystem, 7) heated gas transfer line, 8) capillary gas chromatograph (SRI Instruments, Inc.), 9) photoionization and dry electrolytic conductivity detectors (SRI), 10) rack-mounted computer, 11) signal conditioning punchdown box. Incoming sample lines and gas line purifiers omitted for clarity.

A detailed description of the ASAP components is given in section 4.0, and an overview sketch of the system is shown in Figure 3-1. The ASAP is continually rinsed with VOC free water produced by an Ultra High Purity (UHP) water system. This system takes city water, filters it twice through activated carbon impregnated fiber filters, and then cascades the water through two countercurrent stripping columns sparged with UHP helium that also supplies purge gas to the ASAP, and carrier gas to the gas chromatograph (GC). This subsystem is item 5 in Figure 3-1. The ASAP and the GC are connected by a heated transfer line, that brings carrier from the GC, and returns stripped VOCs at sample injection. Details of this process are provided in Section 4.

A second generation ASAP system (ASAP2) has been built for the OU2 GTS, incorporating additional equipment to support injection of internal standards and surrogates as part of each sample's processing, to increase the robustness of analytical quality control. This enhanced system has undergone initial testing in the laboratory, but has not yet been installed at OU 2, owing to construction delays associated with expansion of the treatment system and the rebuilding of the original GAC system at that plant.

3.3 Chemical Analysis System Installation at OU 1 ICFMS

Micropurging has been shown to have distinct advantages over conventional purge-and-sample approaches, avoiding VOC loss through surging, pressure changes, and inadvertant aeration of samples (Barcelona et al., 1994; Kearl et al., 1992, 1994; Powell and Puls, 1993; Puls et al., 1992, Robin and Gillham, 1987) However, dedicated micropurging sampling pumps have not been coupled with on-line analytical equipment prior to this project. The low-flow pumping and analysis system at OU 1 connects a network of ten wells covering a footprint of over 1000 ft (305 m), and is to our knowledge the largest system of this type assembled to date. The sampling system was designed to be rugged, yet environmentally benign, given its location in part of the Fort Ord site that has been deeded to the University of California Ecological Preserve System. All sample tubing, compressed air lines for sample pumps, and power and signal cables for flow and depth sensors were installed in buried conduit, totaling over 2,300 feet of CPVC piping. Nearly 4,800 feet of malleable, annealed stainless steel tubing was installed for sample transport, including the connection lines from wellheads to the low-flow bladder pumps (Well Wizard pumps, QED Environmental, Inc.).

We moved the original ASAP/OLAS system to the OU 1 Fire Drill Area monitoring facility in the latter part of Spring of 2001, and completed assembly of the system and initial testing in October, 2001. In addition to the filters at the sample inlets to the ASAP used at OU 2, a modified connection to the ASAP primary sample selection valve was made, as follows: each line terminated in a "T," one arm of which connected to the primary sample selection valve on the ASAP (Figure 4-1, Item 15); the other directs flow to one of a bank of flowmeters mounted above the ASAP, that provide a convenient check of pump operation.

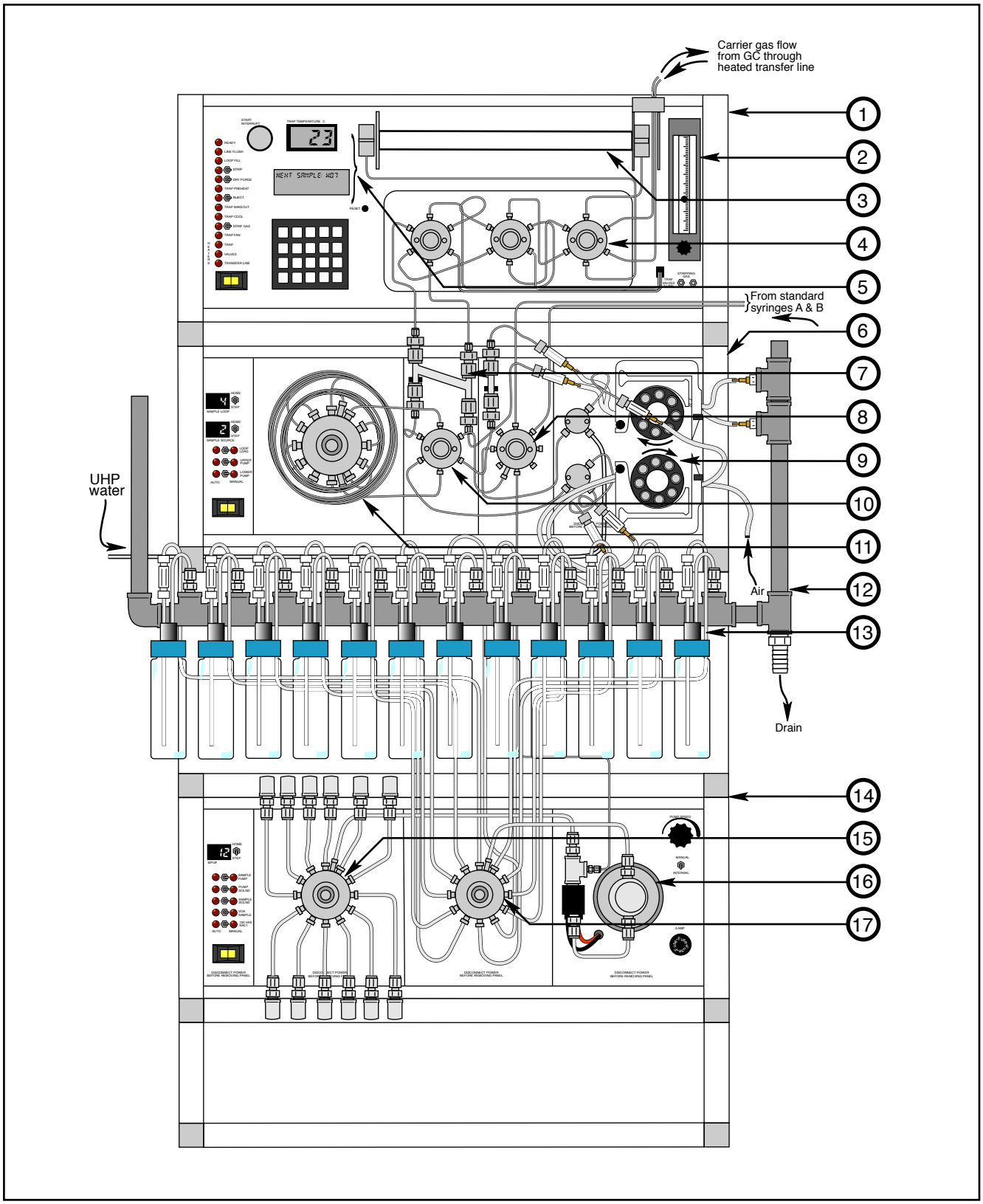

Figure 4-1. Main components of the Automated Sampling and Analysis platform (ASAP, A+RT, Milpitas, CA): 1) gas trapping module, 2) purge gas rotameter, 3) trap, 4) flow switching valves, 5) trap temperature and process stage LCDs, 6) liquid processing module, 7) flow-through stripping cell, 8) source selction valve, 9) drain (upper) and blank rinse supply (lower) peristaltic pumps, 10) liquid process valve, 11) sample loops and loop selection valve, 12) drain standpipes, 13) off-line analysis VOA rack, 14) sampling manifold, 15) primary sample selection valve, 16) sample pump and solenoid, 17) secondary sample valve.

Using the "T" arrangement, all bladder pumps could be operated continuously, and only the short lengths of tubing between the "Ts" and the selection valves need to be flushed to acquire a representative sample. Between adjustment of the bladder pump fill and delivery cycle times programmed at the wellhead controllers, and needle valves at the rotameters, a continuous stream of sample water is supplied at approximately 150 mL/min.

At this time, neither site supports high speed data communications, so all monitoring of analytical system condition must be done at the site. This issue will also be discussed further in a later section.

4.0 ASAP THEORY OF OPERATION

4.1 ASAP Overview

As described above, the ASAP was originally designed to support *in situ* experiments in remediation techniques such as enhanced bioremediation and pulsed pump-and-treat operations. It utilizes multiport selector valves and switching valves to manage high-precision water sample acquisition, VOC stripping, volatiles trapping, and injection into the GC. A sketch identifying the main components of the original ASAP (hereafter, ASAP1) is shown in Figure 4-1. The basic ASAP is comprised of separate modules that manage each part of the process: a sampling manifold that selects from one of the incoming sample lines (Figure 4-1, item 14), a liquid processing module that includes sample loops of several fixed volumes mounted on the Loop Selection Valve (item 11), the sample stripping cell (item 7), and peristaltic pumps that move the sample and standard streams (item 9), and finally a gas trapping module (item 6), that contains the embedded processor that operates the ASAP, gas switching valves (item 4), and the trap and its associated heaters, temperature sensors and controllers (item 3). Our units each have these three units in common, with a fourth in each that offers a specific optional capability. In ASAP1 the fourth module supported a manifold of twelve standard 40 ml VOA vials that could be flushed with sample waters prior to on-line analysis (item 13). In the second-generation ASAP (hereafter, ASAP2), this module was replaced by a unit supporting an additional six-port switching valve and a loop to deliver a fixed volume of internal standard and surrogate compound mixture for enhanced sample-by-sample quality control (Figure 4-10, item 15). The following description of ASAP operation will reference ASAP1, although nearly all the steps are common to both units.

4.2 Sample acquisition

Sample lines are attached to the ASAP sampling manifold primary sample selection valve (Figure 4-1, item 15, and Figure 4-2, item 1). At the point when a sample is taken for analysis, the primary sample selection valve is moved to select from one of the twelve incoming streams. A sample pump and solenoid are actuated, to flush a VOA vial on the off-line sampling rack, through the secondary sample valve (Figure 4-2, item 2). Flushing produces a headspace-free sample

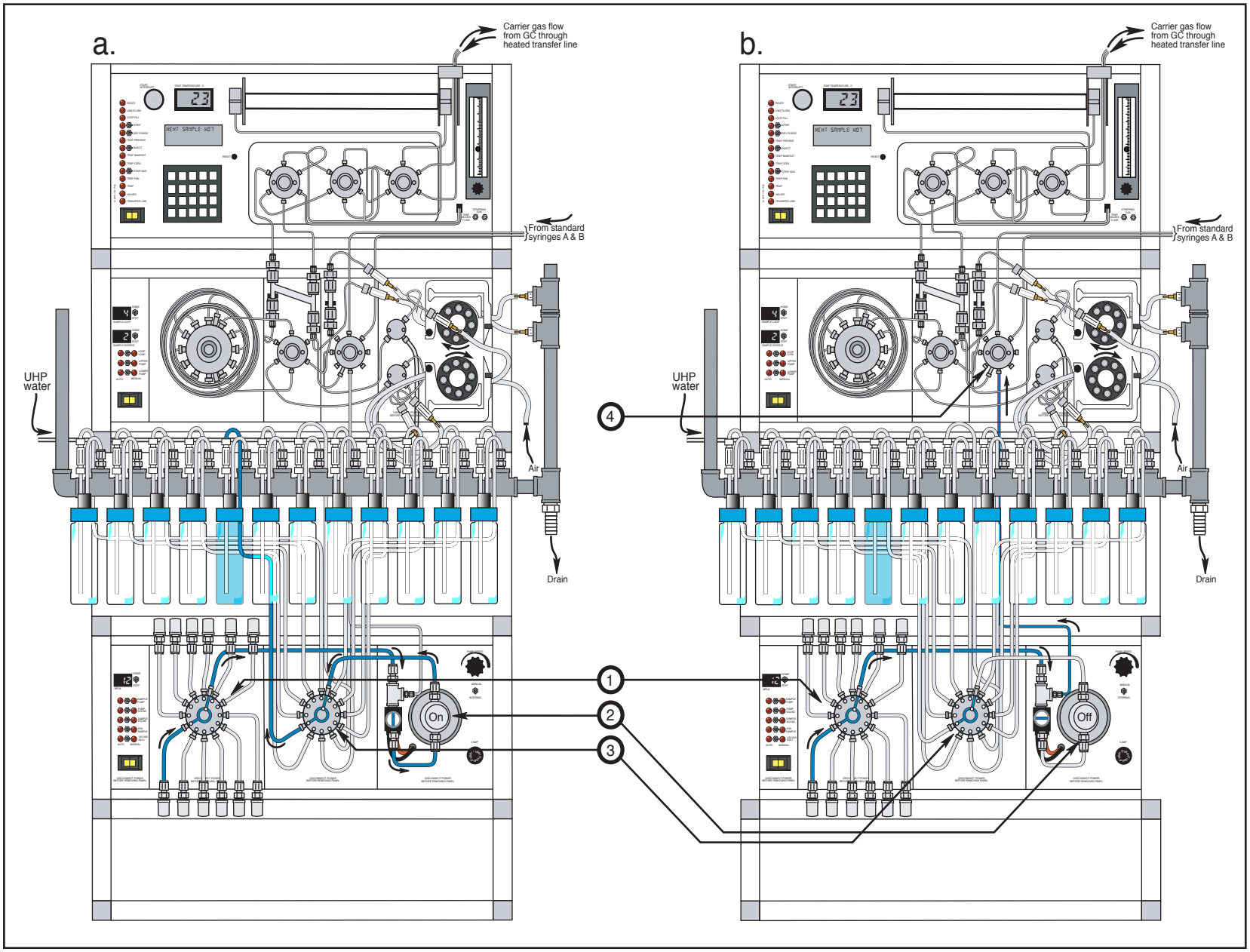

Figure 4-2. Liquid flow of the ASAP1 during sample acquisition: a) primary and secondary sample valves (items 1 and 3) set to sample from port five (lower left), sample pump and solenoid (item 2) on, and open, respectively, to flush VOA off-line analysis vial; b) VOA vial flush ended, flow diverted to source selection valve (item 4). Sample pump is off, and sample solenoid is closed. Blue lines indicate liquid flow paths.

that can be collected for tracer or other analysis. Flushing times (and numerous other parameters pertaining to each sample's source and processing) are executed by the ASAP embedded controller, and are operator programmable with a Visual Basic terminal program supplied by A+RT ("ASAP-QED"). At the OU 2 installation VOA flushing time was generally 20 minutes, to assure static water was purged from sample lines. A similar, single station for collecting an off-line sample is included in ASAP2 (Figure 4-10, item19).

4.3 Sample processing

Following the VOA vial flush, the sample pump solenoid closes, and the sample flows up through 1/16 in (0.159 cm) tubing to the Liquid Processing Module. Figure 4-3 shows the "idle" state of the ASAP after a sample source has been selected. Following a flushing interval, the sample flow is switched by the liquid process valve to flush one of the sample loops (0.17, 0.31, 0.50, 1.0, 2.29, 4.81 and 9.93 ml, respectively for sample loops one through seven, Figure 4-4). Note the small flow cell just to the right of the stripping cell in Figure 4-4. This glass cell and the stripping cell are equipped with optical sensors that detect bubble flow through the tubing. Tracing the flow of either sample (wihout bubbles) or the generated bubble stream, you will note during loop filling bubbles are found in the water flowing through this flow cell, at least until all are displaced from the sample loop by incoming sample. The ASAP controller software monitors this cell to determine the point at which the loop is filled and ready for stripping by detecting the lack of bubbles in this cell.

At this point the sample has filled the loop, and is ready for stripping. The liquid procdess valve switches the direction of flow through the loop, and the sample is pushed back through the liquid process valve by the bubble stream (Figure 4-5). The bubbles ensure that droplets do not adhere to tubing walls. At the same time, the leftmost of the three gas switching valves in the Gas Trapping Module switches, allowing purge gas to flow in the "forward" trapping direction through the trap. VOCs are swept from the sample to the trap by a counter-current flow of helium, as the sample flows through the thin-film stripping cell. The trap is a commercially packed three-component sorbent bed in a 1/8 in (0.32 cm) x 30 cm tube. Two traps were evaluated, a BTEX® trap (Supelco, Inc.), and a Carbopack™-B and Carbosieve™ S-III, Style "8" for Model 2000 purge-and-trap from Tekmar-Dohrmann, Inc. The results of this test will be discussed in a later section.

After the sample has entirely passed through the stripping cell, as determined by the re-appearance of bubble flow in the stripping cell photosensor, the peristaltic pumps are stopped, allowing water to drain from the stripping cell, and the helium purge gas to sweep residual volatiles from the valves and tubing, into the trap (Figure 4-6).

At this point there is an optional, variable dry-purge cycle, during which gas switching valve 2 diverts dry helium through the trap in the direction of sample application (Figure 4-7) to remove residual moisture. This is generally required for GC/MS, which does not tolerate moisture well. In our testing, we found that if dry purging was used, recovery of highly volatile components in standards (e.g.:

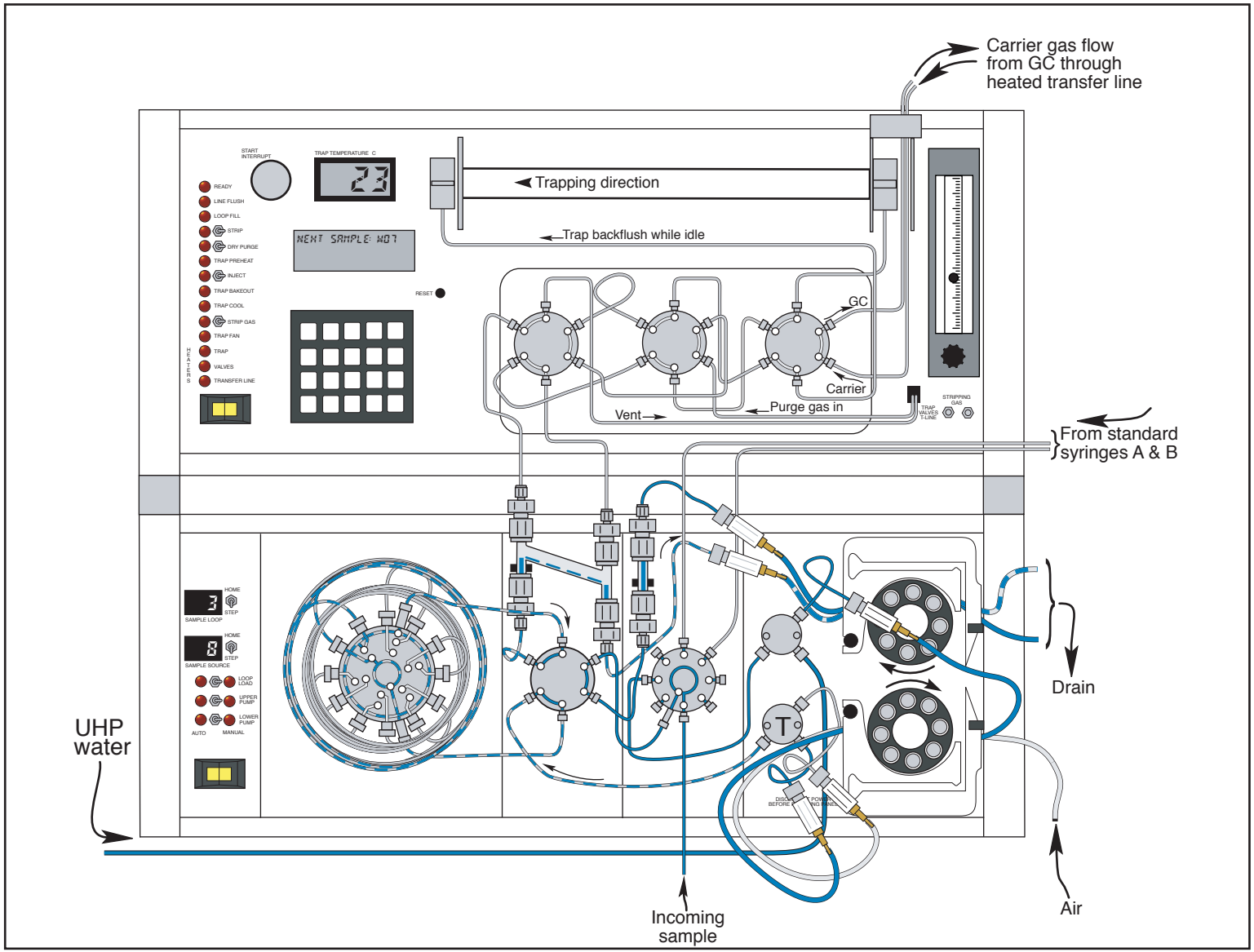

Figure 4-3. Liquid and gas flows of the ASAP1 during sample acquisition and and VOC stripping: idling state between samples. Lower 'T' to left of peristaltics generates bubble stream that sweeps valves and loops. Gas switching valves are set to backflush trap, purge stripping cell.

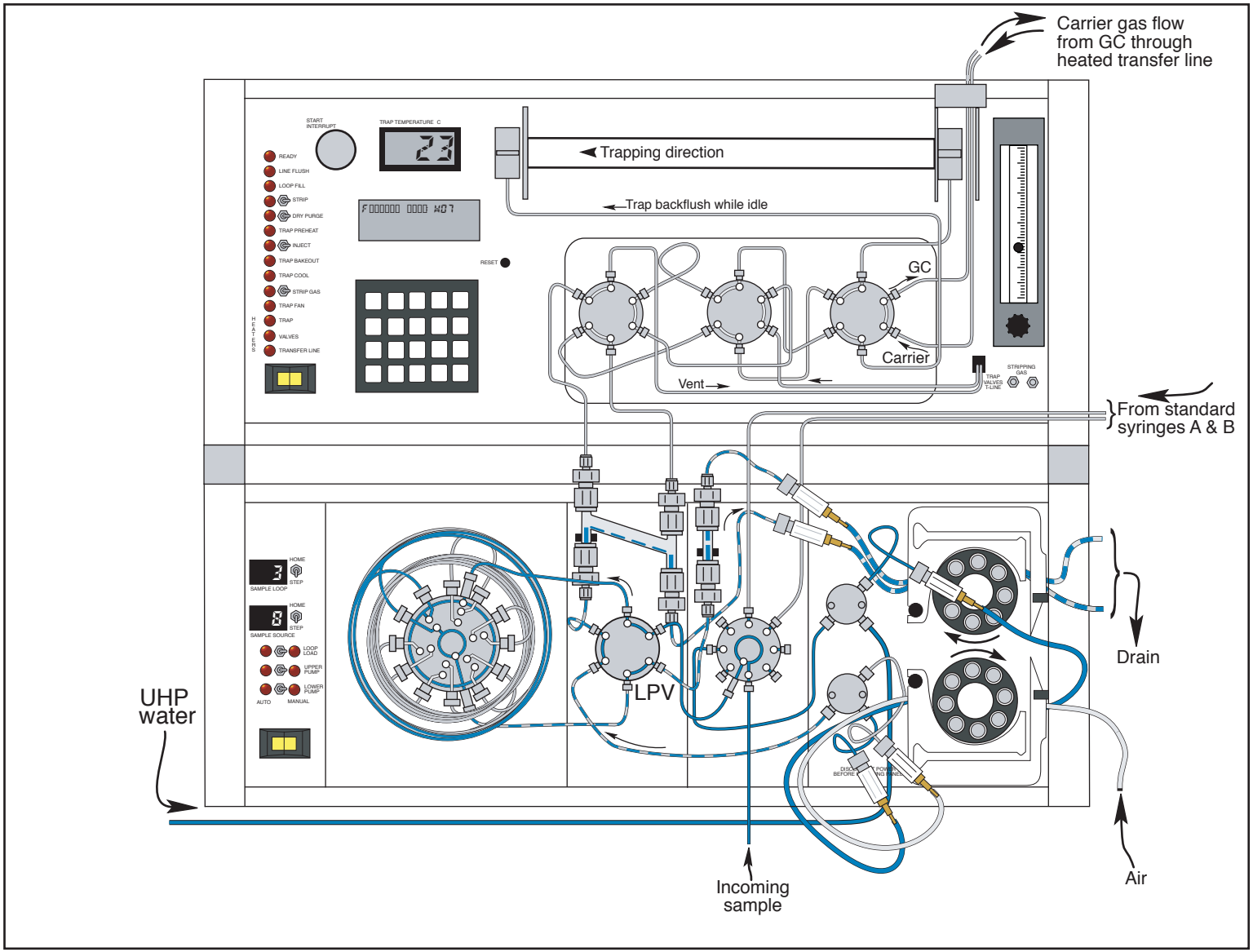

Figure 4-4. Liquid and gas flows of the ASAP1 during sample acquisition and and VOC stripping: loop filling – liquid process valve (LPV) switches to flush loop with next sample. Gas valves unchanged, backflushing trap, purging stripping cell.

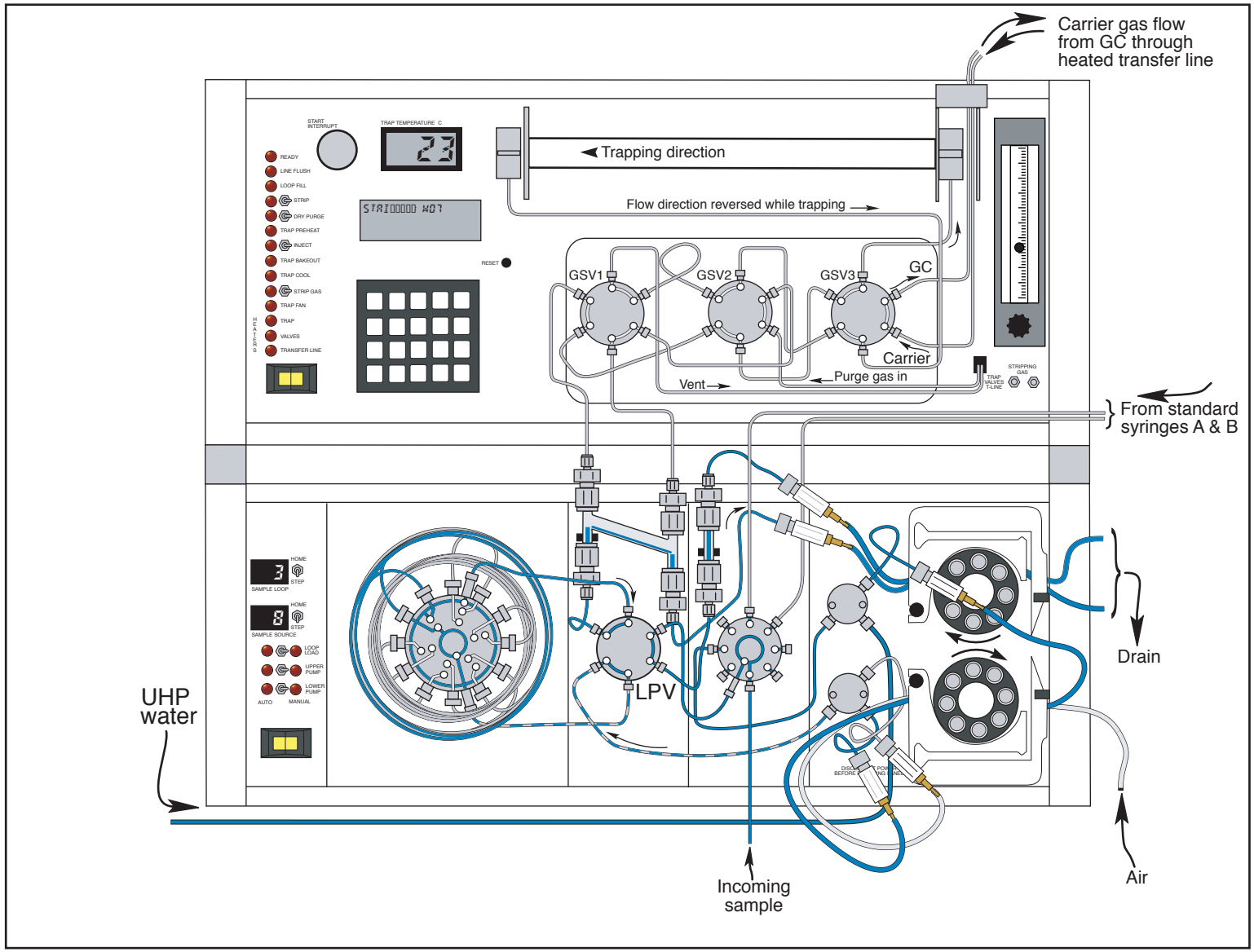

Figure 4-5. Liquid and gas flows of the ASAP1 during sample acquisition and and VOC stripping: sample stripping – liquid process valve (LPV) switches to start pushing loop contents through stripping cell with bubble stream. Gas switching valve 1 (GSV1) switches to reverse purge gas flow direction through trap, transfering VOCs onto trap.

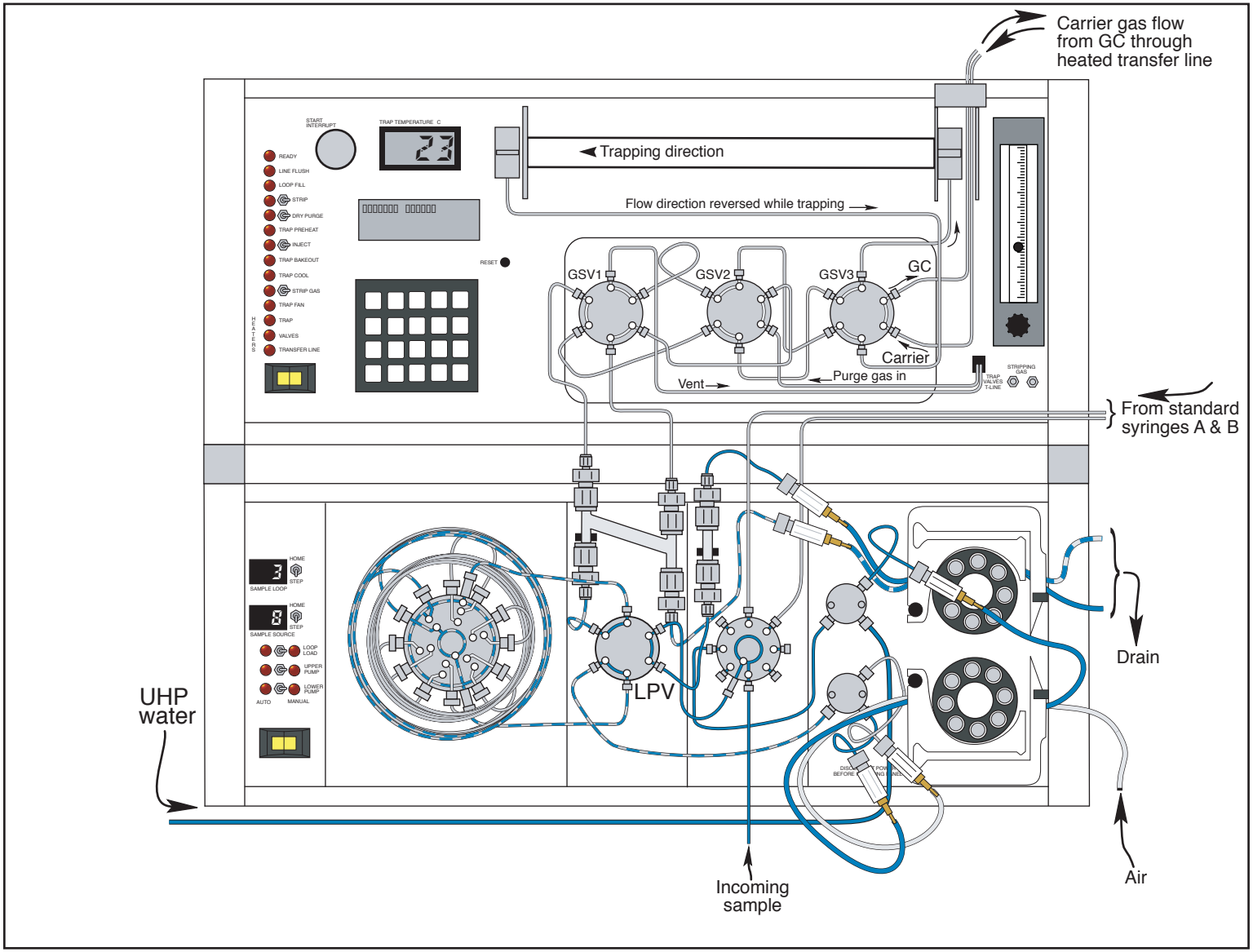

Figure 4-6. Liquid and gas flows of the ASAP1 during sample acquisition and and VOC stripping: valve purging – bubble flow has displaced sample from loop through stripping cell, peristaltic pumps stop allowing stripping cell to drain. Purge gas flushes emaining VOCs through valves onto trap.

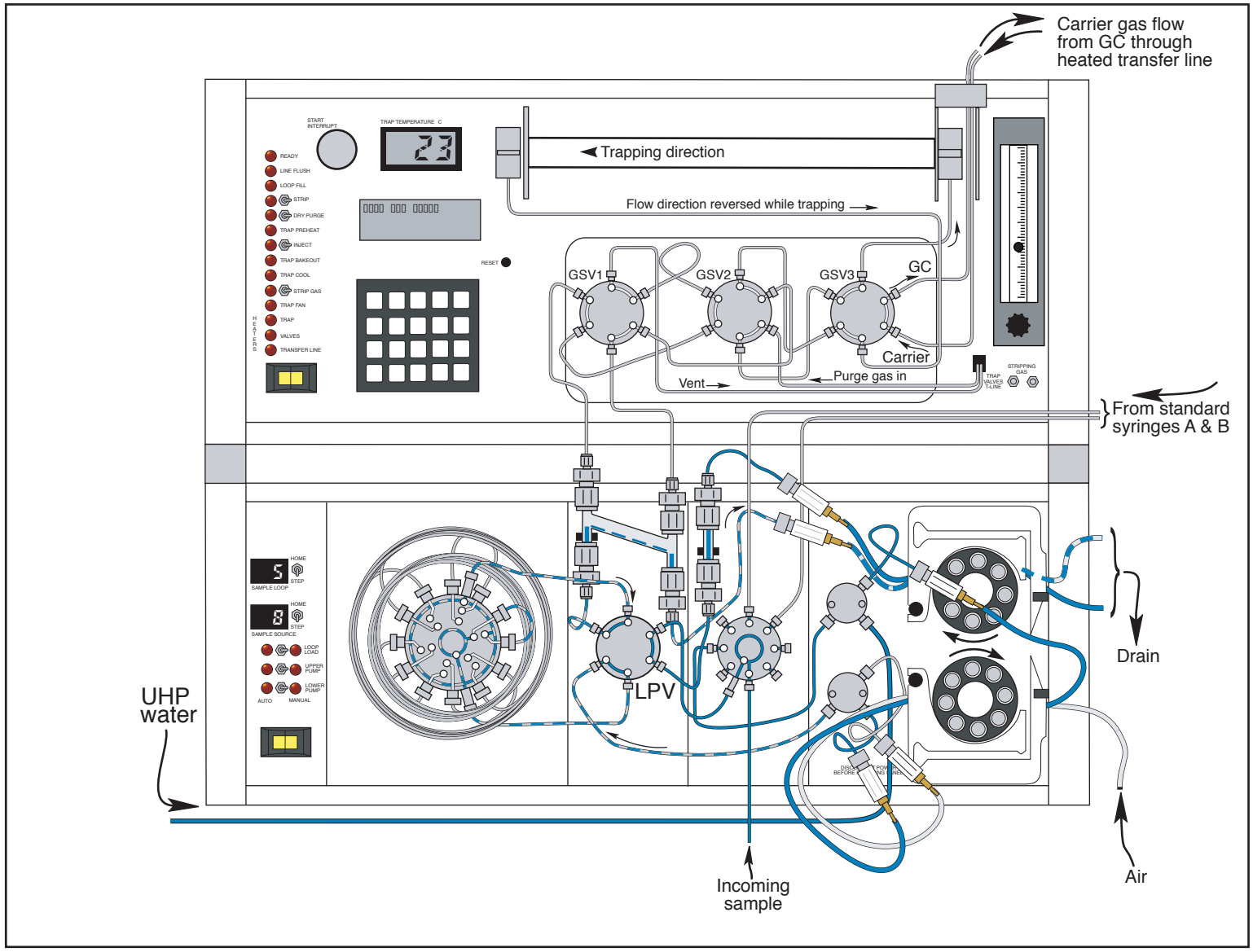

Figure 4-7. Liquid and gas flows of the ASAP1 during sample acquisition and and VOC stripping: trap 'dry' purge – gas switching valve 2 actuates, diverting dry purge gas through trap to remove residual moisture (primarily used with GC/MS applications). Peristaltic pumps restart to start flushing all sample loops with bubble streams; an 0.16 ml sample loop is shown being rinsed.

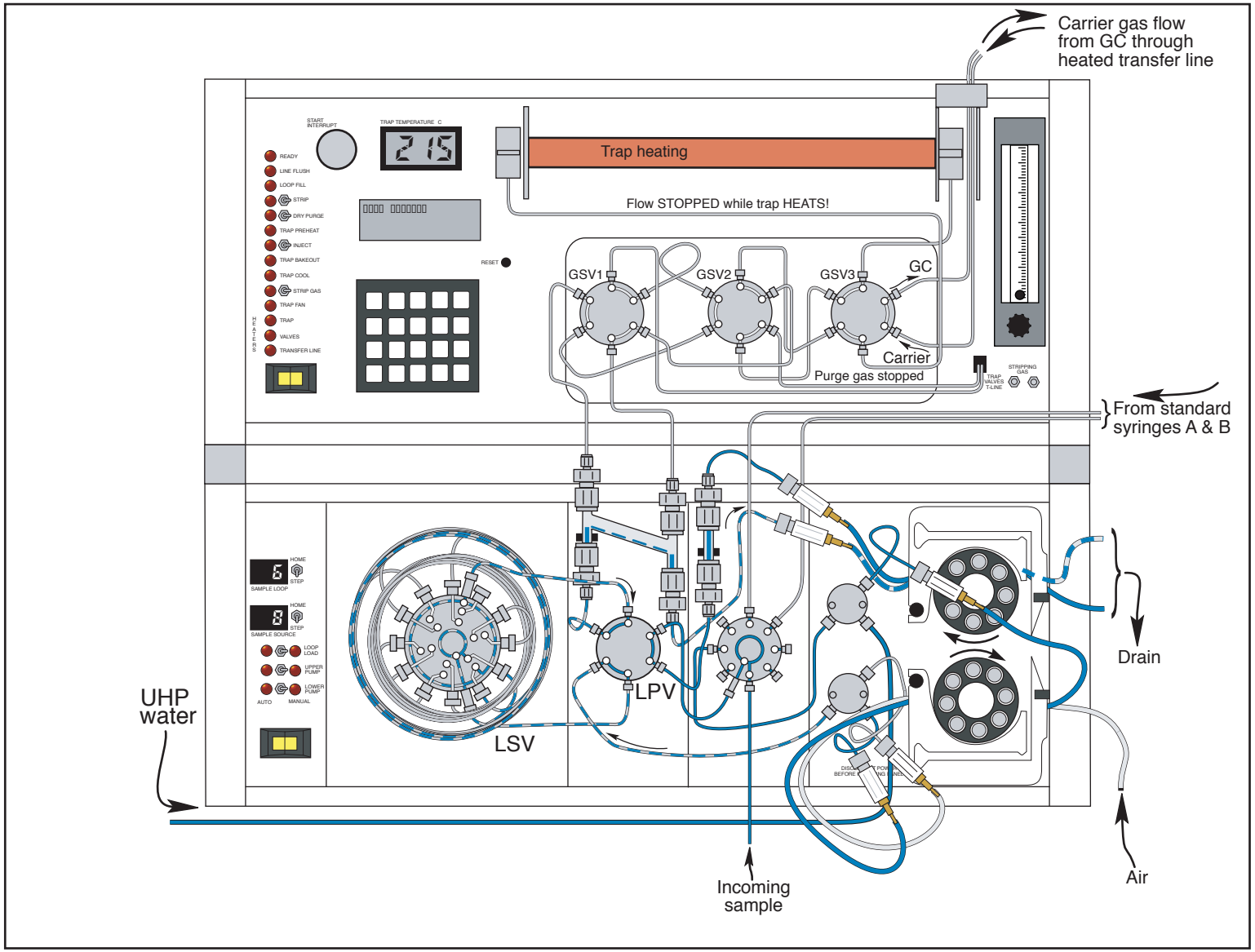

Figure 4-8. Liquid and gas flows of the ASAP1 during sample acquisition and and VOC stripping: trap heating – purge gas solenoid (inside chassis, not shown) closes to stop purge gas flow, isolating trap as it rapidly heats to 215 C, and is allowed to briefly stabilize. Peristaltic pumps continue flushing all sample loops with bubble streams; note that the loop selection valve (LSV) has advanced to the next loop to rinse.

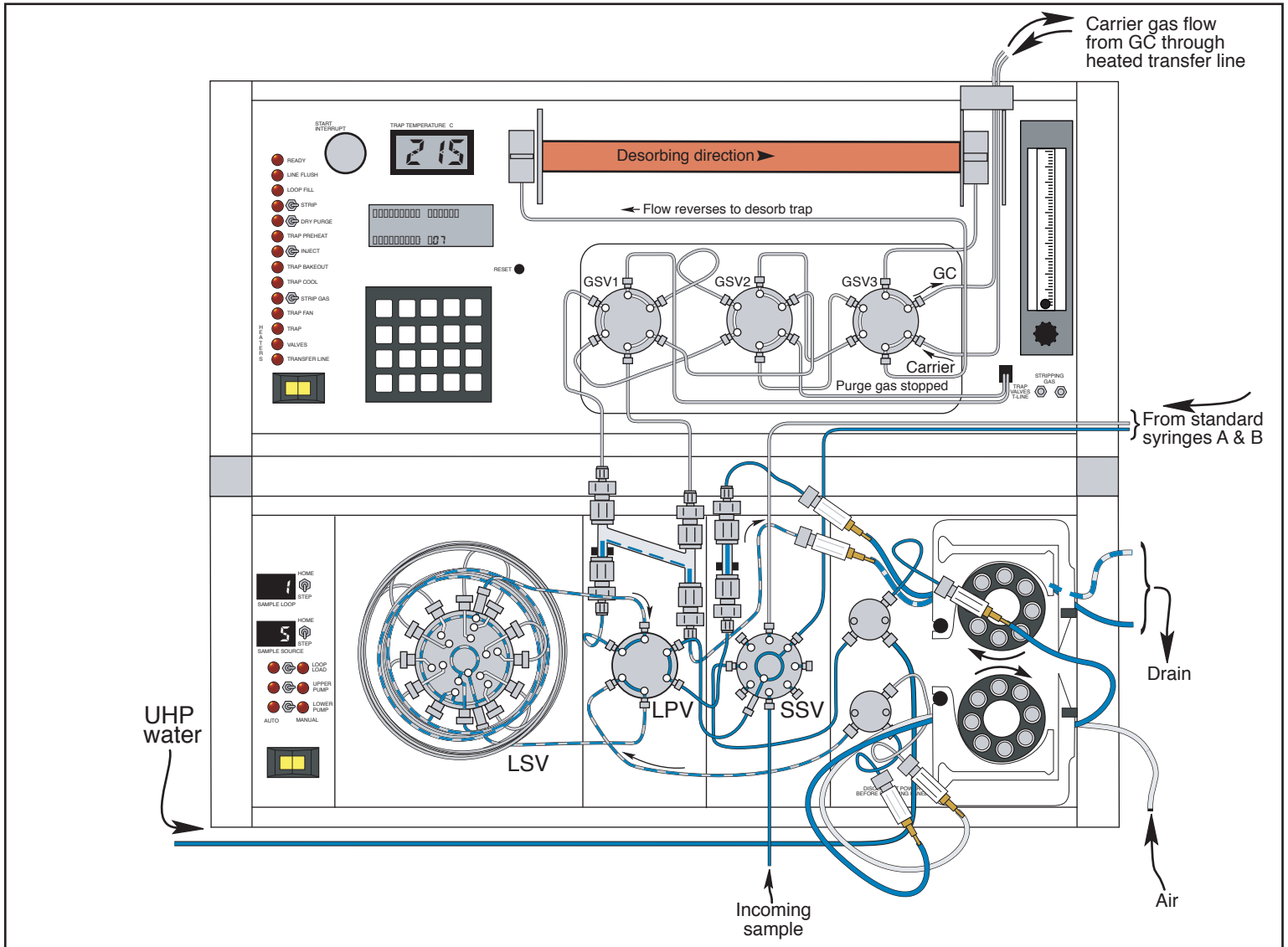

Figure 4-9. Liquid and gas flows of the ASAP1 during sample acquisition and and VOC stripping: trap desorb for GC injection – gas switching valve 3 (GSV3) actuates to place trap in series with carrier flow, and inject trapped compounds onto the GC column. Peristaltic pumps continue flushing all sample loops with bubble streams; note that the source selection valve (LSV) has advanced to sample a standard syringe.

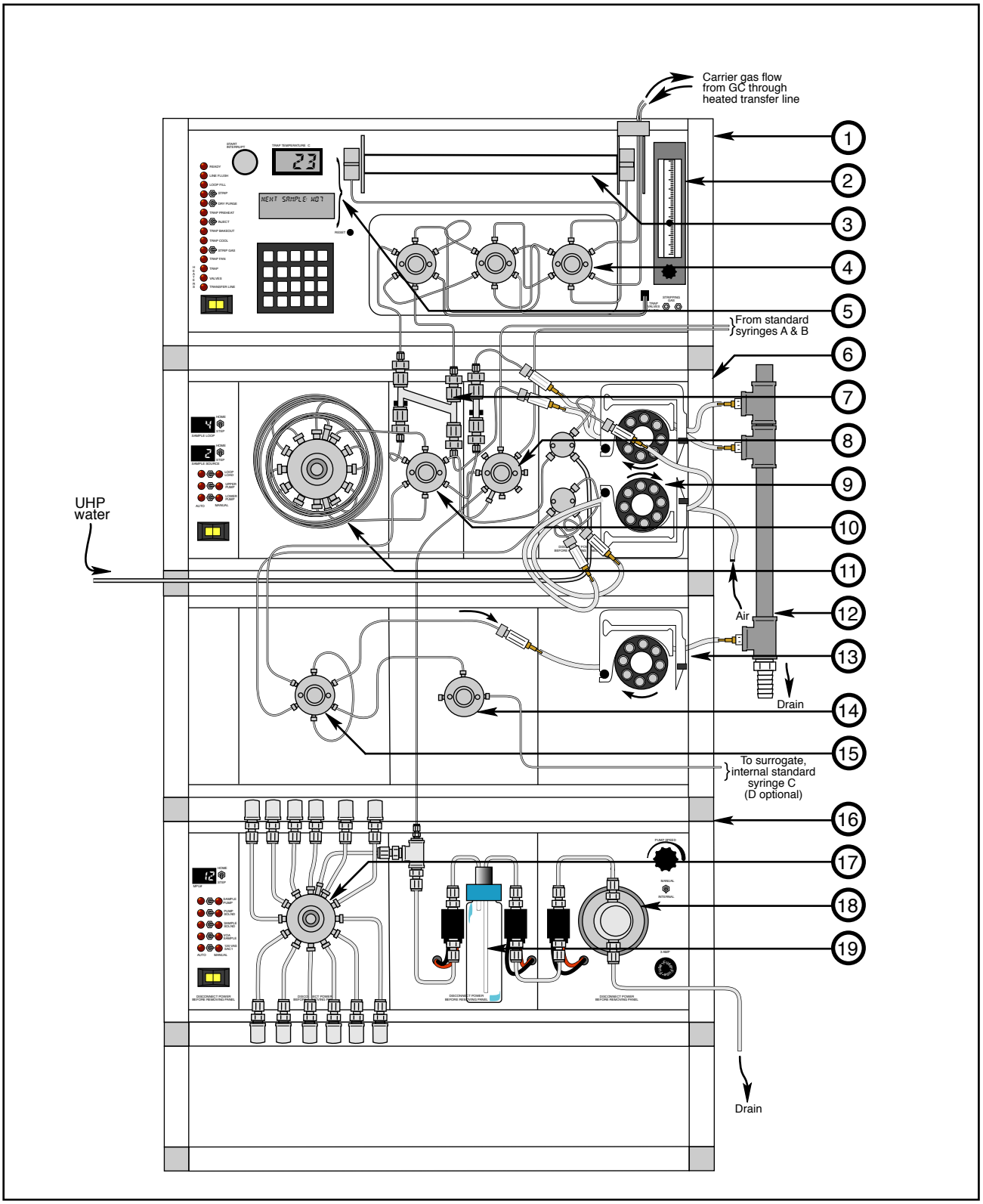

Figure 4-10. Components of the Automated Sampling and Analysis platform (ASAP, A+RT, Milpitas, CA) equipped with additional switching valve and loop for internal standard, surrogate injection: 1) gas trapping module, 2) purge gas rotameter, 3) trap, 4) flow switching valves, 5) trap temperature and process stage LCDs, 6) liquid processing module, 7) flow-through stripping cell, 8) source selction valve, 9) drain (upper) and blank rinse supply (lower) peristaltic pumps, 10) liquid process valve, 11) sample loops and loop selection valve, 12) drain standpipes, 13) internal standard/surrogate peristaltic pump, 14) selection two-way valve, 15) fixed loop injection valve, 16) sampling manifold, 17) primary sample selection valve, 18) sample pump and solenoid, 19) off-line analysis VOA vial and isolating solenoid valves.

choromethane and vinyl choride) was reduced by as much as 40%, without any apparent benefit with our configurations of columns and detectors; consequently dry purging was disabled.

Following the dry purge (if used) the trap is isolated from purge gas flow by the closure of a solenoid on the purge gas line (within the Gas Trapping Module, hidden in Figure 4-8), and heated to the desorbtion temperature of 215 C. The trap is allowed to stabilize for about 10 seconds, then gas switching valve 3 switches carrier flow from the GC in line with the trap, in the desorbtion direction, to flush VOCs from the trap to the gas chromatograph for compound separation and detection (Figure 4-9). At this point the ASAP switches a digital line to the "on" (+5V) state, providing a signal to the GC that the sample has been injected.

5.0 GC OPERATION AND DATA MANAGEMENT

5.1 GC Overview

In both the OU 2 and OU 1 installations a capillary gas chromatograph (8610C GC, SRI Instruments, Torrance, CA) was used. It was outfitted with a combination photoionization/dry elecrtrolytic conductivity detector (PID/DELCD, SRI). During testing, three columns designed for use with EPA volatiles methods were evaluated for separation of commercially available standards and site samples. The columns were a DB-624, 40 m x 0.32 mm ID, 1.8 µm film (J&W Scientific, Inc.); a combination of 20 m of the DB-624 in series with 20 m of DB-VRX (0.32 mm ID, 1.8 µm film, J&W Scientific), and finally an RTX-502.2 capillary column (60 m x 0.32 mm ID, 1.8µm thick film; Restek©, Bellefonte, PA). The combination DB-624/DB-VRX column was evaluated to determine whether 1,2-dichloroethane and benzene (that co-elute from many single columns) could be separated (Rood, 1999). A typical chromatogram from the ASAP/OLAS system using this combination column is shown in Figure 5-1; analyses took 30 minutes following injections. Compound identification was achieved by comparison of chromatograms with vendor-supplied plots, and injection of single compounds, as necessary.

Commercial vendors have started to produce prepackaged standard blends that cover many routine analyses. These have the great benefit of savings of labor, and traceability to NIST standards. We soon realized that the initial strategy of developing a simplified, custom analytical method for the needs of single sites would leave the system vulnerable to mis-identifying compounds, or missing minor components. We elected to examine standard methods supported by capillary GC and PID/DELCD detection, to move the methods supported by the ASAP/OLAS into a closer match with standard laboratory procedures. Target compounds for five relevant EPA methods are given in Table 5-1. The EPA 8021B has the best coverage of compounds with respect to the known compounds of concern at Fort Ord, and is as PID/ELCD, capillary column GC procedure. It does not have quite the extensive compound coverage of the GC/MS methods, such as the EPA 8260B, but appears to be the most useful approach.

Table 5-1. Compound coverage by different EPA methods for volatile organic compounds in groundwater and wastewater. Compounds in bold are identified as "compounds of concern" in OU 1 and/or OU 2 Records of Decision.

Compound	Common Abbrev.	8260B	601	602	624	8021B
acetone	ACE	√				
acrolein	-	√				
acrylonitrile	-	√				
allyl alcohol	-	√				
allyl chloride	-	√				√
benzene	**BEN**	√		√	√	√
benzyl chloride	-	√				
bis(2-chloroisopropyl) ether	-					√
bromobenzene	BEN-Br	√				√
bromochloromethane	CH2ClBr	√				
bromodichloromethane	CHCl2Br	√	√			√
bromoform	CHBr3	√	√		√	√
bromomethane	CH3Br	√	√		√	√
n-butanol	-	√				
t-butanol	-	√				
2-butanone	**MIBK**	√				
n-butyl benzene	n-ButBEN	√				√
t-butyl benzene	t-ButBEN	√				√
s-butyl benzene	s-ButBEN	√				√
carbon disulfide	CS2	√				
carbon tetrachloride	**CCl4**	√	√		√	√
chloral hydrate	-	√				
chloroacetonitrile	-	√				
chlorobenzene	BENCl	√	√	√	√	√
1-chlorobutane	-	√				
chloroethane	C2H5Cl	√	√		√	√
2-chloroethanol	-	√				√
2-chloroethylvinyl ether	2-CEVE	√			√	
chloroform	**CHCl3**	√	√		√	√
1-chlorohexane	-	√				
chloromethane	CH3Cl	√	√		√	√
chloromethyl methyl ether	-					√
chloropropene	-	√				√
3-chloroprorionitrile	-	√				
2-chlorotoluene	-	√				√
4-chlorotoluene	4-ClTOL	√				√
crotonaldehyde	-	√				
dibromochloromethane	CHClBr2	√	√		√	√
1,2-dibromo-3-chloropropane	1,2-DB-3CPA	√				√
dichlorodifluoromethane	CCl2F2	√	√		√	√
1,3-dichloro-2-propanol	-	√				
1,1-dichloropropanone-2	-	√				
1,2-dibromoethane	1,2-DBA	√				√
dibromomethane	CH2Br2	√				√
1,2-dichlorobenzene	1,2-DCB	√	√	√	√	√
1,3-dichlorobenzene	1,3-DCB	√	√	√	√	√
1,4-dichlorobenzene	1,4-DCB	√	√	√	√	√
c-1,4-dichloro-2-butene	-	√				
t-1,4-dichloro-2-butene	-	√				
1,1-dichloroethane	**1,1-DCA**	√	√		√	√
1,2-dichloroethane	**1,2-DCA**	√	√		√	√
1,1-dichloroethene	**1,1-DCE**	√	√		√	√
c-1,2-dichloroethene	**c-1,2-DCE**	√				√
t-1,2-dichloroethene	**t-1,2-DCE**	√	√		√	√
1,2-dichloropropane	1,2-DCPA	√	√		√	√
1,3-dichloropropane	1,3-DCPA	√				√
2,2-dichloropropane	2,2-DCPA	√				√
1,3-dichloropropanol	-					√
1,1-dichloropropene	1,1-DCPE	√				√
1,1-dichloropropanone	-	√				
c-1,3-dichloropropene	c-1,3-DCPE	√	√		√	√
t-1,3-dichloropropene	t-1,3-DCPE	√	√		√	√

Compound	Common Abbrev.	8260B	601	602	624	8021B
1,2,3,4-diepoxybutane	-	√				
diethyl ether	-	√				
1,4-dioxane	-	√				
epichlorhydrin	-	√				
ethanol	EtOH	√				
ethyl acetate	EtOAc	√				
ethylbenzene	Eth-BEN	√		√	√	√
ethylene oxide	-	√				
ethyl methacrylate	-	√				
hexachlorobutadiene	-	√				√
hexachloroethane	-	√				
2-hexanone	2-HEX	√				
2-hydroxyproprionitrile	?	√				
isobutyl alcohol	?	√				
isopropylbenzene	IPA-BEN	√				√
p-isopropyltoluene	p-IPA-TOL	√				√
malononitrile	-	√				
methacrylonitrile	-	√				
methanol	MeOH	√				
methylacrylate	-	√				
methylene chloride	**CH2Cl2**	√	√		√	√
methyl iodide	CH3I	√				
methyl methacrylate	-	√				
4-methyl-2-pentanone	-	√				
methyl-t-butyl ether	MTBE	√		√		
naphthalene	NAPH	√				√
nitrobenzene	-	√				
2-nitropropane	-	√				
N-nitroso-di-n-butylamine	-	√				
pentachloroethane	PCA	√				
pentafluorobenzene	-	√				
2-pentanone	-	√				
2-picoline	-	√				
1-propanol	-	√				
2-propanol	-	√				
propargyl alcohol	-	√				
proprionitrile	-	√				
n-propylamine	-	√				
n-propylbenzene	-	√				√
pyridine	PYR	√				
styrene	STY	√				√
1,1,1,2-tetrachloroethane	1,1,1,2-TCA	√				√
1,1,2,2-tetrachloroethane	1,1,2,2-TCA	√	√		√	√
tetrachloroethene	PCE	√	√		√	√
tetrahydrofuran	TFA	√				
toluene	TOL	√		√	√	√
o-toluidine	-	√				
1,2,3-trichlorobenzene	1,2,3-TCB	√				√
1,2,4-trichlorobenzene	1,2,4-TCB	√				√
1,1,1-trichloroethane	**1,1,1-TCA**	√	√		√	√
1,1,2-trichloroethane	1,1,2-TCA	√	√		√	√
trichloroethene	**TCE**	√	√		√	√
trichlorofluoromethane	CClF3	√	√		√	√
1,2,3-trichloropropane	TCPA	√				√
1,2,4-trimethylbenzene	1,2,4-TM-BEN	√				√
1,3,5-trimethylbenzene	1,3,5-TM-BEN	√				√
vinyl acetate	-	√				
vinyl chloride	**VC**	√	√		√	√
o-xylene	o-XYL	√		√		√
m-xylene	m-XYL	√		√		√
p-xylene	p-XYL	√		√		√

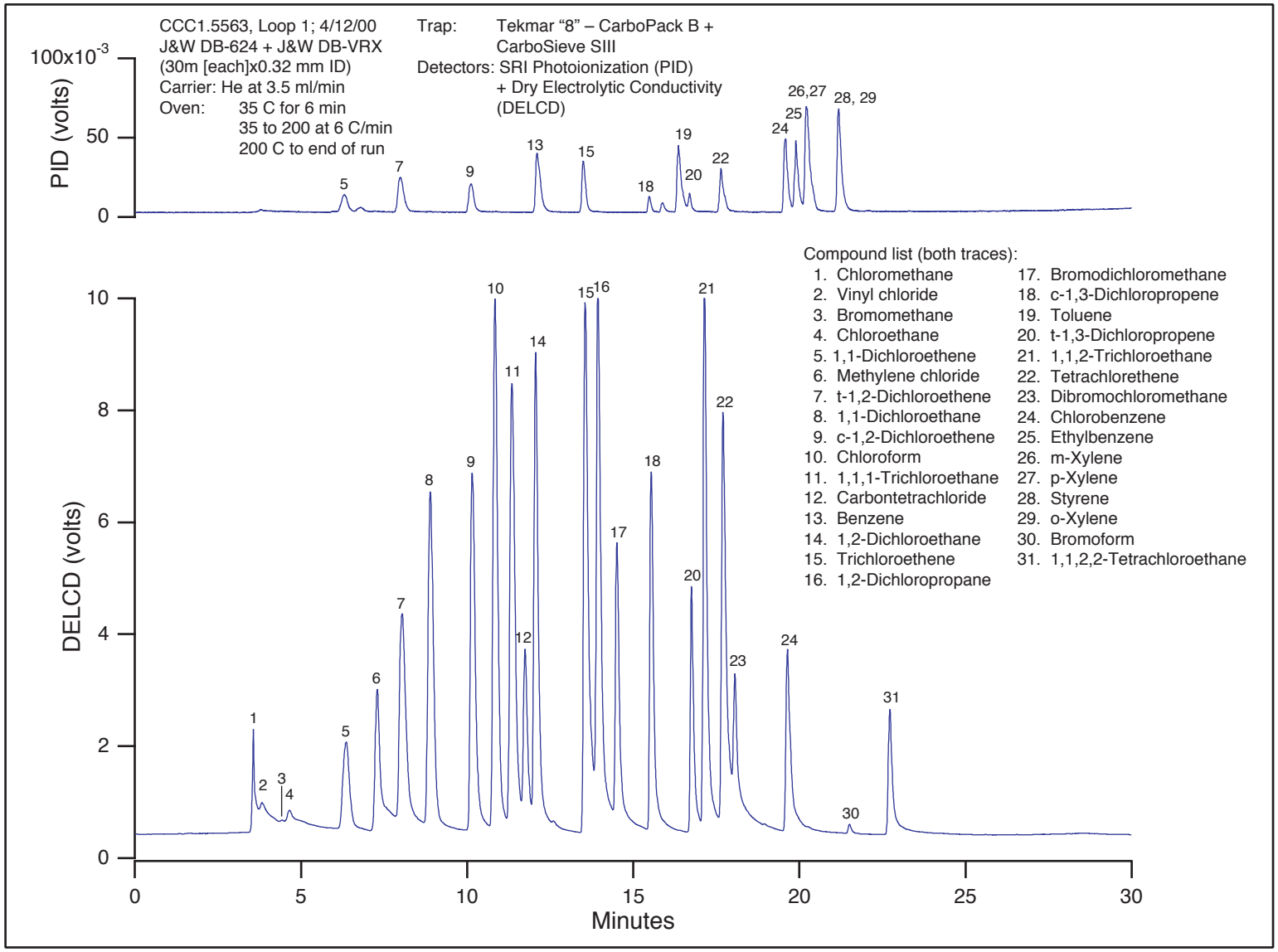

Figure 5-1. Typical ASAP/OLAS chromatogram of Contract Laboratory Program Volatiles Target Compound mixture (CLP-150, Ultra Scientific).

We then evaluated different standard blends that were becoming available. At the start of this phase of the project the Contract Laboratory Program Volatiles Target Compound mixture (CLP-150, Ultra Scientific, Inc., Kingstown, RI) was selected for routine use for its coverage of OU 2 and OU 1 compounds of concern and low cost. Blends for the complete suite of EPA 8021B compounds have become available (e.g.: DWM-580, Ultra Scientific, Inc. Table 5-2), but do not include compounds known to occur at Fort Ord, and are substantially more expensive for routine use. We have procured a limited amount of these latter comprehensive standards for limited study at a later date.

5.2 Instrument Control and Data Archiving

Control of the GC column pressure and oven temperature, and acquisition of detector signals was performed with a custom application developed in LabVIEW (LabVIEW version 6.0.2, National Instrument, Austin, TX). Raw detector signals were saved on disk as binary files in the native format of the Igor plotting software package (version 4.0.2, Wavemetrics, Lake Oswego, OR) for display and reporting. Software was run on a rack mounted Apple PowerMac 9600 equipped with a PC emulation board (OrangeMicro, Anaheim, CA); the latter was used for collection of flow sensor datalogger files, and for low-level programming of the ASAP embedded controller. A multifunction data acquisition board (PCI-MIO-16X50, National Instruments) acquired detector signals, provided digital I/O for handshaking with the ASAP, and analog outputs for control of the GC oven and column head pressures. The user front panels for the LabVIEW GC control and sample sequencing software are shown in Figure 5-2, and the graphical code for the GC control portion is shown in Figure 5-3. All LabVIEW programs use this front-panel/graphical code strategy to produce "Virtual Instruments" or VIs, that can control real-world hardware, or operate independently for computational applications; at present the ASAP/OLAS LabVIEW VIs take both approaches, as will be described below.

Calibration of the ASAP/GC was performed prior to each set of well samples by analyzing six samples from two custom gas-tight syringes mounted on the ASAP. The syringes were filled with ultra-high purity water from the carbon filtered, counter-current helium stripped UHP water subsystem that supplies rinse water to the ASAP (Figure 3-1, Item 4), and spiked with either 20 or 250 μL of a commercially prepared VOC standard (CLP-150, Ultra Scientific, Kingstown, RI).

5.3 LabVIEW Application for Chromatography Analysis

To facilitate rapid retrieval and examination of analytical data, a chronological filing system was incorporated into the LabVIEW software that controls the integrated ASAP/OLAS system . Raw chromatogram data is stored in the native binary format of the plotting package Igor Pro 4 (Wavemetrics, Inc., Lake Oswego, OR.) used to generate all figures in this report. From this file format, other file types can be generated quickly, and even very large data files are rapidly displayed.

Table 5-2. Compounds provided in representative commercial standard blends (Ultra Scientific, Inc.) used in this study. Compounds in bold are identified as "compounds of concern" in OU 1 and/or OU 2 Records of Decision.

Compound	Abbrev.	8021B	EPA-100	CLP-150	DWM-580
acetone	ACE			√	
allyl chloride	-	√			
benzene	**BEN**	√	√	√	√
bis(2-chloroisopropyl) ether	-	√			
bromobenzene	BEN-Br	√			√
bromodichloromethane	CHCl2Br	√		√	√
bromoform	CHBr3	√		√	√
bromomethane	CH3Br	√		√	√
2-butanone	**MIBK**			√	
n-butyl benzene	n-ButBEN	√			√
t-butyl benzene	t-ButBEN	√			√
s-butyl benzene	s-ButBEN	√			√
carbon disulfide	CS2			√	
carbon tetrachloride	**CCl4**	√	√	√	√
chlorobenzene	BENCl	√		√	√
chloroethane	C2H5Cl	√		√	√
2-chloroethanol	-	√			
chloroform	**CHCl3**	√		√	√
chloromethane	CH3Cl	√		√	√
chloromethyl methyl ether	-	√			
chloropropene	-	√			
2-chlorotoluene	-	√			√
4-chlorotoluene	4-ClTOL	√			√
dibromochloromethane	CHClBr2	√		√	√
1,2-dibromo-3-chloropropane	1,2-DB-3CPA	√			√
dichlorodifluoromethane	CCl2F2	√			
1,2-dibromoethane	1,2-DBA	√			√
dibromomethane	CH2Br2	√			√
1,2-dichlorobenzene	1,2-DCB	√			√
1,3-dichlorobenzene	1,3-DCB	√			√
1,4-dichlorobenzene	1,4-DCB	√	√		√
dichlorodifluoromethane	CCl2F2				√
1,1-dichloroethane	**1,1-DCA**	√		√	√
1,2-dichloroethane	**1,2-DCA**	√	√	√	√
1,1-dichloroethene	**1,1-DCE**	√	√	√	√
c-1,2-dichloroethene	**c-1,2-DCE**	√		√	√

Compound	Abbrev.	8021B	EPA-100	CLP-150	DWM-580
t-1,2-dichloroethene	**t-1,2-DCE**	√		√	√
1,2-dichloropropane	1,2-DCPA	√		√	√
1,3-dichloropropane	1,3-DCPA	√			√
2,2-dichloropropane	2,2-DCPA	√			√
1,3-dichloropropanol	-	√			
1,1-dichloropropene	1,1-DCPE	√			√
c-1,3-dichloropropene	c-1,3-DCPE	√		√	√
t-1,3-dichloropropene	t-1,3-DCPE	√		√	√
ethylbenzene	Eth-BEN	√		√	√
2-hexanone	-			√	
hexachlorobutadiene	-	√			√
isopropylbenzene	IPA-BEN	√			√
p-isopropyltoluene	p-IPA-TOL	√			√
methylene chloride	**CH2Cl2**	√		√	√
4-methyl-2-pentanone	-			√	
naphthalene	NAPH	√			√
n-propylbenzene	-	√			√
styrene	STY	√		√	√
1,1,1,2-tetrachloroethane	1,1,1,2-TCA	√			√
1,1,2,2-tetrachloroethane	1,1,2,2-TCA	√		√	√
tetrachloroethene	PCE	√		√	√
toluene	TOL	√		√	√
1,2,3-trichlorobenzene	1,2,3-TCB	√			√
1,2,4-trichlorobenzene	1,2,4-TCB	√			√
1,1,1-trichloroethane	**1,1,1-TCA**	√	√	√	√
1,1,2-trichloroethane	1,1,2-TCA	√		√	√
trichloroethene	**TCE**	√	√	√	√
trichlorofluoromethane	CClF3	√			√
1,2,3-trichloropropane	TCPA	√			√
1,2,4-trimethylbenzene	1,2,4-TM-BEN	√			√
1,3,5-trimethylbenzene	1,3,5-TM-BEN	√			√
vinyl chloride	**VC**	√	√	√	√
o-xylene	o-XYL	√		√	√
m-xylene	m-XYL	√		√	√
p-xylene	p-XYL	√		√	√

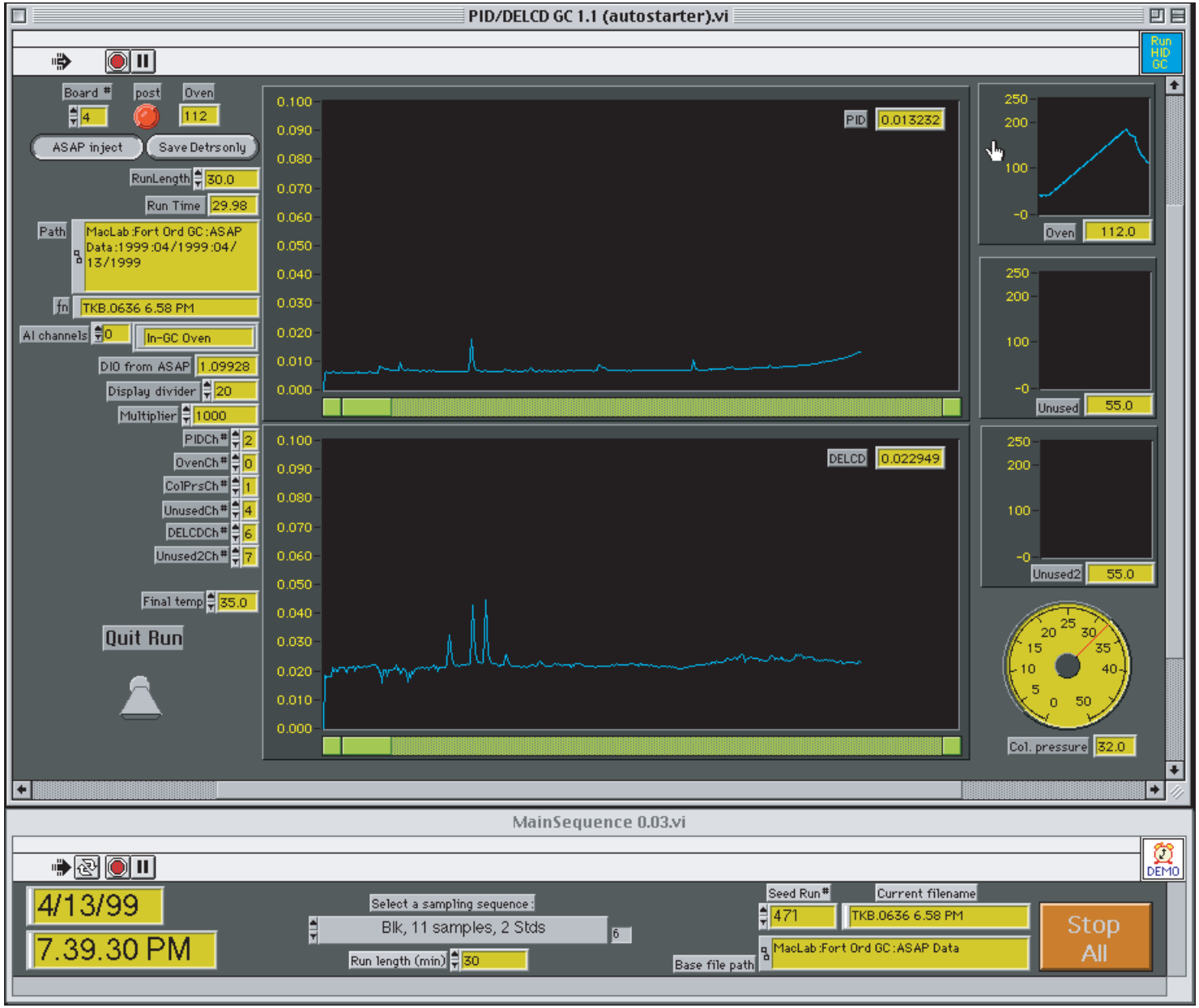

Figure 5-2. Main GC control user interface panels. Central plots show PID and DELCD plots from an effluent sample of OU 1-GTS GAC cannister TKB, with low levels of residual VOCs. Lower panel is "Main Sequence" module that specifies the sample order list, and calls the PID/DELCD control module shown in the upper window. Note plot panels at right that can display ancillary parameters such as column oven temperature, column pressures or other variables. Open nature of code and use of multifunction DAQ board interface permits additional environmental parameters to be logged.

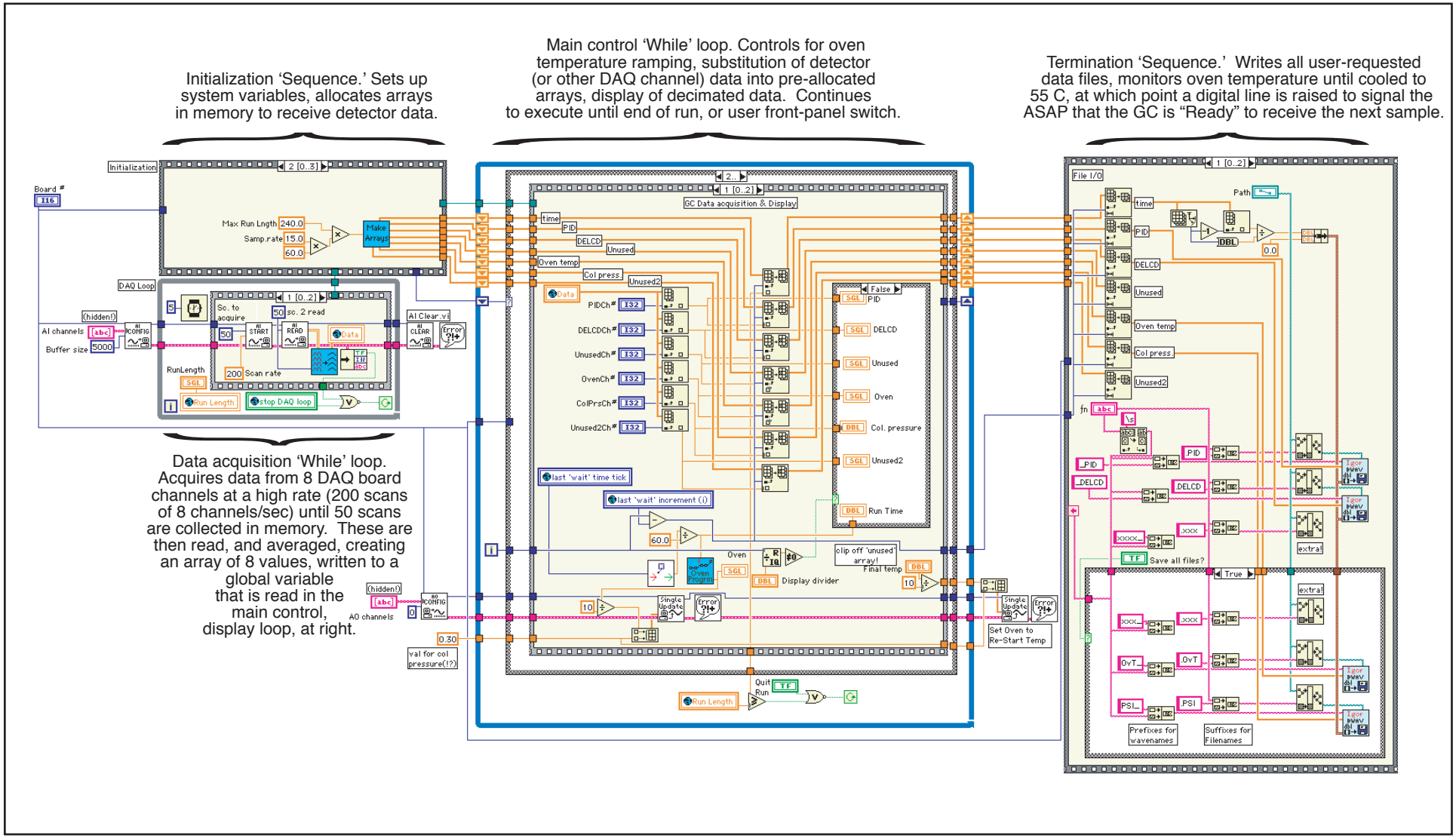

Figure 5-3. Example LabVIEW “Virtual Instrument” (VI) Diagram, showing code for “PID/DELCD GC.VI” (Figure 5-1). Icons are either built-in functions (arithmetic operators, file handling tools, etc.) or user-modifiable subroutines, referred to as “SubVIs,” that each have their own front panels and diagrams. Data pathways are indicated by lines of different colors or patters, e.g.: bold orange lines are floating point numerics, thin blue lines are integers, hatched purple lines are text, etc. The code is intrinsically parallel in operation (e.g.: the “Data acquisition ‘While’ loop” at lower left can freely run at a much higher rate than the “Main control ‘While’ loop,” without an explicit synchronization requirement), and hierarchical, in that a diagram can contain SubVIs that in turn contain one or many SubVIs. The LabVIEW programming environment gives the developer the ability to have an overall view of the program control and data flow on a single page, yet the flexibility to enter any level of lower detail from the same view.

Raw GC binary files are saved in an automatically generated, chronological directory structure. Sampling and sample processing took place in programmable sequences, with standards interleaved with samples. After a GC run, the LabVIEW data acquisition application checks the system clock, and then searches for a directory for the present year in an operator-supplied base directory; if a file for the year is not present (e.g.: C:HardDrive/ASAP files/2001), the subdirectory for the year is created. Similarly, if a subdirectory for the current month and day is not present, those directories are created, so that each day's data files are in a separate subdirectory, identified by date (e.g.: C:HardDrive/ASAP files/2001/ 10_2001/10_31_2001).

Individual raw data files were named to facilitate identification for later review. Following a source prefix is a serial number associated with the GC cumulative history, time of day at which the sample was processed, and detector type that generated the signal in the datafile. For example, a sample taken from MW-OU1-04-A at 3:38 PM, and analyzed with the DELCD detector would be named "W04.10483 3.38 PM.DELCD," and a chemical standard would be named "QCC1.10488 6.55 PM.DELCD," for a standard sample from Syringe B (QCC; low-level dilution of commercial standard blend), using ASAP sampling loop 1, sampled at 6:55 PM. This sample naming and directory storage scheme gives complete identification of individual sample sources, generation times and detector types for future analysis. Note that all OU 2 and OU 1 samples used the largest sample loop on the ASAP, for a uniform 9.9 ml sample size.

5.4 Quantitation and Reporting

Operation of the the integrated ASAP/OLAS system is divided into two general parts: 1) sample selection, processing and GC processing, and 2) peak detection and identification, quantitation, and reporting. At this time, the latter steps performed off-line with a LabVIEW application separate from the GC control and data acquisition application; these two modules will be integrated at a later date.

The "Chromatogram Analyzer.VI" LabVIEW application manages the process of compound identification, quantitation, and report generation (Figure 5.4). The operator starts the analysis process by generating a "standard record" file, with a module called the Edit Standard Configuration.VI (Figure 5-5). The editor produces a data structure with all pertinent information on the chromatography system and standard source in use on any given date, including column type and date of installation, expected analyte retention time, quantity of analyte in the commercially blended standard in use on that date, identified by vendor, catalog number and lot number, and calibration coefficients for each individual analyte's standard curve. For convenience, existing standard files can be easily modified by addition or deletion of compounds (Figure 5-6), so that lengthy compound lists for new blends do not necessarily have to be created from scratch. The editor writes the data structure to disk as a locked, binary file that can only be read and modified within the LabVIEW VI. At this time we have not incorporated permissions for creating or modifying these standard files, although this can be added if deemed necessary. We name these files by the date of calibration runs,

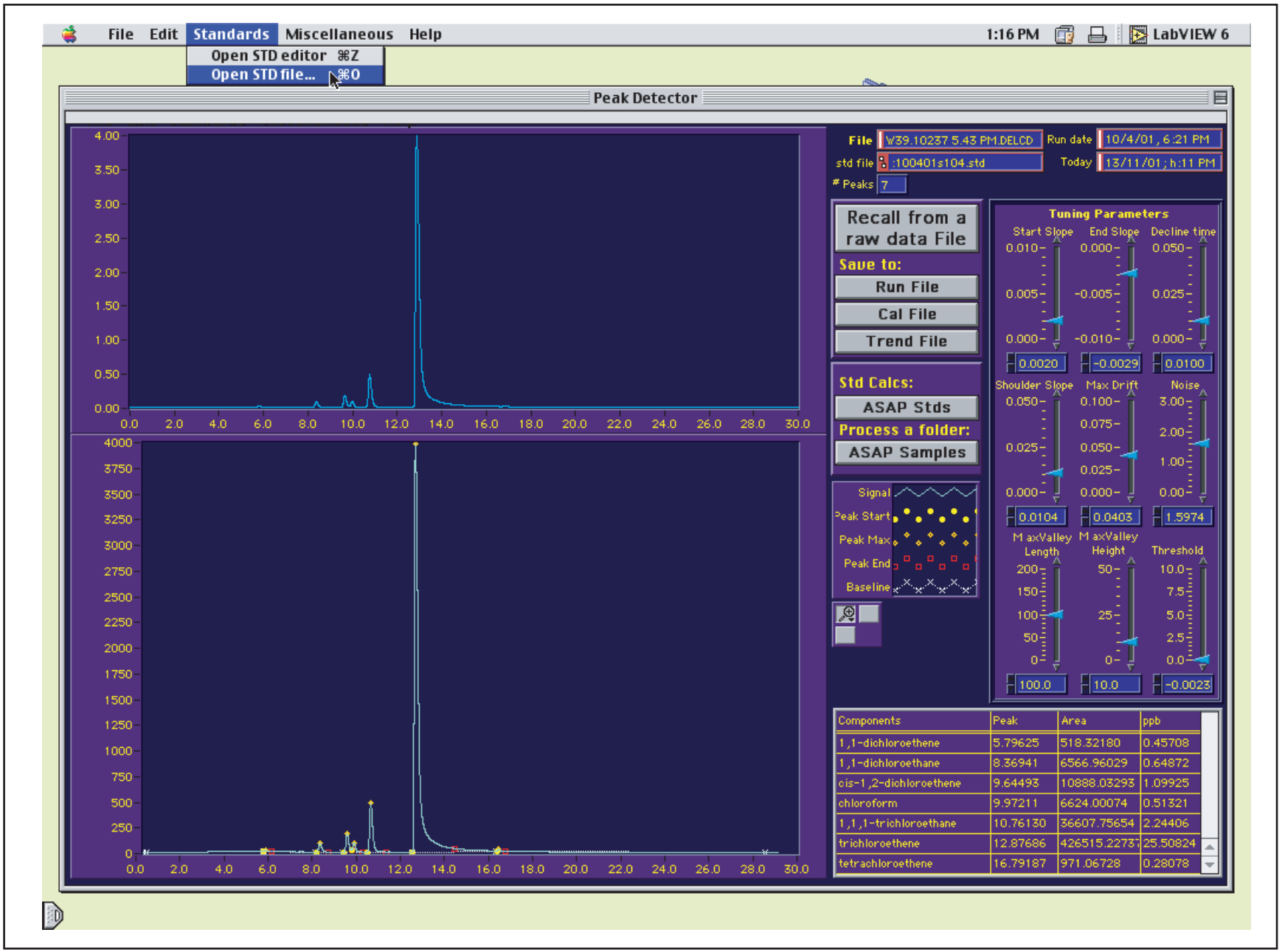

Figure 5-4. Chromatogram analysis starts with opening of a standard file generally named with a date and standard set identifier (e.g.: 100401s104.std, for standard set #104, run on 10/04/01).

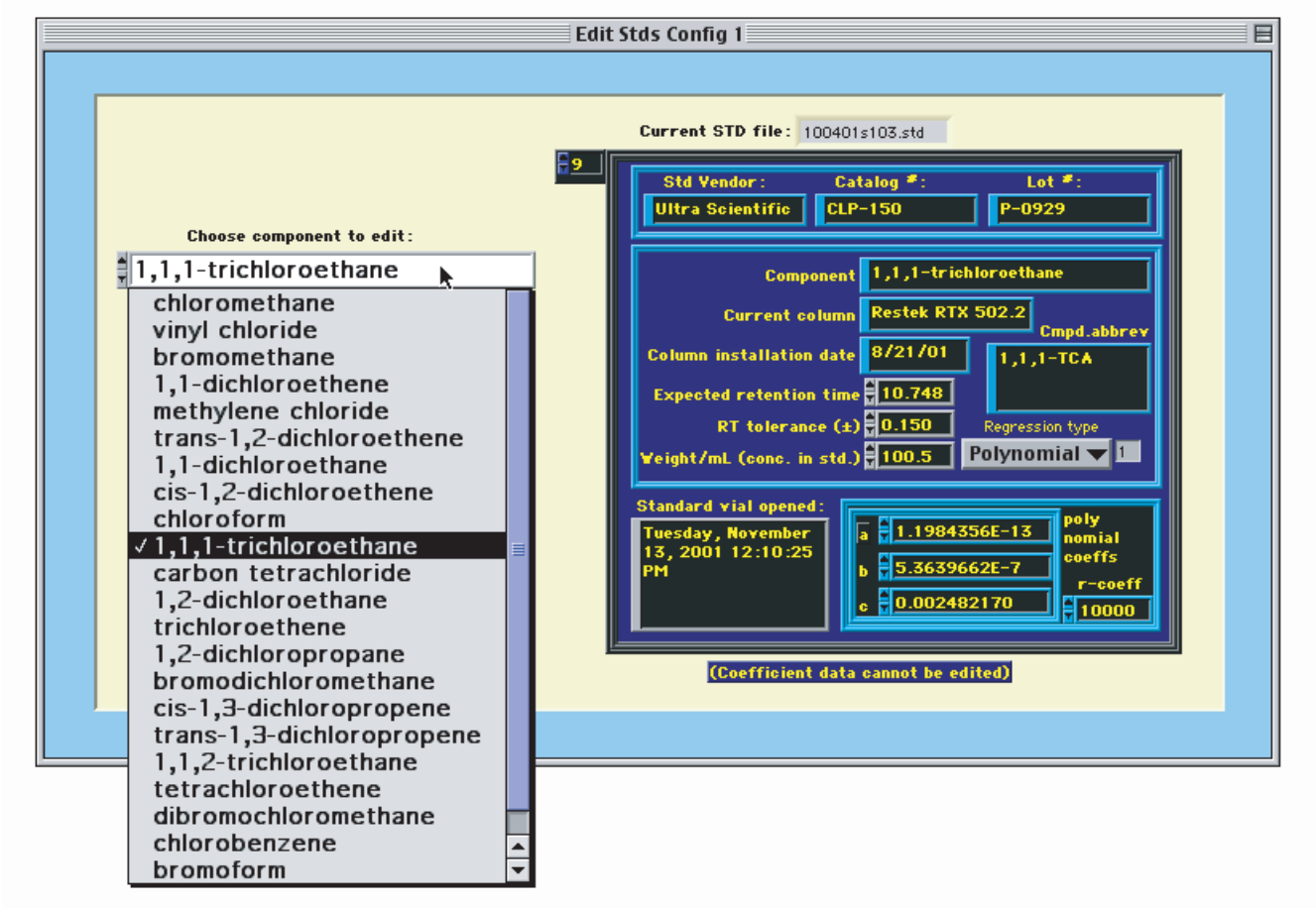

Figure 5-5. The Standard Editor allows viewing and modification of currently defined standard files. Commercial blend vendors, catalog and lot numbers, component names, abbreviations, and weights in blends, may be entered, as well as columns in use, installation dates, expected retention times and type of regression to be generated from calibration files. The calibration coefficients are calculated by the Standard Regressions SubVI, and cannot be edited manually.

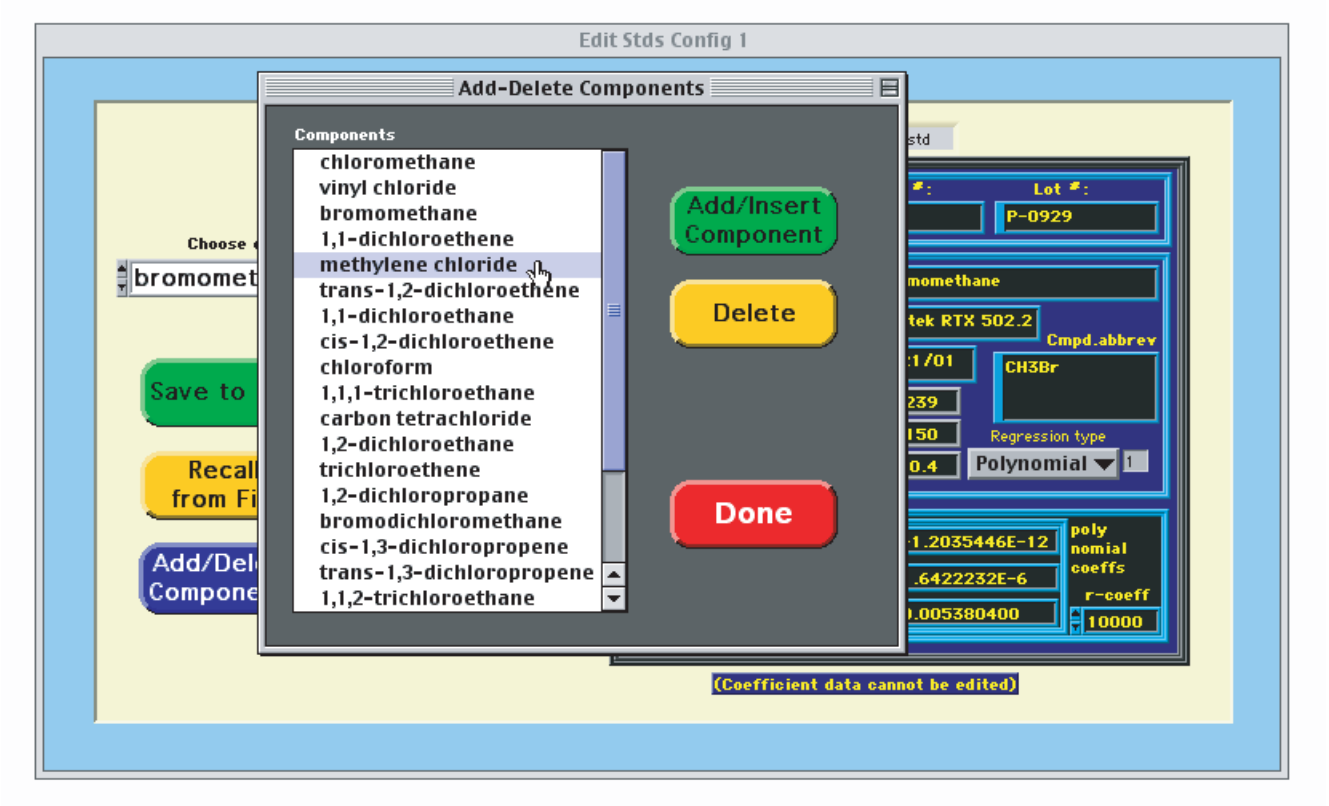

Figure 5-6. The Standard Editor also contains a module for addition or deletion of components, in the event that a new standard blend can more easily created by modiying and renaming an existing one, rather than creating a lengthy list from scratch.

and the sequential standard set run number for the year (e.g.: 100401s104, for calibration standards processed on 10/04/01 in standard set 104).

Once a standard file has been created, it is populated with compound-specific calibration coefficients derived from regression analysis of peak areas from standard runs. Figure 5-7 shows the last of a set of analyses of the CLP-150 Volatiles blend, and the cursor on the "ASAP Stds" button to open the Standards Regression module. Several standard curves produced in this routine are shown in Figure 5-8. Once the regression analysis has been performed, calibration coefficients are inserted into the standard data structure, and can be saved to disk. The user interface does not permit manual modification of these coefficients.

A representative sample chromatogram and quantitative analysis with this package is shown in Figure 5-9. Following analysis of any given chromatogram, one of three ascii (text) report types can be generated: a "Run" file (a typical chromatographer's run report, with parameters identifying the sample and the various thresholds and slope factors relevant to peak quantitiation), a "Calibration" file (summarizing analysis of all analytes, giving only retention time and peak areas) usually generated only for standard analyses, or a "Trend" file, that includes sample identity, sample date and time, and calculated sample concentration. The trend files are structured so that plots can be generated from other software packages, such as spreadsheets or other specialized plotting software.

6.0 OLAS PERFORMANCE

6.1 Compound Identification and Sensitivity

Early in the project we discovered that trap composition had a marked impact on recovery of some compounds. ASAP1 was initially equipped with a BTEX Trap® (Supelco, Inc.), which was not capable of retaining light chlorocarbons, in particular vinyl chloride. This is seen by comparing Figure 6-1a and 6-1b; vinyl chloride is a clearly visible peak eluting at about 2 minutes from the OLAS when equipped with a CarboPack B/CarboSieve SIII trap (Tekmar-Dohrmann, Inc.), but entirely lost from the BTEX Trap®. Although it might be possible to improve light chlorocarbon recovery even more by fabricating custom traps, we have elected to use only commercially available components, and used the Tekmar trap for further work.

MDLs were calculated with the EPA approach: seven analyses of a standard sample with concentrations near the expected MDL are run and processed using the routine quantitation method applied to actual samples; the MDL is the standard deviation of mean for the seven samples. During the operation of the integrated system, this process was performed by selecting the QCC2 runs from seven sequential sets of standards interleaved with well samples, so that the runs were actually performed over about two days. The QCC2 standard analyzes 0.31 ml from standard syringe B (20 µl Ultra Scientific CLP-150 in 88.0 ml total volume). The approximately 7 ng of each analyte, had it been present in the 9.93

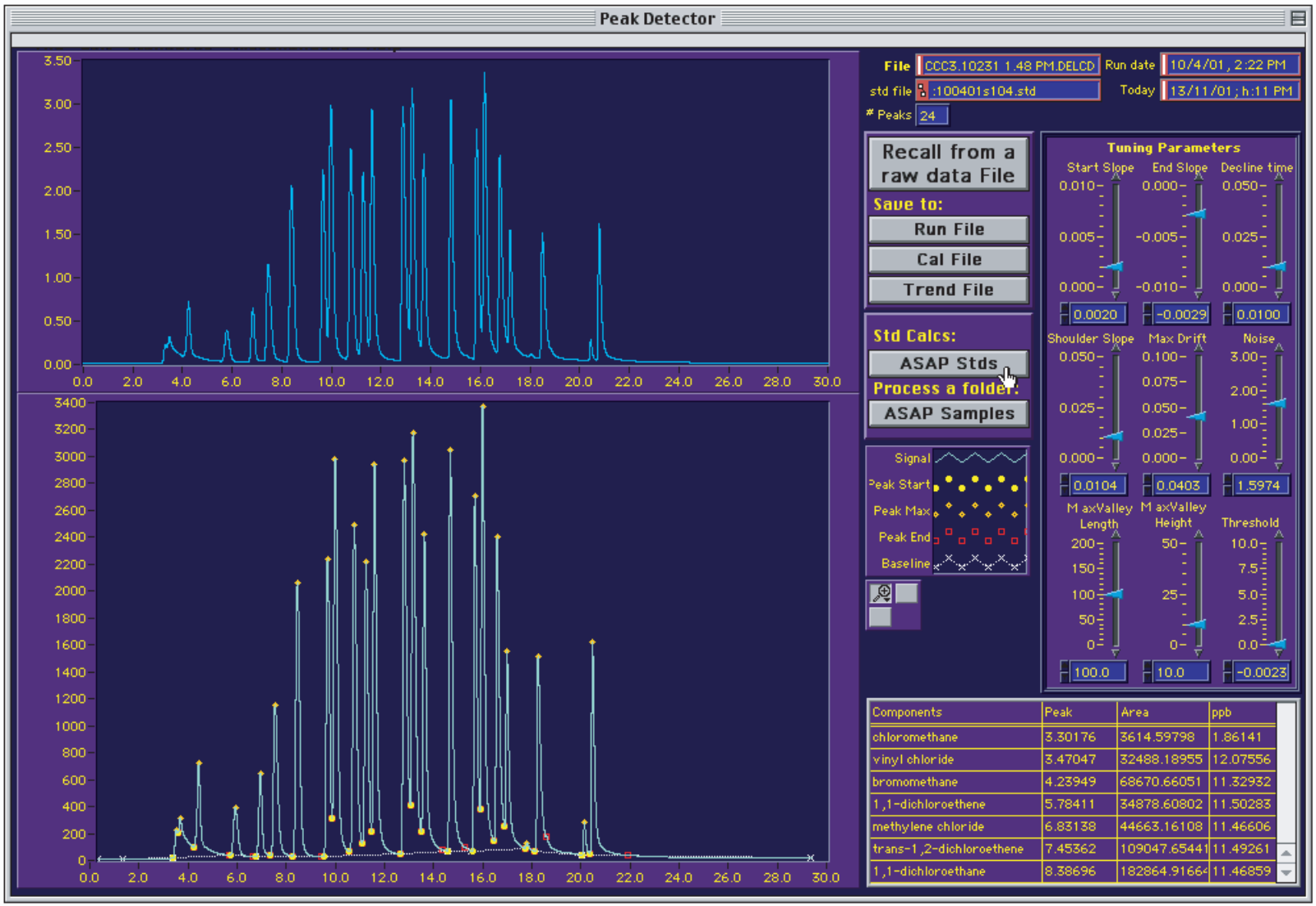

Figure 5-7. Calibration coefficients for standard blend components are calculated after first processing analyses of different loop volumes from the two standard syringes, and saving the peak area data to a "Cal " file (see upper bank of Save to: options). Standard data are displayed, and regressions calculated in the Standards Regression module, by pressinhg the "ASAP Stds" button.

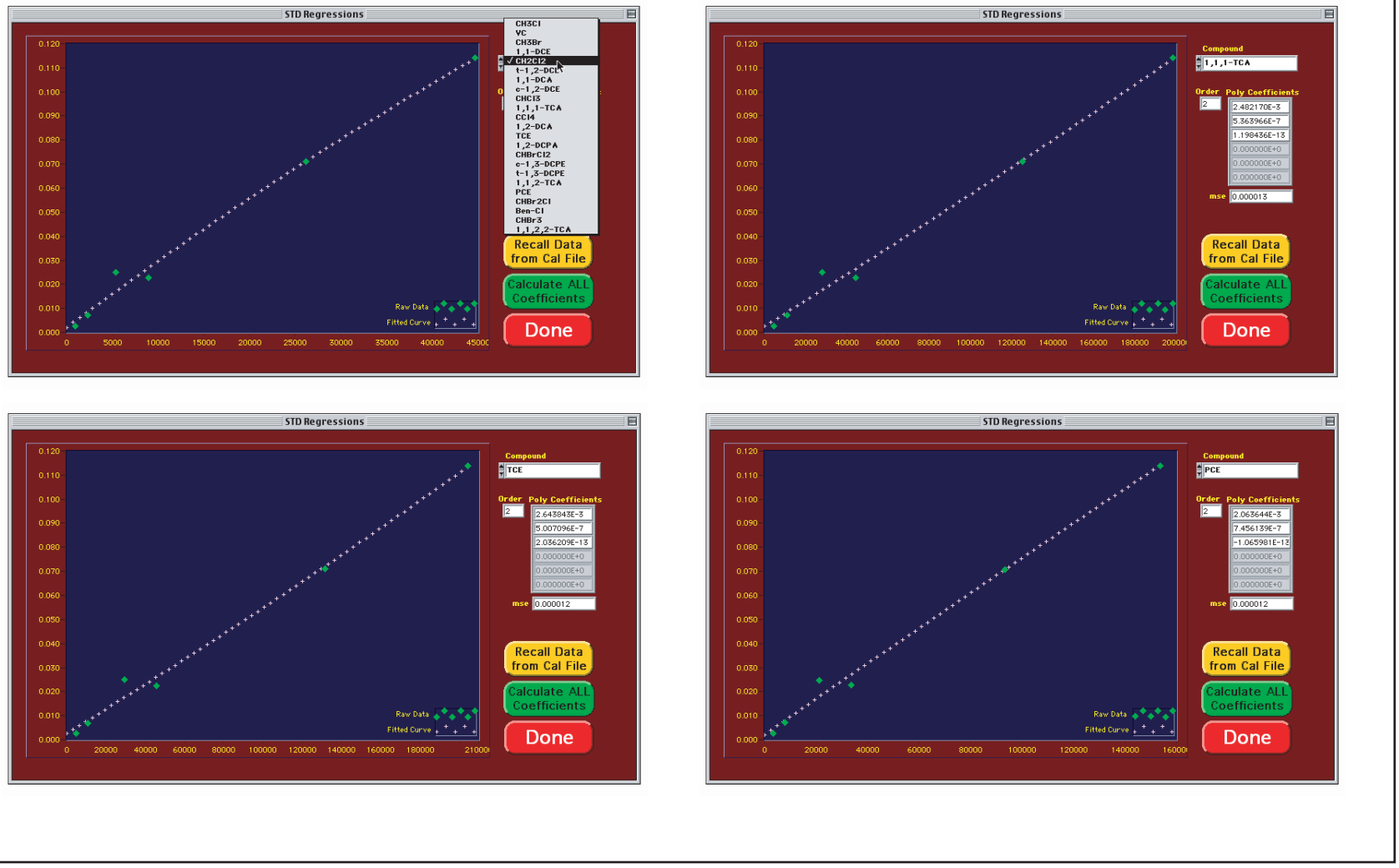

Figure 5-8. Representative standard regressions from chromatograms of Ultra Scientific Contract Laboratory Program Volatiles Target Compounds mixture (CLP-150), run with the ASAP/OLAS equipment at the OU 1 ICMFS. As seen in the upper left, pull-down menus access any component in the standard blend. As in the Standard Editor, the calibration coefficients cannot be manually modified.

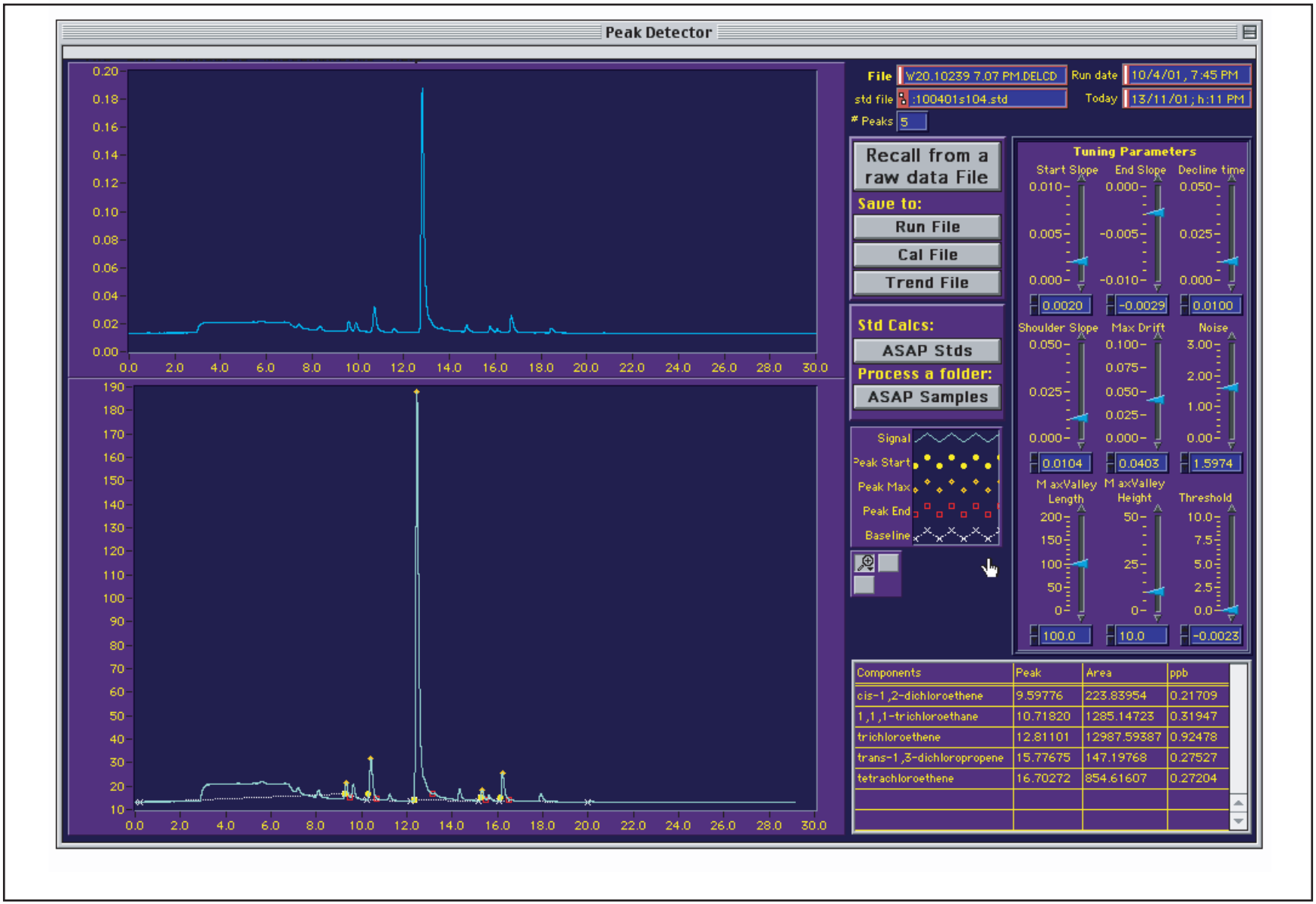

Figure 5-9. Representative chromatogram from a sample of groundwater from MW-OU1-20-A at the OU 1-ICMFS. Note baseline rise that occurs at approximately three minutes into the run. The run date, and date of re-analysis are displayed at the upper right. Data can be written to a "Run" file with all pertinant tuning parameters, standard file used, etc., or appended to an abbreviated "Trend" file with one run per time-stamped line, and compound concentrations arranged in columns, for the purposes of plotting or other analyses.

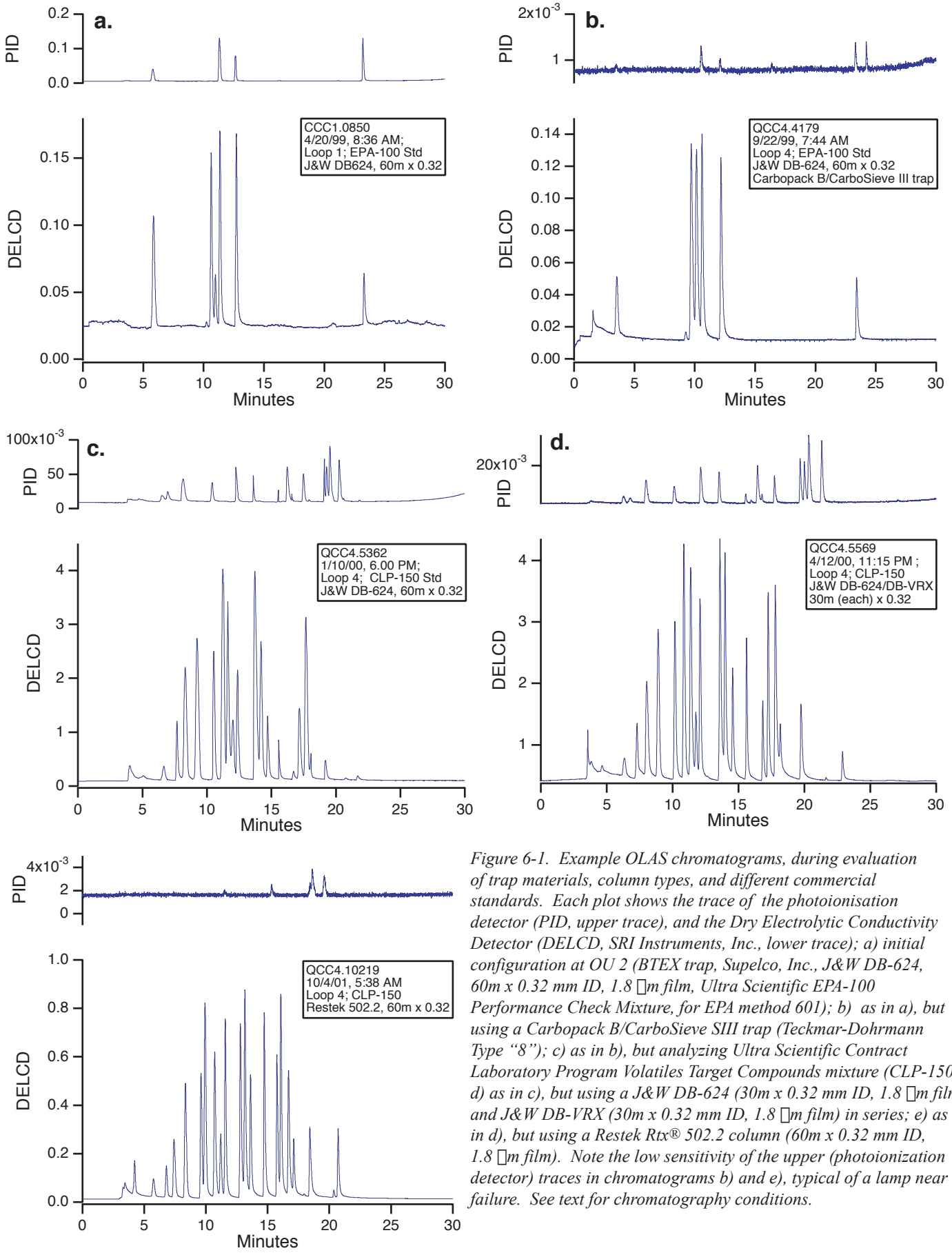

Figure 6-1. Example OLAS chromatograms, during evaluation of trap materials, column types, and different commercial standards. Each plot shows the trace of the photoionisation detector (PID, upper trace), and the Dry Electrolytic Conductivity Detector (DELCD, SRI Instruments, Inc., lower trace); a) initial configuration at OU 2 (BTEX trap, Supelco, Inc., J&W DB-624, 60m x 0.32 mm ID, 1.8 □m film, Ultra Scientific EPA-100 Performance Check Mixture, for EPA method 601); b) as in a), but using a Carbopack B/CarboSieve SIII trap (Teckmar-Dohrmann Type "8"); c) as in b), but analyzing Ultra Scientific Contract Laboratory Program Volatiles Target Compounds mixture (CLP-150); d) as in c), but using a J&W DB-624 (30m x 0.32 mm ID, 1.8 □m film) and J&W DB-VRX (30m x 0.32 mm ID, 1.8 □m film) in series; e) as in d), but using a Restek Rtx® 502.2 column (60m x 0.32 mm ID, 1.8 □m film). Note the low sensitivity of the upper (photoionization detector) traces in chromatograms b) and e), typical of a lamp near failure. See text for chromatography conditions.

ml loop used for all well samples, would represent a sample concentration of about 1 ppb.

Although DELCD MDLs were low for many compounds during testing at the OU 2 installation, the detection limits were variable, and some compounds were not detected reliably (Table 6-1). During testing of the ASAP/OLAS at OU 1, we discovered that there was significant loss of sensitivity when new data were compared with earlier runs. We also found that cycling the reactor temperature of the DELCD (normally operated at 240-250 C) to 300 C for 24 hours not only restored sensitivity in general, bu improved responses to some compounds that had been thought to be relatively difficult to detect. Chromatograms run at this higher detector temperature, however, had distorted peaks for higher-concentration runs, that was determined to be saturation of the detector electronics; this distortion disappeared upon lowering the reactor temperature. Baseline noise was also improved by this procedure

After lowering reactor temperatures, MDLs were recalculated for all halogenated compounds present in the standard blends; all were below 1 ppb, as shown in Table 6-1 (RtX column experiment), and compounds that had not been detected reliably, or with poor reproducibility now gave acceptable results.

6.2 OLAS Operation at OU1

The automated nature of the GC/ASAP system supports a variety of techniques to continually validate performance. In addition to regular estimation of MDLs, the stability of standard analysis can be used to detect detector drift or other problems. In a "well-tuned" state, the integrated system is capable of very stable recover of standards, as shown in Figure 6-2.

In the final testing of the integrated system, standards and samples were processed continuously, starting in early October, 2001. Typical chromatograms from each of the ten wells sampled, and trends for analytes detected above the MDLs are shown in Figures 6-3 through 6-12. Table 6-2 shows that in addition to reliably achieving detection sensitivity comparable to standard laboratory analyses, the ASAP/OLAS detects several compounds not reported in the two previous quarters of manual sampling and laboratory analysis by GC/MS methods (EPA 8260b), and finds other compounds in many wells where conventional sampling did not detect them (note the results for tetrachloroethene in Table 6-2). We suspect that this exposes a previously unappreciated degree of analyte loss in the collective processes involved in manual sample vial filling, transport to remote labs, and storage prior to analysis.

7.0 PROSPECTS FOR FURTHER DEVELOPMENT

7.1 Software Integration for real-time analysis, operator display

The software components for GC control and chromatogram acquisition are separate modules from the Chromatogram Analyzer suite of tools. These can be integrated to support automated trend file generation and live displays for operators, and this combination of code modules is generally straightforward in

Table 6-1. Representative retention times and method detection limits for compounds in a commercial standard blend with two columns and the PID/DELCD combination detector. Compounds in bold are identified as "compounds of concern" in OU 1 and/or OU 2 Records of Decision. Data derived standards interleaved with samples over a three day period at the OU 2 facility (DB-624+DB-VRX column, 5/12/00), and the OU 1 ICFMS (RtX 502.2 column, 10/4/01); MDLs derived from repeated analyses of Contract Laboratory Program Volatiles Target Compound List (CLP-150, Ultra Scientific, Inc.).

		J&W DB-624/DB-VRX, 20+20m		Restek RtX 502.2, 60m	
Compound	**Abbrev.**	**RT**	**MDL**	**RT**	**MDL**
chloromethane	CH3Cl	3.026	0.32	3.301	-
vinyl chloride	VC	3.279	n/a	3.460	0.49
bromomethane	CH3Br	3.902	2.34	4.239	0.43
chloroethane	C2H5Cl	4.133	n/a	n/d	-
1,1-dichloroethene	1,1-DCE	5.186	0.20	5.775	0.47
methylene chloride	CH2Cl2	6.849	1.82	6.831	0.84
trans-1,2-dichloroethene	t-1,2-DCE	7.638	n/a	7.440	0.65
1,1-dichloroethane	1,1-DCA	8.755	0.18	8.366	0.76
cis-1,2-dichloroethene	c-1,2-DCE	9.905	0.06	9.624	0.79
chloroform	CHCl3	10.616	3.61	9.948	0.82
1,1,1-trichloroethane	1,1,1-TCA	11.334	0.05	10.748	0.50
carbon tetrachloride	CCl4	11.729	0.01	11.235	0.45
benzene[1]	BEN	12.073	0.25	-	-
1,2-dichloroethane	1,2-DCA	12.051	0.02	11.601	0.74
trichloroethene	TCE	13.428	0.22	12.846	0.68
1,2-dichloropropane	1,2-DCPA	13.833	0.16	13.215	0.84
bromodichloromethane	CHBrCl2	14.452	0.19	13.683	0.84
cis-1,3-dichloropropene	c-1,3-DCPE	15.516	0.17	14.789	0.81
trans-1,3-dichloropropene	t-1,3-DCPE	16.78	0.002	15.818	0.82
1,1,2-trichloroethane	1,1,2-TCA	17.186	0.79	16.128	0.78
tetrachloroethene	PCE	17.726	0.24	16.761	0.53
dibromochloromethane	CHBr2Cl	18.119	8.53	17.181	0.86
chlorobenzene	BENCl	19.728	0.72	18.491	0.82
bromoform	CHBr3	21.689	n/a	20.450	0.75
1,1,2,2-tetrachloroethane	1,1,2,2-TCA	22.907	n/a	20.799	0.73

[1] PID detection for test with DB-624/DB-VRX column; PID not operated for test with RtX column.

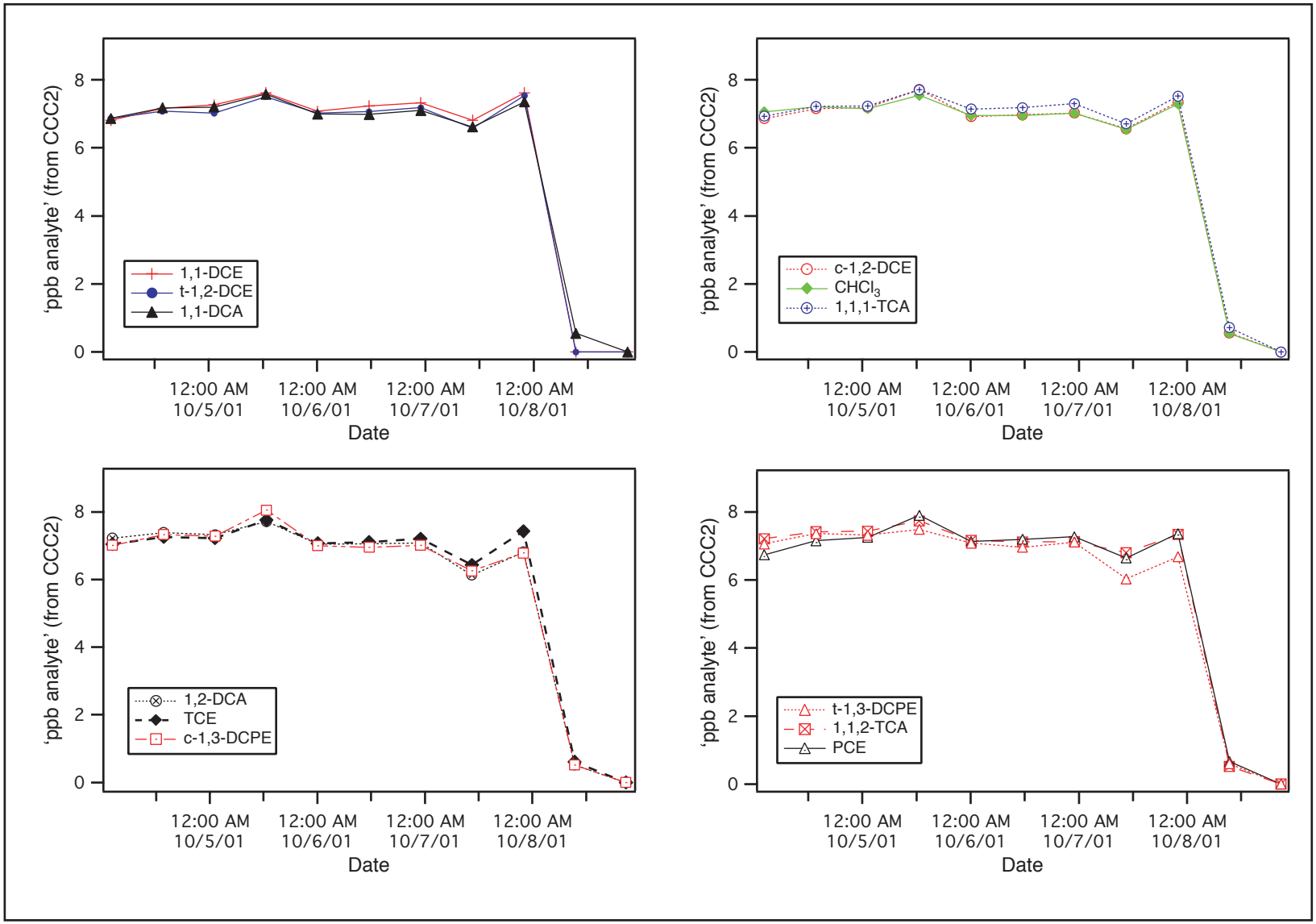

Figure 6-2. Stability of chemical standard analyses with the ASAP/OLAS at the Fort Ord OU 1 ICFMS. Repeated samples from one filling of Syringe A using loop 2 (~70 ng per component of Contract Laboratory Program Volatiles Target Compounds mixture; CLP-150, Ultra Scientific, Inc.) Analytes shown were those detected in OU 1 samples above MDLs. Concentrations calculated as if the individual analyte quantities were present in a sample filling loop 7 (9.928 ml), used for all samples from OU 1 wells.

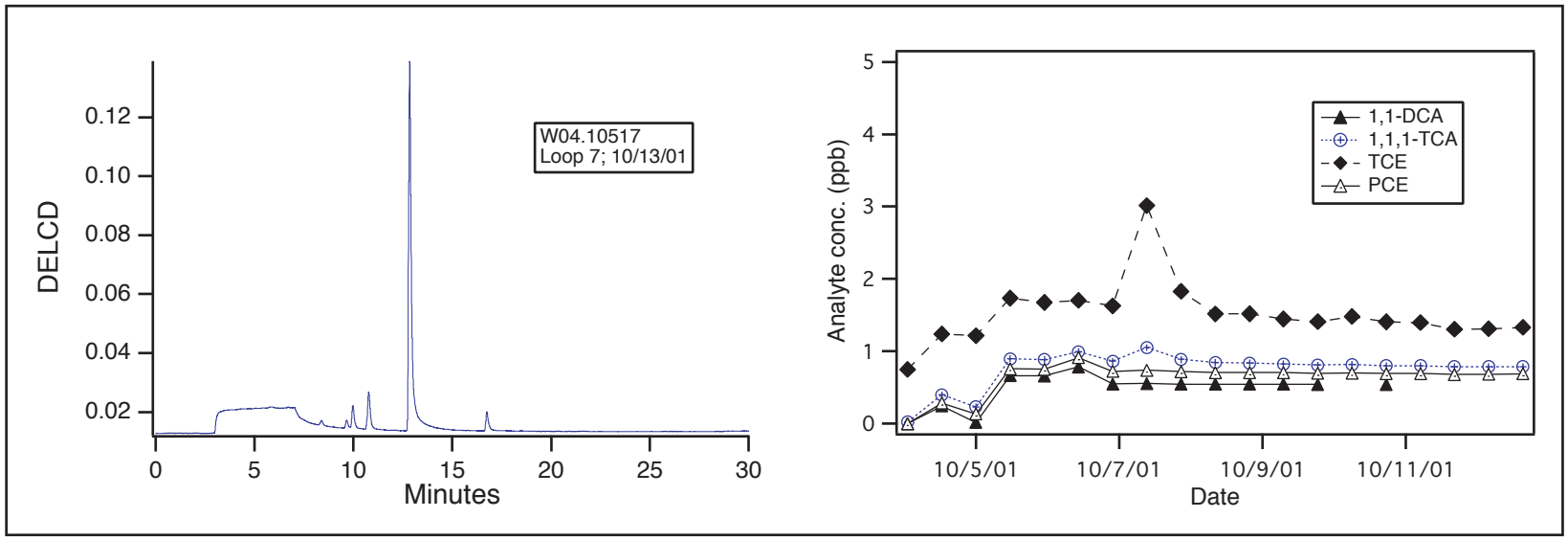

Figure 6-3. Typical chromatogram from Fort Ord well MW-OU1-O4-A (left); trends of analyte concentrations measured during On-Line Analysis System test period (right).

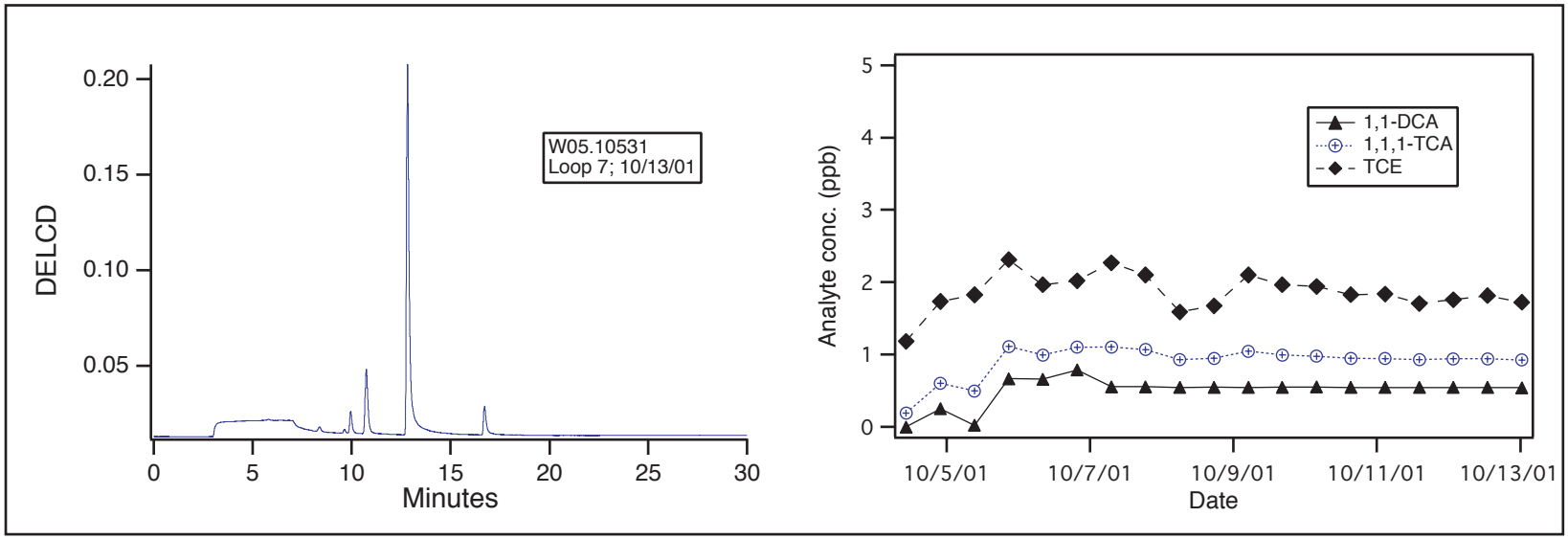

Figure 6-4. Typical chromatogram from Fort Ord well MW-OU1-O5-A (left);trends of analyte concentrations measured during On-Line Analysis System test period (right)).

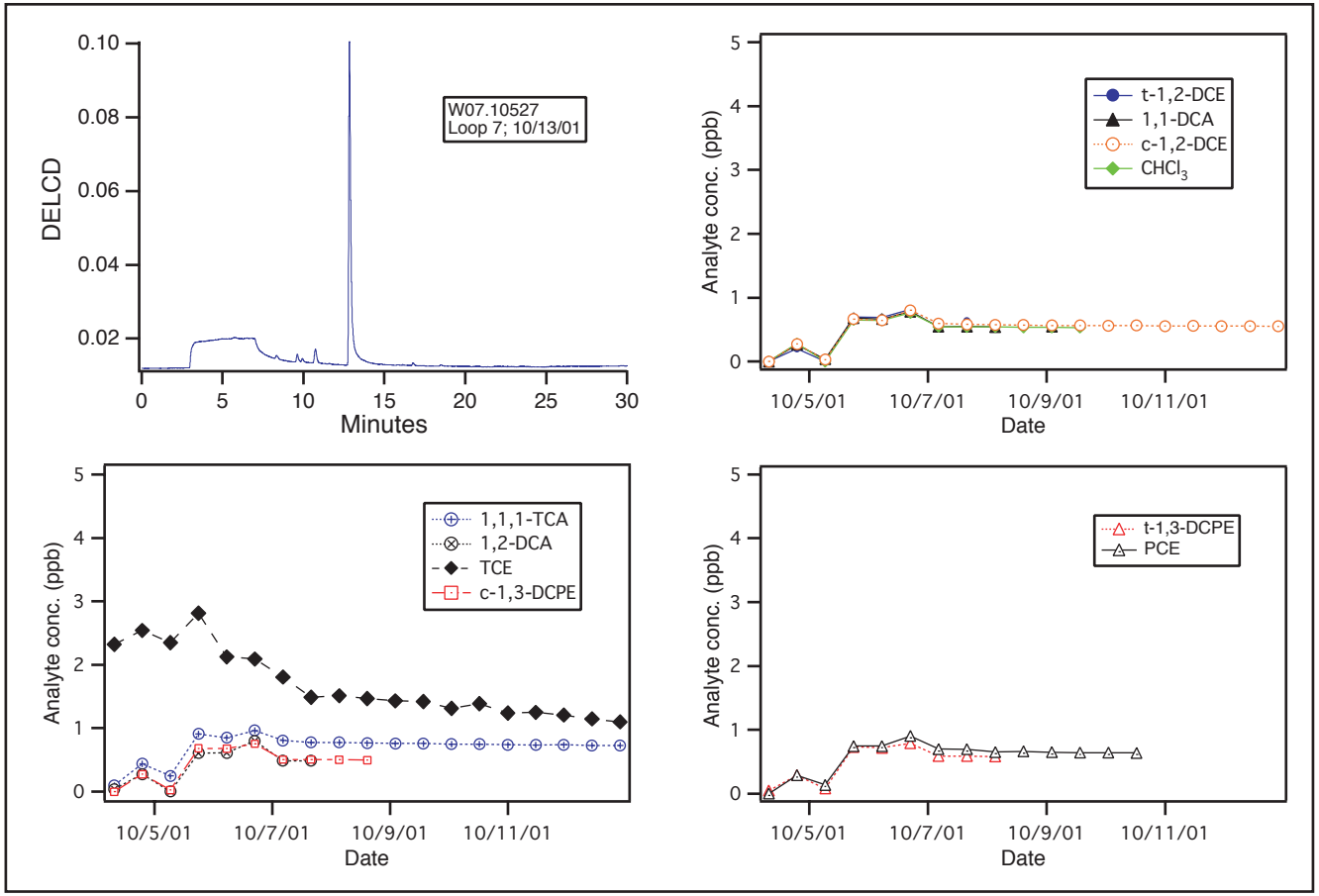

Figure 6-5. Typical chromatogram from Fort Ord well MW-OU1-O7-A (left);trends of analyte concentrations measured during On-Line Analysis System test period (above right, below left, and below right).

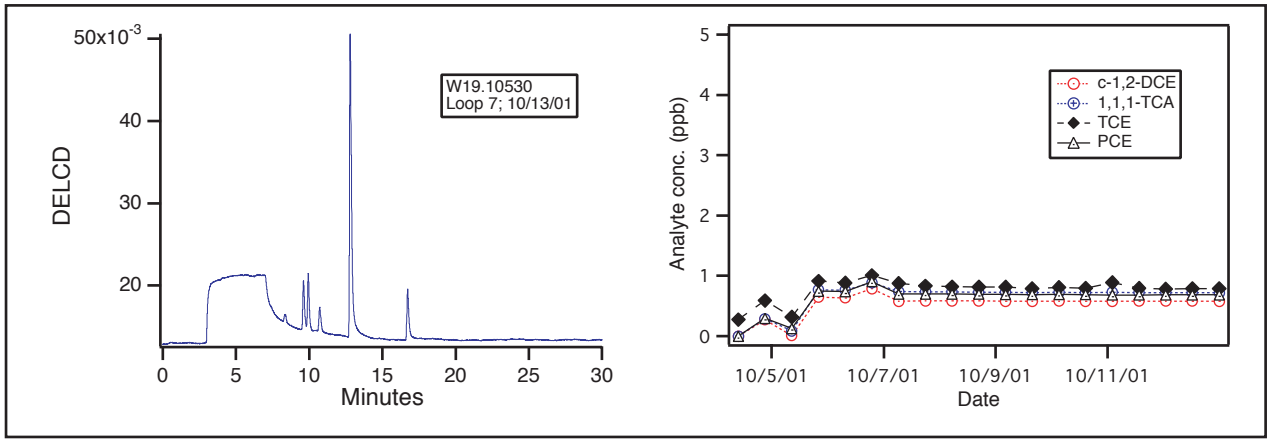

Figure 6-6. Typical chromatogram from Fort Ord well MW-OU1-19-A (left); trends of analyte concentrations measured during On-Line Analysis System test period (right).

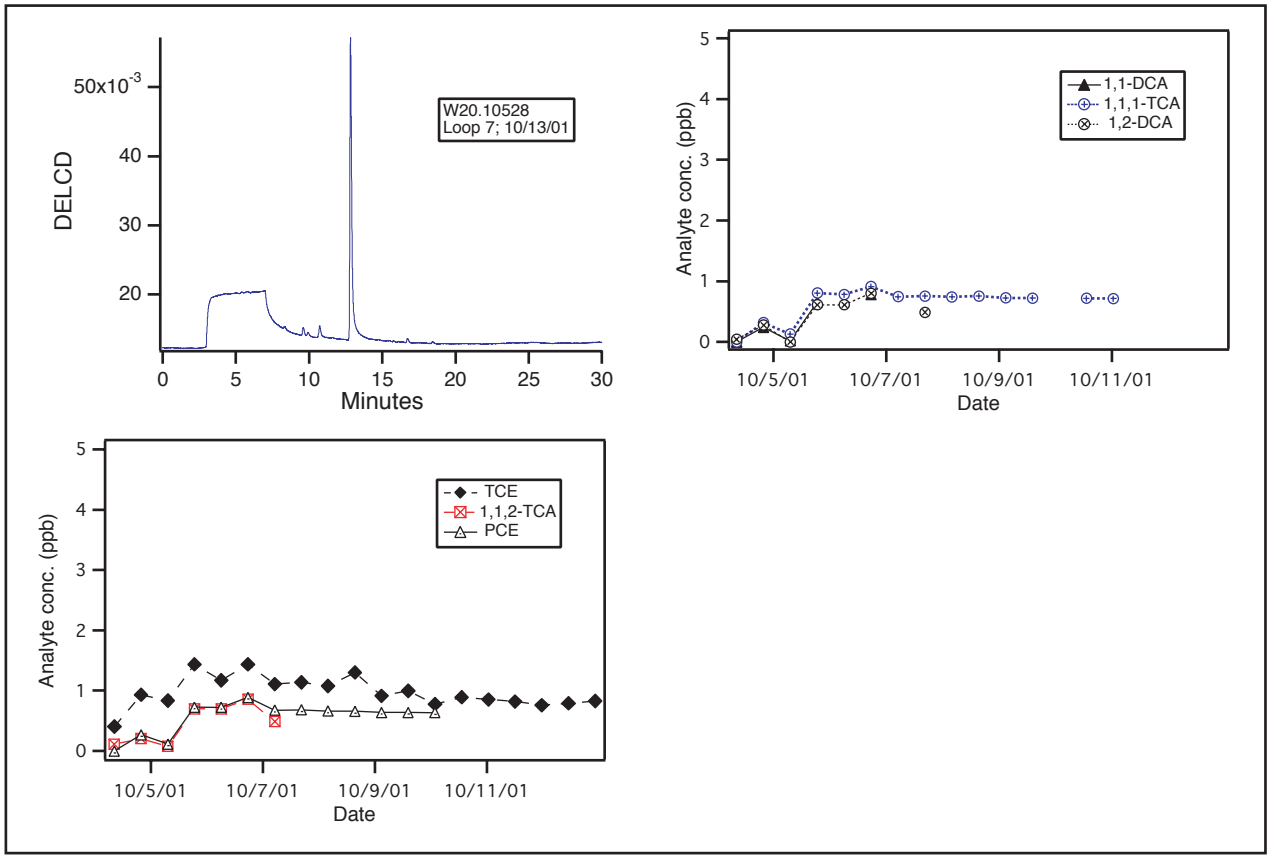

Figure 6-7. Typical chromatogram from Fort Ord well MW-OU1-20-A (upper left);trends of analyte concentrations measured during On-Line Analysis System test period (right, below left).

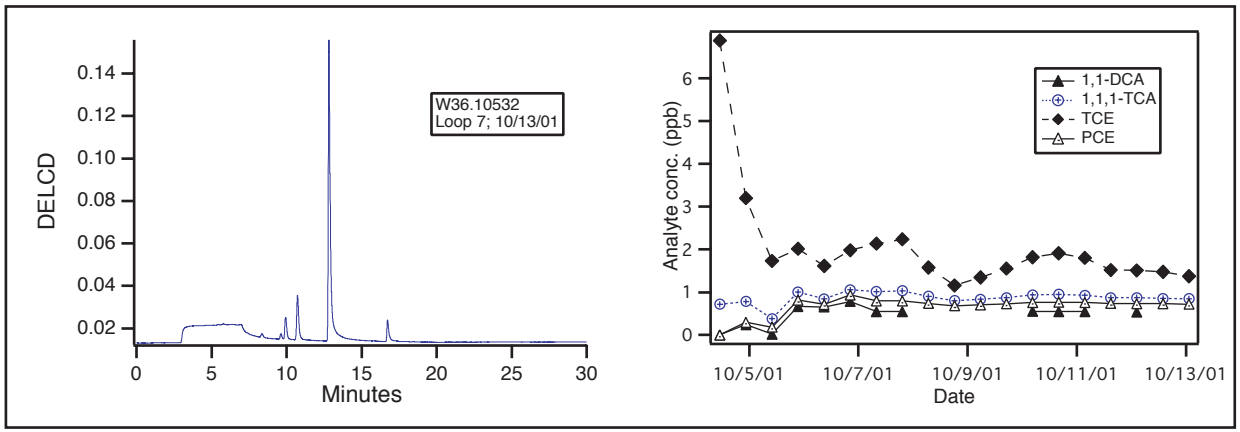

Figure 6-8 Typical chromatogram from Fort Ord well MW-OU1-36-A (left);trends of analyte concentrations measured during On-Line Analysis System test period (right).

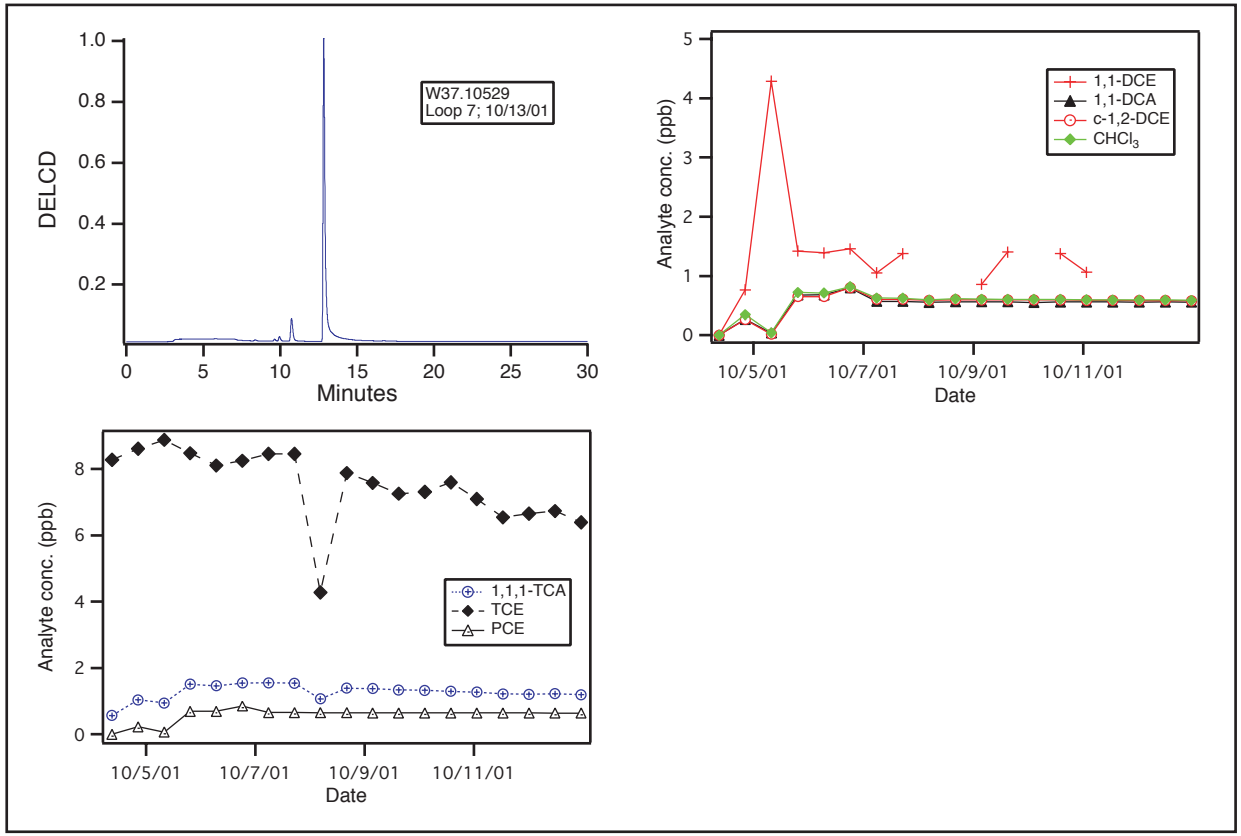

Figure 6-9. Typical chromatogram from Fort Ord well MW-OU1-37-A (upper left);trends of analyte concentrations measured during On-Line Analysis System test period (right, below left).

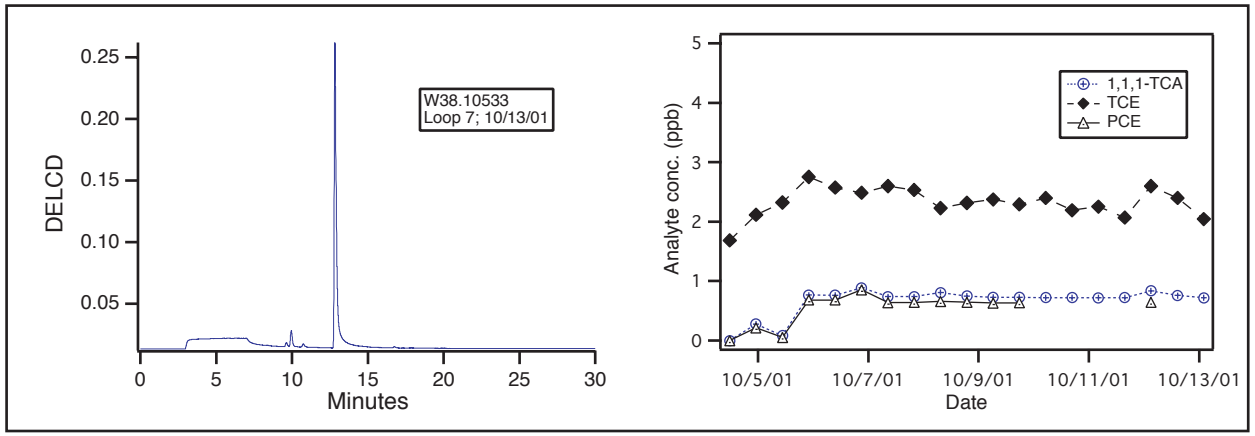

Figure 6-10. Typical chromatogram from Fort Ord well MW-OU1-38-A (left);trends of analyte concentrations measured during On-Line Analysis System test period (right).

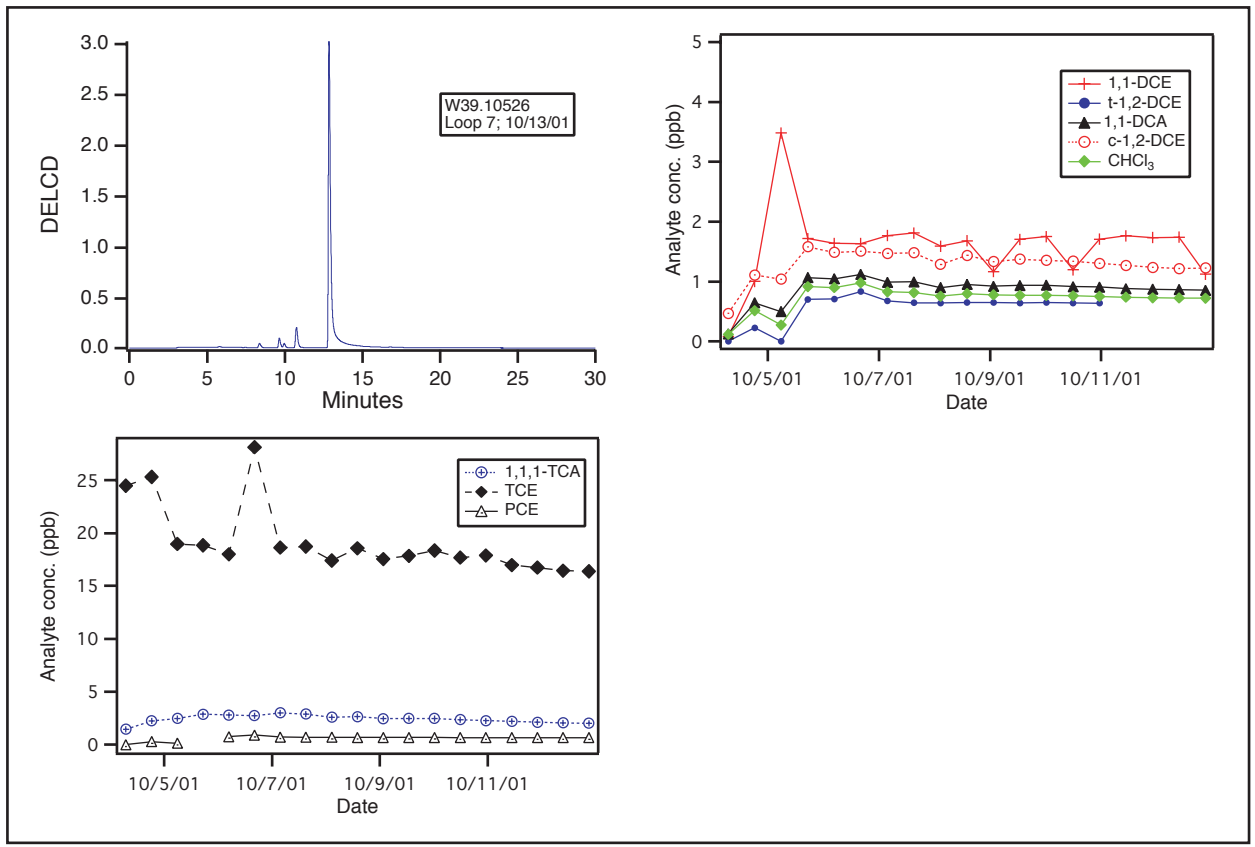

Figure 6-11. Typical chromatogram from Fort Ord well MW-OU1-39-A (upper left);trends of analyte concentrations measured during On-Line Analysis System test period (right, below left).

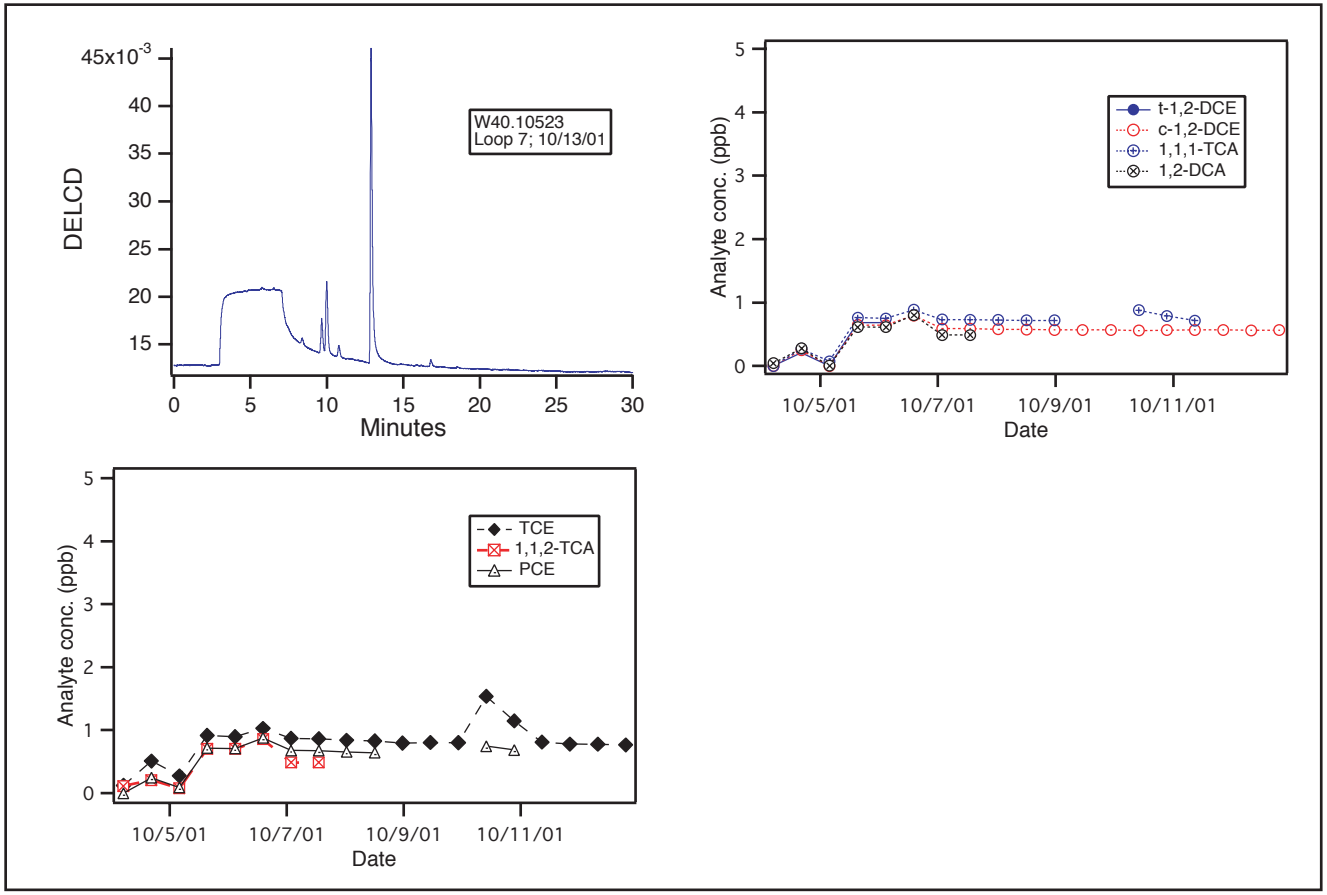

Figure 6-12. Typical chromatogram from Fort Ord well MW-OU1-40-A (upper left);trends of analyte concentrations measured during On-Line Analysis System test period (right, below left).

Table 6-2. Analytes of interest at Fort Ord, OU 1. Shown are compounds in standards used with the ASAP/OLAS, method detection limits (MDLs) measured during continuous operation, wells with compounds detected by manual sampling in the two quarters prior to the automated sampling, and wells with analytes detected with the ASAP/OLAS in October, 2001. Compounds in boldface are identified as "Chemicals of Concern" in either (or both) the OU 1 and OU 2 Records of Decision.

Cmpd	Oct '01 On-line MDL (μg/L)	OU 1 wells with analytes detected in Oct '00 to Mar '01 sampling[4]	OU 1 wells with analytes detected with On-line system at OU1, 10/01
vinyl chloride	0.49		
bromomethane	0.43		
1,1-dichloroethene	0.47	4	37, 39
methylene chloride	0.84		
trans-1,2-dichloroethene	0.65		7, 20[5], 39, 40
1,1-dichloroethane	0.76	4, 39	4, 5, 7, 19[5], 20, 36, 37, 38[5], 39, 40[5]
cis-1,2-dichloroethene	0.79	4, 20, 39	4[5], 5[5], 7, 19, 20[5], 36[5], 37, 38[5], 39, 40
chloroform	0.82	4, 20, 39	4[5], 5[5], 7, 19[5], 20[5], 36[5], 37, 38[5], 39, 40[5]
2-butanone			
1,1,1-trichloroethane	0.50	4, 5, 19, 20, 37, 39	4, 5, 7, 19, 20, 36, 37, 38, 39, 40
carbon tetrachloride	0.45		
benzene			
1,2-dichloroethane	0.74		7, 20, 39[5], 40
trichloroethene	0.68	4, 5, 7, 19, 20, 36, 37,38, 39, 40	4, 5, 7, 19, 20, 36, 37, 38, 39, 40
1,2-dichloropropane	0.84		
bromodichloromethane	0.84		
cis-1,3-dichloropropene	0.81		4[5], 5[5], 7, 19[5], 20[5], 39[5], 40[5]
trans-1,3-dichloropropene	0.82		4[5], 5[5], 7, 19[5], 20[5], 37[5] , 39[5], 40[5]
1,1,2-trichloroethane	0.78		7, 20, 39[5], 40
tetrachloroethene	0.53	39	4, 5[5], 7, 19, 20, 36, 37, 38, 39, 40
dibromochloromethane	0.86		
chlorobenzene	0.82		7[5], 20[5], 39[5], 40[5]
bromoform	0.75		
1,1,2,2-tetrachloroethane	0.73		

[1]RT = retention time for Restek 505.2 column (60m x 0.32 mm I.D., 1.5 μ film).
[2]Chloromethane was detectable in standards, but with a distorted baseline that prevented reliable quantitation; it was not observed in any well samples.
[3]May not be separated from bromomethane; one peak at 4.239 min. reported as bromomethane for this report. No peaks at this retention time observed in any well samples.
[4]MW-OU1-36-A was not manually sampled in either the Oct-Dec '00 or Jan-Mar '01 monitoring periods.
[5]Observed, but not detected above the On-Line MDL.

the LabVIEW environment. However, some work still remains for this to offer acceptable reliability.

Drift in detector response, and more particularly compound retention time, remains an issue. In general, detectors can be expected to decline in sensitivity with use, and strategies for routine maintenance must be enforced, as described above with respect to the heat treatment of the SRI DELCD detector. Identifying the appropriate point to perform these maintenance operations is an important issue. We suspect that the variable response of this detector to different chlorocarbons may be the key to evaluating the need for maintenance, and we will explore this issue.

Another detection related issue is the structure of our use of standards. In this work, we have relied on the use of "external standards," the approach that was used in earlier implementations of ASAP based systems (Roberts et al., 1990). External standards are analyses of known amounts of target compounds with varying concentrations; detector responses (peak areas) are measured, and regressions of peak area against concentration produce functions later used to calculate sample analyte concentrations. A more robust approach is the use of "internal standards," in which a known, fixed amount of a compound related to target analytes, but easily separated from them, is introduced into each sample and standard, usually along with surrogate compounds that are not found in real samples. The chromatogram analysis of the internal standards takes place in both samples and standard runs, but the *ratio* of detector response to sample analyte and internal standard is used in forming a regression against target analyte concentration. This approach is particularly useful in lengthy sample preparation procedures, as any losses of internal standard are expected to mirror losses of targets, yet their ratio is preserved throughout. The use of surrogate compounds further enhances the operator's ability to detect shifts in compound retention time or other performance characteristics The ASAP2 unit was designed and assembled with an additional loop for injection of internal standards and surrogates with this enhancement in mind.

7.2 Data and Control Integration With Site-Wide SCADA Implementation

The Fort Ord environmental restoration program is currently implementing a supervisory control and data acquisition (SCADA) system to link operations of several groundwater remediation systems. The ASAP/OLAS instrumentation has great potential for integration with this site-wide effort, particularly owing to the use of LabVIEW, that supports flexible communications with SCADA systems.

7.3 Data Communications For Integration of Remote Sites

We became painfully aware of the lack of broad-band communications while evaluating the systems described in this report. During development of an automated vapor analysis system that formed the foundation of the GC control system of the ASAP/OLAS, we relied heavily on ethernet communications at the Lawrence Livermore National Laboratory to communicate with an analytical system some fifteen miles from the main Laboratory site (Daley, 1992). Over the network, we regularly used screen-sharing software to view the remote system

screens, transfer data, and support technicians during troubleshooting or maintenance.

Unfortunately this has not been possible at the Fort Ord OLAS sites. The telephone infrastructure at the site is dated, and cannot be reliably used for data communications. However, both cable and digital subscriber line (DSL) installations are taking place, and there are conventional ethernet installations in parts of the base.

Connecting the analytical stations to these network hubs, however, can be prohibitively expensive, particularly for very remote sites like the OU 1-FDA. We have monitored with great interest the growth in industry acceptance of new wireless networking standards, especially IEEE-802.11b wireless ethernet operating in the 2.4 to 2.6 GHz frequency bands. We are confident that with the use of readily available directional antennas and repeaters, analytical stations such as the ASAP/OLAS could be efficiently linked to site wide communications backbones and greatly facilitate reliable and sustained operation of the on-line hardware.

8.0 CONCLUSIONS

8.1 Software and Hardware development for improved acceptance of OLAS

Software was developed to manage analytical standards and automate chromatography data reduction. Good Laboratory Practices such as locked standard file types and incorporation of chromatography system configurations was incorporated to bring the integrated software system into congruence with common commercial laboratory procedures.

A second generation ASAP/OLAS sampler that provides optional introduction of internal standards and surrogates for improved analytical reliability was designed and built. Owing to construction delays associated with the rebuilding of the OU 2 groundwater treatment plant, this system has not been installed at that plant.

8.2 Installation and testing of chemical On Line Analysis System

An automated water sampling and analysis system was developed and tested at two sites at Fort Ord. The analytical equipment successfully supports relatively unattended operation for extended periods, and has demonstrated stability, sensitivity and precision comparable to formal analytical laboratory instruments over at least the time scale of weeks. Moreover, since samples are transported through a highly inert, all-metal sampling system, they apparently arrive at the analytical hardware in a relatively undisturbed state, as analytes not detected with manual sampling and formal laboratory analysis were frequently detected, and other compounds, although previously found at the site, were detected in wells where they had not been previously observed. Although during testing data

acquisition and subsequent quantitation and reporting were separate processes, these can be integrated in the future to provide integration, and instantaneous updates of contaminant distributions.

9.0 RECOMMENDATIONS

We would like to offer the following recommendations:

1) We recommend that the ASAP1/OLAS system should be operated at the OU 1-FDA/ICFMS site to support experiments to enhance our understanding of the impact of groundwater pumping patterns and treated water disposal. We further recommend installation of the ASAP2/OLAS at OU 2 as soon as construction at the site allows, so that the capabilities of this unit can be evaluated during routine operation.
2) We recommend that since site installation construction at the OU 1-FDA/ICFMS and OU 2-GTS sites is essentially complete, and analytical software has been initially validated, that the focus of operations should shift to intensive operation of the analytical hardware to improve long-term performance. This will require more attention to regular maintenance using techniques discovered in this project. We recommend that alternate operators already assigned to tasks at the two sites (GTS operators, etc.) receive training in ASAP/OLAS routine maintenance operations (cleaning and filling standard syringes, maintenance of peristaltic pumps, inspection of standard recoveries, etc.), to assist in keeping the analytical hardware in the best working condition, and to integrate the resulting data into the management processes of these two sites.
3) We strongly recommend installation of wireless networking, to allow remote data collection, viewing of operator interfaces, and facilitate troubleshooting and maintenance operations. If this cannot be readily accomplished, we recommend an alternative manual transfer of data (email, file uploads to an FTP site, etc.) by facility staff, so that system operation can be more regularly reviewed.
4) We recommend integration of data streams from the ASAP/OLAS stations with the SCADA plans at the site. While further software development may be required, this is a realistic proposal supported by the use of LabVIEW by the analytical stations, and related products from the same vendor for the site SCADA system. A detailed review of data types supported by the ASAP/OLAS systems in their present configuration, and areas of prioritized data needs of the SCADA implementation should take place as soon as possible, so that a systematic strategy for implementing and testing software extensions can be developed.

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