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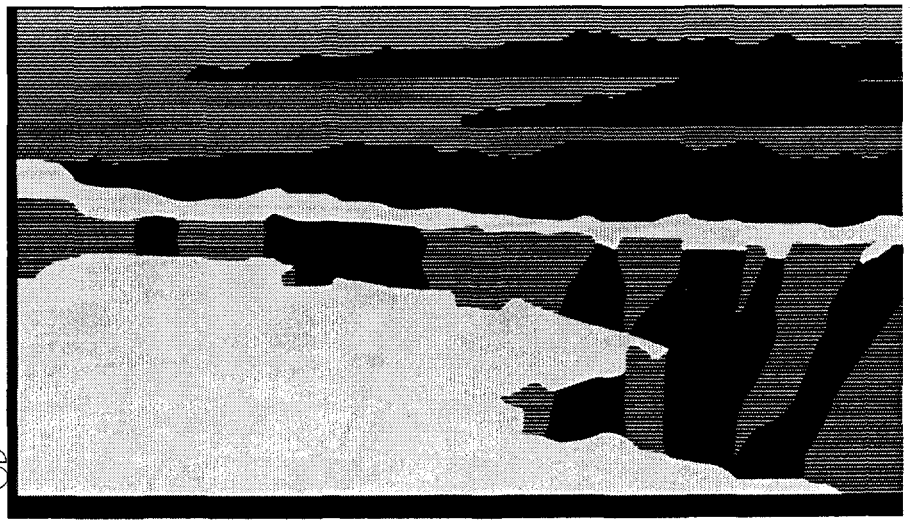

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Beta Test Results for the CAA Mini-SAM System
By R. Conrad Johnson and Matthew Monagle

Introduction

The mission of the Chemical Analysis Automation (CAA) Program is to automate methods for chemical analysis of environmental samples. To accomplish this mission, the CAA team has developed automated laboratory systems based on a plug-and-work strategy for integrating components. Realizing that standardization is the key to implementing this strategy, CAA has developed, demonstrated, and encouraged commercialization of standards for laboratory automation. While the CAA mission is driven by the analyses in support of the extensive remediation programs of the Departments of Energy and Defense, it also impacts any industry that depends upon high volumes of repetitive chemical analysis.

A Standard Analysis Method (SAM) is any collection of hardware and software used to automate part or all of a method. The method automated for the Mini-SAM testing is EPA Method 3550, which outlines semivolatiles extraction by sonication. The list of semivolatiles includes the polychlorinated biphenyl (PCB) analytes of interest (commercially known as Aroclors 1242, 1254, and 1260).

The basic building block of a SAM is the Standard Laboratory Module (SLM™). For the Mini-SAM test an automated sonication SLM and an automated concentration SLM were configured to perform the extraction and concentration processes. The Mini-SAM differs from the Full-SAM in that a fully automated delivery of materials, samples and extracts is not required. The robot arm and Task Sequence Controller associated with the Full-SAM were not installed.

The intent of the Beta Test of the Mini-SAM was threefold. Firstly, the Mini-SAM Beta Test met a milestone mandated by the Department of Energy in the course of the program effort. Secondly, the CAA Program secured an independent assessment of the equipment and its capabilities from Assagai Analytical Laboratory. Lastly, the Program captured real-world sample data. The independent assessment, coupled with CAA observation of equipment performance, was used to determine strengths and weaknesses of the Mini-SAM and to compile possible modifications for CAA engineers to address.

Experimental

The Mini-SAM system consisted of a second-generation automated sonication extraction module and a second-generation high-volume concentrator. Further information on the sonication module is given in "A Standard Laboratory Module for Performing Sonication Extraction (EPA Method 3550)," by T.H. Erkkila in The Journal of Laboratory Robotics and Automation, Volume 6, No. 2, 1994. Modifications to this sonicator include an on-board CPU and keypad interface, larger internal diameter extract transfer tube, and teflon transfer system. The high-volume concentrator (HVC) is an automated, self-cleaning concentration system. It consists of an input beaker port (into which the beaker containing about 300 mLs of extracted solvent from the sonicator is placed), a glass boiling chamber with column (which mimic the Kuderna-Danish and Snyder column process), a glass transfer chamber, an output port (into which a 20 mL glass vial is placed for collection of the 10 mL final concentrate), and various teflon lines and valve blocks for the transfer of solvent and sample. The process involves a vacuum transfer of the extract from the input beaker to the boiling chamber via a stainless steel tube. The beaker is rinsed with 20 mLs clean solvent dispensed from the same tube, the rinseate is transfered to the boiling chamber, and the process is repeated three times. The extract and rinseate are concentrated in the boiling chamber by two heaters: an upper heater (which operates on the majority of the volume) at 90 degrees Celcius, and a lower heater (which handles the final 10 mLs of the volume) at 80 degrees Celcius. The system is operated at a vacuum of negative six pounds per inch relative to atmospheric pressure. The concentrator utilizes a series of fiber-optic sensors attached to the boiling chamber to determine when the correct concentration end-point is reached. The concentrate is allowed to cool and the residual volume (about one mL) is then transferred to the transfer chamber. Clean solvent

(40 mLs) is delivered to the boiling chaber at the top of the column and the rinseate is concentrated and transfered to the transfer chamber in the same manner. This wash cycle is repeated two more times. The extract in the transfer chamber is then brought to volume (10 mLs in this application) and the final volume transfered to the output vial where it is ready for analysis or manual cleanup. A final wash step is initiated, with solvent flushing out all transfer lines and valve blocks, the boiling chamber, transfer chamber, and output chamber to waste. All waste solvent is captured, including the vaporized solvent from the concentration stages, in a condensor-equipped waste container.

This system was placed in a ventilated benchspace at Assagai Analytical Laboratory (Albuquerque, NM) and used typical laboratory utilities such as 110V power and compressed nitrogen. Service to the Mini-SAM system was performed by technicians from within the CAA program as well as designated technicians from Assagai. Service included the preparation of samples and transfer of extracts through the stages of the system as well as maintenance required in the operation of Mini-SAM system.

Prior to daily analytical operations, the concentrator was cleaned with acetone by transfer procedures, followed by a straight hexane concentration run. All glassware was washed thoroughly with soap and water and rinsed with de-ionized (DI) water, acetone, and hexane, in that order.

The Mini-SAM system uses a 1:1 mix of acetone and hexane in the sonication SLM as the extraction solvent and pure hexane in the concentration SLM as the exchange solvent. The hexane used was a pesticides grade Chempure Brand obtained through Curtin Matheson Scientific (Houston, TX). The sodium sulfate was a 12-60 mesh granular type of 'Baker Analyzed' grade, while the acetone was 'Baker Resi-Analyzed' (Phillipsburg, NJ).

The surrogate and spike mixtures were prepared to a final concentration of 1ppm. The surrogate used was a tetrachloro-*m*-xylene (TCMX)/decachlorobiphenyl (DCBP) mix at a stock concentration of 200 ppm made by Accustandard Incorporated (New Haven, CT). The mixture used for the pre-operation setup of the concentrator was an Aroclor 1242 spike made from a stock concentration of 1000 ppm. The spike mixture for the blank and sample matrix spike duplicates was Aroclor 1260, also at a stock concentration of 1000 ppm. Both Aroclor standards were made by Chem Service Inc. (West Chester, PA).

The CAA Program Validation Team requested that sample soils contaminated with PCB's at or above the limit of quantitation (.05 mg/mL) be provided by Assagai. A split was portioned off from each contaminated soil sample previously manually extracted by Assagai for their customers. The samples were heterogeneous in nature; waste-treatment sludges, pieces of asphalt, and rocky soils represent three of the soil matrices comprising the test selection. All of the samples had a high moisture content.

Prior to extracting samples, recovery tests were performed in order to verify the working condition of the equipment and to establish optimal operating parameters for the HVC. The operating temperatures for the boiling chamber and operating vacuum for the system were established so that maximum recoveries could be obtained. Once the optimal parameters were determined, they were programmed into the HVC, and actual sample runs were performed.

An aliquot (30 grams) of the soil sample was weighed into a 500 ml sample beaker, the weight of the sample recorded, and 60 grams of sodium sulfate added. The two portions were mixed by hand to a fine, dry consistency. If moisture was still evident, an excess of sodium sulfate was added to the sample. When the sample was completely mixed, it was spiked with surrogate compounds and, where appropriate, a matrix spike mixture. The sample was then ready for extraction.

The prepared beaker was placed within the automated sonicator system along with a solvent-rinsed 500 ml output beaker and the automated analytical procedure was then initiated. Solvent was added to the sample and the extraction process began. Intervention in the transfer of fluids from the input beaker to the output beaker on the sonicator was not considered a system failure in this beta demonstration. The failure to transfer was, however, recorded as an error in the sample handling in order to track this particular manipulation error. At the completion of the sonication operation, the solvent output beaker was removed from the sonicator and manually inserted into the

automated concentration system. The sonicator system was then restored by hand in preparation for the next sample.

Along with the sonicator output beaker with extract, a 14 dram sample vial was placed within the automated concentrator and the procedure initiated. The product of the concentrator was an extract of 10 ml in the 14 dram vial. This sample was then ready for manual cleanup by using a Florisil column cleanup technique (EPA Method 3620A) and by administering a sulfuric acid shakeout (EPA Method 3665). A 1 ml aliquot of the final cleaned extract was consequently separated for GC/ECD analysis.

Analysis of the extracts was completed by Assagai Analytical Laboratories using an Hewlett-Packard (Palo Alto, CA) 5890 Gas Chromatograph with an HP 19233 Electron Capture Detector and a DB5 column by J&W Scientific (Folsom, CA). Analysis was performed in a manner consistent with SW-846 methodologies. Daily standards, sequence logs, and other appropriate information was maintained regarding the sample batch that was processed with the Mini-SAM system.

Results and Discussion

Thirteen environmental soil samples were extracted,and concentrated using the mini-SAM over a two-day period with five of the samples run twice, resulting in a total of eighteen extracts prepared for analysis. Three of the soil samples were found to have no detectable PCB contamination at the method detection limit; the remainder of the samples were contaminated with Aroclor 1254, Aroclor 1260, or a combination of the two. Additionally, a commercially available QC sample, two blanks, a blank spike duplicate set, and a matrix spike duplicate set were extracted and concentrated, bringing the total number of samples run to twenty-five. The QC and five of the environmental samples were not analyzed due to a mix-up at the analytical lab, however, limiting the data set to thirteen environmental samples.

A comparison of the results of the conventional and the automated processes includes the PCB contamination and surrogate recoveries. Percent relative recovery of surrogate was determined by dividing the Mini-SAM recovery by the conventional method.

SURROGATE RECOVERIES, % **% RELATIVE RECOVERY**

		Mini-SAM			Conventional			
Sample	Dilution	TCMX	DCBP	Dilution	TCMX	DCBP	TCMX	DCBP
1A	1	**73**	**93**	1	**66**	**62**	**110**	**150**
2B	5	**85**	**135**	5	**95**	**110**	**89**	**123**
3B	1	**69**	**73**	1	**72**	**75**	**96**	**97**
4A	5	**80**	**85**	5	**80**	**100**	**100**	**85**
5A	5	**85**	**120**	5	**90**	**105**	**94**	**114**
6A	10	**100**	**120**	10	**80**	**110**	**125**	**109**
7A	100	**100**	***300***	50	**100**	***150***	**100**	**200**
8A	25	**100**	**150**	25	**100**	**125**	**100**	**120**
9A	10	**100**	**90**	10	**80**	**100**	**125**	**110**
10A	1	**103**	**104**	1	**77**	**84**	**134**	**124**
11A	1	**91**	**89**	1	**85**	**90**	**107**	**99**
12A	1	**83**	**80**	1	**81**	**0**	**102**	**N/A**
14A	5	**90**	**105**	5	**90**	**100**	**100**	**105**

There is a clear correlation of the surrogate recoveries of the Mini-SAM in relation to the conventional method. The exception is Mini-SAM sample 7A, which was so highly contaminated with co-extracted material that the Assagai analyst determined that the final conventional dilution (which in all other cases served as the initial Mini-SAM dilution) was not sufficient and

subsequently diluted the sample to 100:1. Both the Mini-SAM and conventional extracts of this sample were at much higher dilutions than the rest of the sample extracts and similarly had much higher apparent values for DCBP. Both the conventional and Mini-SAM DCBP concentrations for sample 7A are out of criteria (QC limits for DCBP are 60 to 150 %), which may be due to detection of this surrogate at the lower limit of the calibration curve. In addition to this anomaly, DCBP was not detected in the conventional extract of sample 12A. This analysis was done several weeks prior to the Mini-SAM test and no explanation was given by the analytical lab. However, the overall surrogate recovery trend is definite; the mean percent relative recovery for TCMX is 106 and for DCBP is 120. Also, there is comparatively minimal surrogate interaction with matrix. These facts indicate that the extraction efficiency of the Mini-SAM is certainly comparable to the conventional method.

ANALYTE RECOVERIES, mg/Kg

	Mini-SAM				**Conventional**			
Sample	Dilution	1254	1260		Dilution	1254	1260	
1A	40	**ND**	**ND**		1	**ND**	**ND**	
2B	5	**ND**	**0.2**		5	**ND**	**0.22**	
3B	1	**ND**	**0.04**		1	**ND**	**0.02**	
4A	5	**ND**	**ND**		5	**ND**	**0.11**	
5A	5	**0.11**	**0.13**		5	**0.28**	**0.21**	
6A	10	**0.4**	**0.45**		10	**0.82**	**0.56**	
7A	100	**2.8**	**1.8**		50	**5.4**	**1.8**	
8A	100	**2.8**	**ND**		25	**1.1**	**ND**	
9A	100	**2.1**	**2.8**		10	**0.25**	**0.33**	
10A	1	**ND**	**ND**		1	**ND**	**ND**	
11A	1	**ND**	**ND**		1	**ND**	**ND**	
12A	1	**ND**	**ND**		1	**ND**	**ND**	
14A	5	**ND**	**ND**		5	**ND**	**0.05**	

Interpretation of the analyte results between the Mini-SAM and the conventional samples is complicated by dissimilar dilutions required by significant matrix interferences in the Mini-SAM extracts. In these cases (Mini-SAM samples 1A, 7A, 8A, and 9A) relevant peaks are measured at the lower detection limit of Assagai's calibration curve. This factor may contribute to the differences in the reported values between the Mini-SAM and the conventional analyses.

Many additional factors may effect the comparison of recoveries and explain discrepancies between the Mini-SAM and the conventional extract analyses. First, electron capture detectors have been noted as having a limited linear range. Second, the relevant calibration curves utilized quadratic equations which inherently describe a non-linear range, thus decreasing precision and accuracy at the limits of quantitation. Additionally, the analytical lab involved establishes a new initial calibration every week. Several curves were in place between the analyses of the conventional extracts, and those of the Mini-SAM. All of these factors may combine to result in the slight differences observed between the Mini-SAM and the conventional analysis. For instance, in samples 3B, 5A, 6A, and 8A the Aroclor recoveries from the Mini-SAM are roughly half those of the conventional method, yet the peak areas are approximately five percent those of the conventional extract analyses. Surrogate areas for these samples are identical both in the Mini-SAM and in the conventional analysis.

It should be noted that the presence of contaminants in the conventional extracts are verified by Mini-SAM results except in the samples 4A and 14A. The presence of these false negatives is disturbing. Aroclor 1260 patterns are discernible by the analyst, but the peaks are obfuscated by an elevated baseline which is the result of significant matrix interferences. The resultant peaks are below the limit of detection at this dilution, and so were not reported by the analytical lab.

Sample 9A was extracted on the second day of operation (September 15, 1996) as a matrix spike and matrix spike duplicate in addition to the original sample cut. In addition, a blank spike and blank spike duplicate (LCS and LCSD) were extracted on September 14 as requested by Assagai personnel. Results are given below.

ANALYTE RECOVERIES, mg/Kg

	Mini-SAM				Conventional		
Sample	Dilution	1254	1260		Dilution	1254	1260
9A	100	**2.1**	**2.8**		10	**0.3**	**0.38**
9A MS	10	**0.42**	**0.83**		10	**0.26**	**0.52**
9A MSD	10	**0.41**	**0.39**		10	**0.27**	**0.75**
LCS	1		**0.026**				
LCSD	1		**0.025**				

SURROGATE RECOVERIES, %

Sample	TCMX	DCBP
9A	**100**	**90**
9A MS	**120**	**140**
9A MSD	**100**	**110**
LCS	**87**	**78**
LCSD	**77**	**71**

The comparative recoveries of the blank spike and spike duplicate demonstrate reproducibility of the extraction and concentration of a single homogenous blank (in this case, simply 30 grams of sodium sulfate spiked with a .0333 mg/Kg Aroclor 1260 solution). As is the case with surrogate compounds, the Aroclor does not interact strongly with blank spike and blank spike duplicate samples since they are only sodium sulfate overspiked with the Aroclor standard. There is little interaction between the surrogate comounds and the sample matrix; these compounds are therefore easily dissolved when placed into the extraction process. From the results of the sample, matrix spike, and matrix spike duplicate, it is immediately clear that matrix effects due to inhomogeneity are indicated. The Mini-SAM matrix sample 9A, at a dilution an order of magnitude greater than the other five samples, reports contamination levels that are similarly elevated. The conclusion of both the analytical lab and the CAA analysts is that matrix effects are indicated.

Other problems encountered by the CAA Mini-SAM were results of co-extracted material. During the test, silt and organic material clogged the valves and contaminated the glass elements (boiling chamber and transfer chamber) in the HVC and plugged the filter apparatus in the sonicator. The sonicator method was changed to include filter paper advances more often. This action solved the problem of the sonicator filter plugging.

The filtering system on the sonicator operates under vacuum, with the extracted solvent being drawn through the filter. This results in less thorough capture of co-extracted particulates. These particulates form a film within the HVC which inhibits valve performance and contaminates much of the system, thus introducing possible analyte carry-over. After the first sample was concentrated and this contamination was visually evident, the HVC system was washed extensively with soap and water, DI water, acetone, and hexane. A manual filter step was introduced between the extraction and concentration processes. This procedure prevented further contamination of the HVC. The sonicator filtration issue is currently being investigated by CAA staff at Idaho National Engineering Laboratory.

As a standard operating procedure, the HVC is cleaned with neat acetone prior to each days' run. This was the only additional purging procedure that was needed for the duration of the test. This process has been incorporated in the third generation HVC, with a secondary solvent option included in the automated method.

In addition to particulate contamination, problems were encountered with the sensing capabilities of the HVC given certain types of extracts. Several of the samples, it was noted earlier, were waste-treatment sludges; they were heterogenous in nature and probably contained detergents in matrix. An emulsion formed during the boiling of the extract in the HVC and the consequent foaming led to problems in detection of the concentration end point. This issue has yet to be addressed thoroughly due to difficulty in reproducing the same effect without the original sample extracts. It should be noted however that all blank samples processed through the Mini-SAM system showed no sign of contamination greater than the lower detection limit for this analysis.

4.0 Conclusion

Given the small data set, the results of the test are conclusive only for the surrogate extraction. The recoveries are comparable and higher than those of the conventional method. Analyte recoveries are non-conclusive, with analytes being detected as per the conventional method, but without a definite correlation in concentration. However, several analytical issues were identified. There were differences in the detector calibration curves between the conventional and the Mini-SAM and the curves used were not a linear but rather a quadratic curve. Furthermore, many of the analytes quantitated were at the limits of the curves' "linear range". These factors, in addition to matrix non-homogeneity, may account for the differences in values reported for the aroclors. Extensive testing at Los Alamos National Laboratory proved extraction and concentration accuracy and precision prior to the Beta Test at Assagai. The reliability of the equipment given a wide array of environmental soil sample types will be addressed as the primary concern in future tests.

During the Mini-SAM test the issue of reliable performance was only effected by real-world environmental sample matrix. The matrices were non-homogenous and dissimilar to each other and to prior CAA environmental samples. Subsequently the results of the processes of extraction and concentration were unpredictable. With proper adherence to method guidelines (drying and thoroughly grinding the sample) and manipulation of instrument parameters, however, many of the problems encountered were minimized and unassisted operation was possible.

Conclusions from Assagai personnel were favorable given the reduced size of the equipment footprint (1/3 of the space of the conventional system requirements), the ability to collect waste solvent (which can then be distilled for re-use), the closed-system format (reducing analyst exposure to hazardous chemicals and fumes), and the potential for unattended runs. They were concerned with the problems in automation caused by some of the sample matrices, however. They observed that the efficient removal of fine particles by the sonicator and consistent detection of concentrate by the HVC are critical to the practical use of the system. These concerns are paramount to the CAA Team and efforts have been redoubled to provide absolute reliability as well as exceptional recovery performance.
