BENZENE MONITOR SYSTEM REPORT (U)

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BENZENE MONITOR SYSTEM REPORT (U)

SUMMARY

Two systems for monitoring benzene in aqueous streams have been designed and assembled by the Savannah River Technology Center, Analytical Development Section(ADS). These systems were used at TNX to support sampling studies of the full-scale "SRAT/SME/PR" and to provide real-time measurements of benzene in Precipitate Hydrolysis Aqueous(PHA) simulant. This report describes the two ADS Benzene Monitor System (BMS) configurations, provides data on system operation, and reviews the results of scoping tests conducted at TNX. These scoping tests will allow comparison with other benzene measurement options being considered for use in the Defense Waste Processing Facility (DWPF) laboratory. A report detailing the preferred BMS configuration statistical performance during recent tests has been issued under separate title: Statistical Analyses of the At-line Benzene Monitor Study, SCS-ASG-92-066.

The current BMS design, called the At-line Benzene Monitor (ALBM), allows remote measurement of benzene in PHA solutions. We have demonstrated the ability to calibrate and operate this system using peanut vials from a standard HydragardTM sampler. The equipment and materials used to construct the ALBM are similar to those already used in other applications by the DWPF lab. The precision of this system ($\pm 0.5\%$ Relative Standard Deviation(RSD) at 1 sigma) is better than the purge & trap - gas chromatography reference method currently in use. Both BMSs provide a direct measurement of the benzene that can be purged from a solution with no sample pretreatment. Each analysis requires about five minutes per sample, and the system operation requires no special skills or training. The analyzer's computer software can be tailored to provide desired outputs. Use of this system produces no waste stream other than the samples themselves (i.e. no organic extractants).

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INTRODUCTION

In January 1992, the DWPF need for a benzene analysis method was first discussed with ADS. This measurement is needed to provide the benzene content of PHA before transfer from the Precipitate Reactor(PR) to the Precipitate Reactor Bottoms Tank(PRBT). The benzene concentration needs to be less than 30 parts per million(ppm) before transfer in order to guarantee that benzene vapor in the PRBT off gas system does not exceed the benzene Lower Explosive Limit(Reference 2). The sample from PR will contain approximately one weight percent suspended solids. This sample(PHA) will be at about 50 degrees centigrade (°C), have an acidic component of about 0.1 molar(M) formic acid, and a salt content of around 0.5 M(Reference 3). The PHA solids are black in color and prevent direct measurement of benzene in solution by absorption spectrophotometry.

ADS experience with absorption spectrophotometry has demonstrated its usefulness for remote process measurements(Reference 4). This technique is well adapted to remote measurement by use of fiber optics. To minimize the amount of space required in the shielded cells and the number of contaminated system components, only the sample interface is contained in the shielded cells. Electrical control lines and fiber optics provide the connection to system components located in the clean area.

In addition to the size requirements imposed by available equipment space inside the DWPF shielded cells, plumbing changes in the current DWPF sampling system are strictly limited. The first BMS delivered to TNX in mid March was an online analyzer designed to operate unattended in a continuous mode. This analyzer would make measurements based upon operator-selected sampling frequency and control the instrument's process interface. This first analyzer (Figure 1) worked satisfactorily to support initial mixing & sampling tests on the PR (Reference 5). This system was capable of meeting the size restrictions given by DWPF but would require plumbing changes. Several key problems were identified in this first system: 1) solenoid valve failures resulted from sample plugging and corrosion, 2) sample vessel filling and emptying were dependent on process flows and pressures that were difficult to control, and 3) quality control(QC) checks would require an additional valve and fluid pump.

The most recent design is called an At-Line Benzene Monitor(ALBM). This system: 1) requires no DWPF plumbing changes, 2) uses no valves, and 3) uses a standard DWPF sampling vial for each measurement (Figure 2). This new design allows for QC samples and recalibration when needed without any changes from the sample measurement configuration. However, process solutions must be manually sampled using existing laboratory sampling techniques. This sample is then transferred to the ALBM and measured from the sample container. User input is required to initiate analyzer measurement of each sample. Training requirements are minimal for the cell operators and lab analysts because the ALBM prompts the user at each step.

The ALBM described above was delivered to TNX in July 1992. This system was used for additional testing of the PR sampling system and documentation of benzene loss rate from the full scale SRAT/SME/PR. Similar results for benzene loss from PR were obtained from the ALBM system as from earlier use of the online analyzer(Reference 1). The online analyzer measured one sample every four minutes while the ALBM system required about six minutes per sample. The recent statistical studies conducted by Defense Waste Processing Technical(DWPT), Applied Statistics Group (ASG) and ADS show that the ALBM system is capable of excellent precision and accuracy even under process conditions. In summary, the ASG report documents that the ALBM is capable of making bias free benzene measurements in the needed concentration range. The statistical study also provides an evaluation of instrument calibration, a comparison of synthetic and process solutions, and documentation of process studies. With the current ALBM, the 95% confidence interval for a 30 ppm standard is 28.9 to 32.0 ppm.

DISCUSSION

Operation of the online and ALBM systems are based upon the same principles:

1. Volatile organic compounds can be purged from aqueous solutions using air or other gases.
2. For fixed volumes of liquid and gas, the vapor concentration of a volatile organic has an equilibrium value.
3. The equilibrium concentration of volatile organic in the confined space above a solution is related to the initial concentration of volatile organic in solution.

The benzene concentration of PHA cannot be measured directly in the sample solution by absorption spectrophotometry because not enough light can get through the sample solution (too black). To get around this problem, the ALBM uses a pump to recirculate air through the liquid sample in closed loop. The air containing purged benzene vapor is continuously pumped through an optical cell and back into the sample container where it bubbles through the sample solution (Figure 3). This process is called a "Recycling Purge". The UV spectrum of benzene is very unique(Figure 4) and can be readily identified for quantitation using an ultraviolet-visible (UV-Vis) spectrophotometer. The concentration of benzene in a sample is directly related to the amount of UV light absorbed at certain wavelengths as light passes through the optical cell. Figure 5 explains the principles used in absorption spectrophotometry for calculating component concentrations from absorption data.

We can monitor the change in benzene concentration versus time from start of purge sequence(i.e. measurements are started when the recirculating air pump is switched on). The change in benzene concentration with time is called a purge profile (Figure 6). The purge profile is affected by sample temperature, gas flow rate, salt content of sample and analyzer gas volume. The purge profile can be used to detect leaks in tubing or other analyzer components, because under normal operation the benzene vapor concentration will reach a maximum and stay at this

level until the system is vented. In a leaking system, the benzene vapor concentration will reach a maximum then decline at a rate determined by the leak size.

The ALBM uses the peanut vial sample container as the purge vessel. In this system, the purge time is set at three times the equilibrium time indicated by purge profiles for a given sample type. This 3X factor allows for minor differences in sample temperature, ionic strength and purge gas flow rate. The vapor volume of the ALBM system is about ten times the sample volume. This causes most of the benzene to be extracted from a typical PHA sample (~90% at 30 ppm). The ALBM's attainable sensitivity and detection limit are functions of 1) analyte extraction efficiency/sample volume relationship and 2) the optical cell path length.

The optical cell is maintained at a set temperature ($\pm 0.1^{\circ}\text{C}$) above the maximum sample temperature to prevent condensation of sample on the optical cell windows. Condensation on optical components causes scattering of light similar to fogging-up a bathroom mirror. Increasing optical cell temperature above the maximum dew point has a negative effect of reducing the benzene absorption signal. Observation of the online system benzene measurements plotted against time, before temperature control was stabilized ($\pm 5^{\circ}\text{C}$ swings), revealed a sawtooth pattern that correlates with optical cell temperature. As optical cell temperature increased, the measured benzene concentration decreased thus demonstrating an inverse relationship between absorption signal and optical cell temperature. Benzene absorption, in the expected concentration range (up to 100 ppm in solution) is linear with concentration (Figure 7). Because samples in this concentration range behave according to Beer's Law, increasing path length will give lower detection limits and greater sensitivity. Air flow through the optical cell is stopped for absorption measurements except when collecting a purge profile.

The pump used to move the air/benzene mix through the ALBM is a miniature diaphragm pump. The diaphragm and seals are made of viton and the other wetted components are Kynar. This pump operates on 6 - 12VDC for flow control. Pump speed is set to minimize transfer of sample solutions from the purge vessel into the sample vial interface which also serves as a vapor-liquid separator. Connections between the pump, optical cell, and sample vial interface are made with approximately 3/32 inch inside diameter (ID) Viton tubing (#14). This size allows excellent friction fit with 1/8 inch outside diameter (OD) stainless steel tubing. The optical cell (Figure 8) and sample vial interface (Figure 9) are manufactured from stainless steel and have Swagelok tube connections for analyzer plumbing. The purge tube is fitted with a 2 μM stainless steel frit supplied by Mott Metalurgical Supply Company to produce small air bubbles. This process reduces the time required for benzene to reach equilibrium in the vapor space.

The connections to the optical cell are 1/8 inch tubing for air/benzene flow and 1/2 inch Swagelok stainless fittings for fiber optic lens assemblies. The fiber optic lens assembly (Figure 10) provides a seal for the optical cell and allows light from the fiber optic to pass through the air/benzene mix. Light from a UV-Vis light source (located outside the cell) is focused onto the end of a fiber optic. This fiber optic is

run into the shielded cell and attached to the first lens assembly. Light from this fiber is collimated by the lens, travels through the optical cell and is refocused by a second lens onto another fiber optic. The second fiber optic is attached to a Diode Array Spectrophotometer(DAS) on the outside of the shielded cell. The DAS(Hewlett Packard 8452), IBM PC compatible computer, pump power supply & temperature control (supplied by SRTC Equipment Engineering Section), and light source are housed in a single cabinet outside the shielded cell. For UV measurement applications, the current spectrophotometer is limited to about 20 meters of fiber optic cable in each direction(i.e. a total of 40 M).

Cables from the optical cell temperature control and pump power are run into the shielded cell along with the fiber optics. The optical cell is heated with two 150 watt cartridge heaters that operate on 110 volt(v) alternating current(AC). The optical cell temperature is measured by a Resistance Temperature Detector(RTD) and controlled with a proportional temperature controller (Figure 11). Temperature is maintained independently without input from DAS or computer. The pump is switched on/off by using pin #25 of the DAS serial part. This pin of the DAS is software controlled, and allows +5v direct current(DC) supplied on another pin of the serial interface to complete a circuit to ground when closed. Completing this circuit closes a relay to supply current at selected voltage to the air pump (Figure 11).

An IBM Industrial Computer with HPIB (IEEE-488) interface controls the DAS. Any IBM PC compatible computer may be used although a 16MHz or faster machine with math coprocessor is recommended. Sample absorbance data and instrument control signals are passed back and forth via the HPIB interface. Sample measurements are made based upon software set-up parameters. These parameters include wavelength range, integration time, and number of scans for the spectrophotometer. The spectrophotometer uses this data to control a shutter on the UV-Vis light source.

The ALBM measures the absorption signal of benzene between a wavelength range of approximately 240 and 270 nanometers(nM). The light source is a deuterium lamp that has high UV output between 190 and 350 nM(Figure 12). This lamp is held in a housing that allows alignment of the lamp filament so that light can be aligned and focused with appropriate spot size on a fiber optic. The spectrophotometer shutter is mounted between the focusing optics and the fiber optic adapter. The lamp is provided with a power supply that provides very stable light intensity. This type lamp typically has a 1500 hour lifetime and a one year shelf life. Alignment and focusing of the light source is aided by software supplied with the ALBM.

The software used on this analyzer is a revision of code used for several years at SRTC. This program provides many options for system operation, but has been adapted for specific user interface needed by the ALEM. In general, this code (1) reads instrument setup parameters from disk, (2) requests necessary user input like sample identification, number of samples and timing information for start of analysis then (3) controls sample measurement sequence and (4) calculates benzene

concentration from absorption spectrum. Benzene concentration is calculated based upon a Principle Component Regression(PCR) model calculated during instrument calibration. The PCR model is essentially a multidimensional calibration curve that compensates for the effects of other sample constituents on benzene concentration.

Calibration of ALBM will not be needed on a frequent basis. Because absorption spectrophotometry uses a ratio technique, corrections are continuously made for changes in lamp intensity, plus fiber and other optical changes. A new calibration may be required to compensate for changes in system configuration like replacing spectrophotometer or optical cell. Other changes like lamp, fibers, pump, shutter or computer should not require a new calibration. The process of building calibration models for prediction of unknown samples' benzene concentration includes data processing to enhance the benzene signal.

Because the benzene signal has relatively narrow peaks, a second derivative can be used to separate benzene signal from large slowly changing background signal (Figure 13). This improves the quality of benzene measurements especially in the presence of other organic vapors like formic acid. Since this type model uses many different wavelengths to compute benzene concentration, the computer is able to provide a warning signal when the measured spectra do not "look" like benzene. Compounds similar to benzene like toluene or phenol have very different absorption spectra(Figure 4) and would produce a large residual ratio. The residual signal is a goodness of fit statistic used to alert operators of possible interfering chemicals.

Samples are measured on the ALBM according to the following general steps:

- 1) Sample is collected using the normal Hydragard™ sampler then placed one at a time in the ALBM sample vial holder.
- 2) The ALBM computer is provided with the sample ID and told to initiate measurement sequence. The instrument begins by making a reference measusrment with air containing no benzene in the optical cell.
- 3) The operator is prompted to raise the sample holder using a lever action like found on the Hydragard™ sampler. This engages the sample vial with the ALBM sample vial interface, and the sample analysis is started.
- 4) The sample is purged by recirculating air through the sample. An absorption spectrum of benzene in air is measured after a set purge time, and this spectrum is used to calculate sample benzene concentration.

This same data collection sequence is followed for each sample. When standards are measured for instrument calibration, the absorption spectrum is saved on disk for later calculation of a calibration model. Software for creating calibration models also runs on the IBM PC or compatible computer. To maintain QC charts, a standard is substituted for a sample in the above sequence and analyzed in the same manner as a sample.

Normal operation of the ALBM should include analysis of QC standards. The most logical concentration of standard to assure excellent instrument performance is 30 ppm because this is the benzene level established for the safe transfer of PHA from PR to PRBT. Standards prepared in 10% methanol solution have been shown to have similar characteristics to standards prepared in PHA(Reference 1). The first step in preparation of these standards is dilution of pure benzene to approximately 1760 ppm in pure methanol(1 part in 50). This allows preparation of 30 ppm standard by addition of approximately 3.4 ml stock solution for 200 mL of standard. These standards are stable for at least two (2) hours when kept in peanut vials with viton solid septa and nearly zero head space. The 1760 ppm stock solution has been stored for up to 2 weeks in a freezer without noticeable change.

Operating experience and system evaluation conducted at TNX has provided excellent operational insight. The primary component of error that must be controlled by procedures is filling of the sample vial. Visual checks and/or solution mass checks should be used to make sure vials are filled within specified limits. Small variations in sample volume will not cause measurements to exceed control limits when peanut vials are completely filled. The fill volume is a parameter that must be matched with calibration because fill volume affects vapor/gas volume, total benzene available for purge and air extraction efficiency. Efforts to correct for these volume changes(i.e. half filled vials) have not been effective.

As currently used at TNX, the ALBM does not produce any waste other than the samples themselves. Therefore, this instrument has the added benefits of supporting waste minimization and the resulting cost savings over solvent extraction methods. The components selected for use in the shielded cells should be functional at high dose rates for reasonable lengths of time (up to 50 megarads for lenses). This system shows promise for being packaged with a very small footprint design that can be maintained for daily operation.

The next ALBM model (beta test unit) will incorporate features necessary for shield cell installation and maintenance. These fixtures include:

1. Individual components with weights < 12 lbs.
2. Quick disconnect fittings for power/control cables.
3. Sealed components for corrosion protection of motor windings, etc.
4. Longer pathlength optical cell with 1/2" diameter light path.
5. Wing nuts for access to in cell system components.
6. Customized software based upon DWPF operating requirements.
7. Use of a faster(386) PC compatible computer.

The changes in optical cell(#4 above) are desirable because: 1) The current system uses an air volume expander tube to improve air extraction efficiency. This additional volume is better used in the optical cell. 2) Increasing light path diameter will improve light throughput thus allowing a longer pathlength and faster measurements. 3) The increased path length will help improve analyzer sensitivity and detection limit. However, the pathlength will also have to be balanced with required length and quality of fiber optic cable to be used. To circumvent this

difficulty, a different spectrophotometer and detector could be substituted for the Hewlett Packard DAS. Use of this improved detector will allow extension of fiber optic beyond the present 20 meter limit.

Additional work should be done before completion of the ALBM Beta test model to optimize the system vapor volume. Some adjustment of this parameter is provided by the optical cell light path diameter and length; however, these dimensions must be balanced against the limits given for component size and weight that can be moved into the shielded cells. Optimum vapor volume can be measured using the current ALBM and then divided between the optical cell and sample interface during design of the beta test unit.

At present, we view use of this system like any other lab instrument for QA purposes. The software is documented by comments in source code and a manuscript user's manual (Reference 6), and the system reliability will be checked by repeat measurements of QC standards.

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9	Liquid-Vapor Seperator/Sample Vial Interface
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12	Deuterium Lamp Spectrum
13	Benzene Absorption Spectra - 2nd Derrivative Correction for Background Signal

FIGURE 1

ONLINE BENZENE MONITOR SYSTEM COMPONENTS

FIGURE 2

ONLINE ANALYZER SAMPLE INTERFACE

FIGURE 3

ATLINE BENZENE MONITOR SAMPLE INTERFACE

FIGURE 4
UltraViolet Spectra of Aromatic Compounds

FIGURE 5

Absorption Spectroscopy

$$A(\nu) = - \text{Log} (I(\nu) / I_0(\nu))$$

$$\text{Conc.} = A(\nu) * E(\nu) / \text{Pathlength}$$

Measure Intensity of light at many colors
without sample present -- $I_0(\nu)$
and with sample present -- $I(\nu)$

FIGURE 6

FIGURE 7

FIGURE 8
Optical Cell Drawing

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FIGURE 10
Fiber-Optic Lens Assembly

- (1). Mount 1/2" barrel of reducer in lathe - remove 1/4" fitting
- (2). Drill and tap reducer for 1/4-36 tap - install SMA adapter
- (3). Ream inside of reducer with #8 tapered ream (.3971-.5050)
- (4). Tap 1/2" reducer with 1/8" MPT tap
- (5). Smooth ID of reducer with 450 grit emory cloth
- (6). Srink TEFLON tubing on lens and trim
- (7). Press lens and tubing into reducer until flush
- (8). Heat assembly to 150 deg C - then press lens into reducer again
- (9). Repeat step #8 until lens no longer creeps during heating

FIGURE 11
Temperature & Pump Control Circuits

Temperature Control

Pump Control

FIGURE 12

FIGURE 13

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