# REGULATORY OFF-GAS ANALYSIS FROM THE EVAPORATION OF HANFORD SIMULATED WASTE SPIKED WITH ORGANIC COMPOUNDS

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#### ABSTRACT

After strontium/transuranics removal by precipitation followed by cesium/technetium removal by ion exchange, remaining low activity waste in the Hanford River Protection Project Waste Treatment Plant is to be concentrated by evaporation prior to being mixed with glass formers and vitrified. To provide a technical basis to permit the waste treatment facility, a relatively organicrich Hanford Tank 241-AN-107 waste simulant was spiked with 14 target volatile, semi-volatile and pesticide compounds, and evaporated under vacuum in a bench-scale natural circulation evaporator fitted with an industrial stack off-gas sampler at the Savannah River Technology Center. An evaporator material balance for the target organics was calculated by combining liquid stream mass and analytical data with off-gas emissions estimates obtained using EPA SW-846 Methods. Volatile and light semi-volatile organic compounds (<220°C BP, >~1 mm Hg vapor pressure) in the waste simulant were found to largely exit through the condenser vent, while heavier semi-volatiles and pesticides generally remain in the evaporator concentrate. An OLI Environmental Simulation Program evaporator model successfully predicted operating conditions and the experimental distribution of the fed target organics exiting in the concentrate, condensate and off-gas streams with the exception of a few semi-volatile and pesticide compounds. Comparison with Henry's Law predictions suggests the OLI ESP model is constrained by available literature data.

#### **IMPLICATIONS**

While the EPA SW-846 off-gas sampling methods are typically used for determination of plant emissions below regulatory limits, this study appears to be one of the first attempts to extend this methodology for closing a unit operation material balance, particularly on the bench-scale for multiple classes of compounds. If successfully applied, these methods such as Methods 0010 and 0031 in combination with others can also be used to obtain detailed process information sufficient for process validation and process model building, both valuable to plant designers as well as oversight and regulatory bodies.

#### **INTRODUCTION**

At the Hanford Site, 56 million gallons of aqueous low activity waste (LAW) are currently stored in over 177 single- and double-shell storage tanks<sup>1</sup>, some of which were suspected to be leaking

and sending plumes of radioactive waste toward the Columbia River. In the coming years, the Hanford River Protection Project Waste Treatment Plant (RPP-WTP) pretreatment and vitrification processes will be designed and built to process this waste into an immobilized form. The current RPP-WTP process for Hanford tank supernatant liquids generally calls for: 1) filtration to remove precipitated strontium (Sr-90) and transuranic (TRU) metals, 2) Cs and Tc ion exchange processes using elutable organic resins, 3) concentration by evaporation of the decontaminated waste, followed by 4) vitrification of the concentrated waste mixed with glassformers. Prior to the filtration step, precipitation of some wastes, the so-called "Envelope C" waste in Tanks 241-AN-102 and 241-AN-107, with strontium and permanganate solutions will be required due to high strontium and TRU levels and poor filterability of raw supernatant liquids. Since the wastes have been found to contain low levels of regulated organic compounds<sup>2</sup> originating from the PUREX<sup>3</sup> solvent and laboratory wastes dumped into the tanks, low activity waste melter feed evaporation has been regarded as an important source of emissions to be included in the RCRA (Resource Conservation and Recovery Act) off-gas emissions permit application to the State of Washington. The purpose of this work was to provide an experimental basis for emissions estimates from the evaporation of aqueous wastes contaminated with various classes of organic compounds, and provide data for the development of computer process models that will also be used for the permit application process and risk assessments. Other outputs from this work were preliminary evaporator operating data for flow sheet development and evaporator design, such as operating pressure and temperature, expected concentration endpoints, foaming and scaling potential, compositions of the evaporation condensate and concentrate, distribution of fed organic compounds into the aqueous output streams, and physical properties of the product concentrate. The knowledge gained and the model developed based on this study can be applicable elsewhere in the Hanford RPP-WTP process, such as ion exchange eluate evaporation and possible pre-processing waste concentration, and also served as the working basis for bench-scale radioactive evaporator testing using an actual Hanford Tank 241-AN-102 waste sample<sup>4</sup>.

The EPA (Environmental Protection Agency) SW-846 off-gas sampling methods were developed under the authority of Title III of the Clean Air Act Amendments in 1990<sup>5</sup>. These methods are typically employed for sampling plant emission stacks for determination of

regulated compound concentrations, although these and similar techniques have been used for other activities such as ambient air sampling<sup>6</sup> and tank vapor space sampling<sup>7</sup>. Sorbent cartridge-based off-gas sampling methods quantify both mass of analyte captured from the off-gas and off-gas sample volume, both of which can be completely diverted to an off-gas sampler from small bench-scale equipment, as well as offer good capture efficiencies and recoveries for a wide range of organic compounds. If combined with mass and organic concentration data from aqueous streams, a potentially viable extension of these off-gas sampling techniques was for use to obtain a material balance on fed organics for an operating bench-scale evaporator. A reasonable literature search did not reveal similar use of the EPA SW-846 Methods in the recent published technical literature, particularly the combination of industrial-scale sampling and bench-scale equipment as was demonstrated here.

#### EXPERIMENTAL

### Setup

The Hanford RPP-WTP low activity waste melter feed evaporator will be a forced circulation type similar to the Hanford 242-A evaporator that is currently used to concentrate Hanford supernatant wastes<sup>8,9</sup>. The evaporator is a forced circulation evaporator that is designed to operate at an absolute pressure of 40 to 80 torr<sup>10</sup>. A bench-scale thermosiphon evaporator (Figure 1) was used in this investigation to best mimic the plant-scale evaporator design on a laboratory-scale. Construction was mainly of glass and polytetrafluoroethylene (PTFE) to minimize potential organic absorption/adsorption losses, with the metal parts limited as much as possible to little- or non-contact surfaces. Thermocouples and resistance temperature detectors measured the evaporator (T2), condensor (T3) and condensate (T4) temperatures, and an Incoloy<sup>®</sup> heating rod (with internal thermocouple T1) served as the heating element in this natural circulation evaporator. Pressure (PG) and temperature measurement devices of stainless steel construction as well as material addition/removal ports were secured using stainless steel fittings mounted in PTFE plugs. Feed, condensate and concentrate were introduced into or removed from the system through PTFE lines and valves (V1-V3). Continuous feed addition and concentrate removal (semi-batch for condensate) at a nominal 9.6 and 6.6 mL/min, respectively, was performed using peristaltic pumps equipped with a segment of Viton<sup>®</sup> tubing.

Natural leak rates of as low as 0.2 mL/min (STP) were achieved for this ~5200 mL internal volume system without the use of vacuum grease. A measured air in-leakage was added using a mass-flow controller to create a total evaporator in-leakage (11.5 ml/min) scaled on a percentage of system volume basis for expected air in-leakage in the full-scale plant.

#### **Simulant Development**

Although this work is part of a series of evaporation studies, the AN-107 waste represented a "worst-case" where interactions between high organic content in the waste and the regulated organic compounds were expected to be most significant. Actual AN-107 waste contains relatively high concentrations of organic complexants added for strontium and cesium recovery during PUREX waste reprocessing, and this characteristic is reflected in the simulated waste. Precipitated and filtered AN-107 ("Envelope C") simulated waste feed material at 5.5 M Na was introduced into the evaporator from 1L polyvinyl fluoride (PVF) bags. Prior to processing, each simulated waste bag was injected with an acetone spiking solution containing 14 target volatile, semi-volatile, and pesticide compounds to a target of 1 ppm, similar to maximum concentrations in actual wastes observed by Klinger et al.<sup>2</sup>. The 14 selected compounds were a reduced list from the 20 organic indicator chemicals<sup>11</sup> selected from an original list of 192 based on limited tank data and regulatory lists<sup>12</sup>. Chemical instability in caustic waste solutions led to the elimination of some species, while toxicity concerns led to the replacement of the polychlorinated biphenyl (PCB) and dioxin/furan chemical classes by a semi-volatile surrogate, bis(2-ethylhexyl)phthalate (BEHP), selected based on thermal stability and vapor pressure criteria. Direct addition of these target organic compounds into the aqueous simulated waste solution was not possible due to the low levels and low solubilities of many of the analytes. Hence, a spiking solution containing the 14 target analytes required development. Acetone was selected for the spiking solution solvent after careful consideration and experimentation balancing many factors such as sufficient solubility of all compounds in a single solvent, high aqueous solubility, and non-interference with regulatory analyses. Anti-entrainment of liquid to >99% was achieved using a rolled stainless steel mesh (supplied by Koch-Otto York Corp.) mounted above the evaporator, and was experimentally verified. Saito et al.<sup>13</sup> describes in further detail the spiked feed development, experimental setup, design, and planning.

#### **Sample Analysis**

The total evaporator condensor vent gas (off-gas) and PTFE-diaphragm vacuum pump bleed air, ~400-450 mL (STP)/min used to adjust evaporator pressure, were sent to a volatile organic sampling train coupled with a metering console that is designed for use for EPA SW-846 Methods 0010 and 0031. Method 0031 was selected over Method 0030 for volatiles off-gas sampling since actual Hanford waste was suspected to contain volatile organic compounds (VOC's) that are more volatile, polar, and difficult to collect than those for which Method 0030 was designed. Two Tenax<sup>®</sup>-GC and one Anasorb<sup>®</sup>-747 sorbent tube were mounted in the offgas sampler for volatiles sampling as called for in Method 0031 "Sampling Method for Volatile Organic Compounds". The three-tube train was replaced with a single XAD-2<sup>®</sup> sorbent tube as specified in Method 0010 "Modified Method 5 Sampling Train" for off-gas sampling of the semi-volatiles and pesticide classes as well as PCB's and dioxins/furans via a surrogate. Tenax<sup>®</sup>-GC, Anasorb<sup>®</sup>-747 and XAD-2<sup>®</sup> sorbent tubes each contained 1.6, 5.0 and 4.6 g of sorbent, respectively, with each glass sorbent tube measuring approximately 10 cm x 1.6 cm ID. After an initial boildown to raise the evaporator concentration from 5.5 to 8.0 M Na, steady state operation ( $50 \pm 3^{\circ}$ C,  $60 \pm 8$  mm Hg,  $40 \pm 1^{\circ}$ C condensor) was performed for ~75 hours continuously, with the total run time divided equally between each off-gas sampling method. The ~75 hour steady state operation was dictated primarily by the need to generate 6 liters each of condensate to follow semi-volatile and pesticide EPA SW-846 Method regulatory liquid analysis protocols rigorously. Splitting the long run time permitted collection of approximately 25 L (STP) of condensor vent gas during each off-gas sampling event, fulfilling the 20 L requirement for Method 0031 and coming as close as reasonably possible for Method 0010's 3000 L (3 m<sup>3</sup>) sampling volume requirement. To minimize run time and to remove any potential effects from evaporation shutdown and restart, an "on-the-fly" transition from volatiles (Method 0031) to semi-volatiles/pesticide off-gas sampling (Method 0010) was accomplished in less than 35 minutes as the evaporator continued operation. For the post-experiment material balance, regulatory liquid samples were collected simultaneously with the off-gas samples, and together were sent to an EPA-qualified vendor laboratory for EPA SW-846 regulatory analysis. As required by the customer, all regulatory sampling and sample analyses were performed per the strictest interpretation of the SW-846 protocols as was permitted by the experiment.

#### **RESULTS AND DISCUSSION**

Prior to the regulatory evaporation experiment, critical operating parameters were estimated by process modeling as was done successfully for earlier Hanford waste simulant runs<sup>14</sup>. After resolving charge balance issues caused by conflicting analytical data, an electrolyte process model using the Environmental Simulation Program (ESP) licensed by OLI Systems, Inc. (henceforth called the "OLI model") was formulated to predict the evaporation temperature and pressure, and the bulk saturation point for the simulant. The bulk solubility limit of a multi-electrolyte solution is defined here as the point where the solution becomes either saturated with one or more of the major salt species, or supersaturated with other minor salt species to the extent that the total insoluble solids formed exclusively out of minor constituents exceeds 0.5 wt% of the entire solution. The predicted operating pressure of -27.6 in Hg vacuum (60 mm Hg) at 50°C was experimentally verified in a preliminary boildown experiment, and the predicted bulk solubility limit of 11.4 M Na was remarkably within ~10% of the observed ~10.3 M Na. Based on these results, an evaporation endpoint of 8.0 M Na for the concentrate was selected to meet customer specifications to concentrate up to 80% bulk solubility.

Overall, 38.9 L of spiked simulant was fed producing approximately 27.4 L of concentrate and 12.6 L condensate, which was within 2.5% of the target as verified by evaporator concentration factors. Generally, the experiment went smoothly with the system operating the majority of the time at the desired steady state conditions. On a few occasions, the concentrate produced became either too dilute or concentrated by  $\pm 1.2$  M Na at the extreme, generally caused by changing pumping flow rates as the experiment progressed. These effects were minimized by periodic material balance checks and concentrate density measurements by pycnometer. Mass of spiked feed material fed into the evaporator and mass of concentrate and condensate extracted were recorded throughout the experiment. Overall mass and volume balance closures on the 75 hour steady-state evaporation (Table 1) were to within 2%, with closures to within 5% and 1% for the volatiles and semi-volatiles off-gas sampling portions of the run, respectively. The densities assumed for the volume balances are from experimental measurements of the feed before experiments and of the concentrate during the experiment. Efficient operation of the evaporator was verified by the high decontamination factors (DF = ratio of the concentration of analyte in the evaporator feed and condensate) calculated for both major and

minor analytes (Table 2). Additional supporting evidence for high DF's are the non-detectable levels (<0.01-10 mg/L) of metals (except Si) and anions in the condensate when analyzed by inductively-coupled plasma emission spectroscopy (ICP-ES) and anion ion chromatography (IC). In fact, many of the calculated DF's were limited to relatively low numbers by analyte minimum detection limits in the condensate samples. More sensitive analytical methods such as ICP-mass spectroscopy (ICP-MS) and pH would be required to accurately evaluate evaporator performance.

Approximately 130 regulatory off-gas and liquid samples were collected and sent for analysis during the two off-gas sampling events. Review of the regulatory process, field, trip and reagent blank data shows that contamination was a minor issue in 22 of the approximately 72 blanks, with most detected analytes being only slightly above detection limits or at levels far below those detected in associated samples. The remainder did not show detectable quantities. Many of these "positive" results never impacted results since "positive" trip blanks were discounted due to non-detectable levels in associated field blanks, and one case was a water reagent blank for dilution that was never needed. As a result, only about 10 sample results had to be adjusted slightly as a result of detected contamination. After an in-house quality assurance review of the regulatory data supplied by the vendor analytical laboratory, the corrected regulatory analytical data was then combined with the experimental mass balance data to understand the fate of the 14 target organic compounds fed into the evaporator. Table 3 lists the average concentrations of the 14 target organic compounds detected in the feed using best available data. Table 4 lists the calculated quantity and standard deviation of each target organic compound entering or leaving through each evaporator stream for the overall experiment.

Given the 20-130% acceptable analyte recoveries specified for this work, acceptable mass balances (-30 to 80% mass closure) were obtained for all species except for 1,2-dibromoethane, 1,2,3-trichloropropane and pentachlorophenol where small measured quantities and/or large analytical losses were expected for these compounds due to hydrolysis<sup>15</sup>. Typical acceptable recoveries are of order 50-150% with of-order relative deviation of 25%, with actual method-specific precision and accuracy usually determined by repeated testing with the actual system in the field. Future regulatory evaporation studies should consider excluding halogenated aliphatic

compounds given the rapid degradation in caustic solutions observed within the short experimental exposure times relative to the age of the Hanford tank wastes. Similar material balances were performed individually for both the volatiles and semi-volatiles/pesticide off-gas sampling periods and were not found to change the results or trends significantly.

Table 4 shows the target organic volatiles and the more volatile semi-volatiles (1,2,4)trichlorobenzene and naphthalene) with  $<220^{\circ}$ C boiling points (BP) and  $>\sim1$  mm Hg vapor pressures largely exit the evaporator through the condensor vent, generally leaving small quantities in the concentrate and slightly greater quantities in the condensate. The remaining semi-volatiles (BP>242°C) were found to predominantly remain in the evaporator concentrate with small quantities being captured in the condensate. No significant quantities of the lessvolatile semi-volatiles were detected in the off-gas sampling train, although a few percent of the hexachlorobenzene and pyrene fed were found to have condensed in the condensor vent line. The shaded *italic* cells in Table 4 signify that there is analytical uncertainty (lack of accuracy/precision) in the values due to data qualification by the vendor analytical laboratory and/or the Savannah River Technology Center (SRTC) Environmental Geochemistry Department. Regulatory feed analyses for 4-methyl-2-pentanone (methyl iso-butyl ketone, MIBK), 1,2-dibromoethane, and pentachlorophenol were qualified as inaccurate, which could explain the discrepancies in the material balances observed. The same is true for hexachlorobenzene in the condensate. The quantity of 1,2,3-trichloropropane fed into the evaporator during the experiment is a calculated value based on previous aging studies. The actual quantity was expected to be between the analytical laboratory 800 µg/L minimum detection limit and the 140 µg/L obtained by delayed analysis of an in-house sample. The vendor analytical laboratory also expected that the recovery of 1,2,3-trichloropropane in the offgas sampling tubes would be low due to chemical degradation on the sorbent material or during extraction. Shaded/italicized pesticide numbers were deemed uncertain as insufficient sample was set aside for these analyses leading to high detection limits. MIBK totals are thought to be higher than the theoretical input due to extraction of this compound, often used for plastic coatings, from the PVF bags.

The regulatory data from the vendor analytical laboratory were used to the maximum extent possible. However analytical problems and issues required that some of the data be replaced by analytical results from in-house analysis of identical samples, or that regulatory data be used that were qualified as inaccurate or "uncertain" by the vendor Quality Assurance Department or the SRTC's Environmental Geochemistry Department. Regulatory semi-volatiles and pesticide analytical results for both feed and concentrate samples were replaced by SRTC in-house analytical results. The EPA SW-846 Methods require that semi-volatiles and pesticide samples be acidified to pH=2 prior to analysis. However the vendor laboratory noted that the samples bubbled on acidification, emitting a brown gas thought to be NO<sub>x</sub>, and that much lower than expected target semi-volatile organic compound concentrations were obtained. It is believed that the added acid is reacting with the abundant nitrite in the Hanford AN-107 simulated waste to form the highly reactive nitrous acid which is oxidizing and consuming the target organics. As the SRTC analytical method concentrates the analytes through the use of liquid-liquid extraction with methylene chloride, the in-house results for both feed and concentrate semi-volatiles and pesticides were deemed more accurate and were used in the analysis, except pentachlorophenol. It is believed that sample acidification is necessary to render the phenol in the more hydrophobic protonated form that would then be more readily extracted by methylene chloride.

The volatiles off-gas data were deemed uncertain for two primary reasons. First, low surrogate recoveries, average 8% for Anasorb sorbent tubes and an acceptable but low 34% average for Tenax sample tubes, were initially reported. A regulatory sample Tenax and the Anasorb tube had to be methanol-extracted according to soils and solid waste SW-846 Method 5035 since the quantities of target components on the first thermally-desorbed Tenax tube overloaded the analytical equipment detector. As the low quantities of spike material (50  $\mu$ g each component) combined with permananent sorption losses onto the sorbent material were thought to be causing the reported low recoveries, recovery testing using the maximum quantity of analyte observed on each regulatory sample tube (3000  $\mu$ g on Tenax, 30000  $\mu$ g on Anasorb) was performed by BWXT Services, Inc. The recoveries obtained with these larger spiked quantities improved to 15% for Anasorb and 88% for Tenax. The low average surrogate recovery for Anasorb are due to <11% recoveries of benzene, toluene, and chlorobenzene by methanol extraction. The recoveries, as is

standard practice. Second, due to the sorbent tube analysis difficulties, the obtained analytical volatiles quantities for one volatiles Tenax sample tube is known to be approximate and low due to detector overload. As a result, all sorbent tube recovered quantities were deemed approximate, although the target organic compound distribution trends appear unaffected and reasonable material balances were obtained since the bulk of the analytes were on the Anasorb tube. An important note is that all Anasorb and one sample Tenax tube were solvent extracted to yield the analytical results. Hence, the process, field, and trip blank Tenax tube results were thermally desorbed for analysis and those results (where significant) were not affected by the aforementioned difficulties.

While the material balance results for the 14 target organic compounds was satisfactory given the experimental design, clearly improvements can be made to reduce the variabilities in the target analyte recoveries from the off-gas stream. First, this experiment was to serve as the first of two attempts to obtain this data, but customer schedule did not permit a second test. Additionally, the EPA SW-846 Methods call for repetition of the test until variances are reduced. Therefore, this single test addressed several issues simultaneously such as equipment functionality, sampling, and analyte distribution without the benefit of feedback to improve the process. Second, subsequent review of the technical literature revealed that the experimental reliance on the Anasorb-747 tubes to capture the bulk of the volatiles in the Method 0031 off-gas sampling was not recommended by the EPA Method developers. Fuerst et al.<sup>16</sup> found that Anasorb-747 sorbent efficiently traps non-gaseous volatile organic analytes but does not quantitatively release them by thermal desorption, and strongly recommended that Method 0031 be utilized to capture the bulk of the analytes on the two preceding Tenax sorbent tubes. Attempts to achieve quantitative recovery by increasing thermal desorption temperatures from 180°C to 350°C were unsuccessful<sup>17</sup>. Given the aforementioned low spike recoveries, methanol solvent extraction of the Anasorb-747 used in this investigation is suspected to have encountered similar but unquantifiable difficulties. In future testing, obtained Tenax sorbent capacities will be combined with the distribution data in Table 3 to shorten volatiles sampling times, and multiple off-gas samplings to different sorbent loadings will be used to account for possible analyte breakthrough. Another possible experimental improvements include lowering the spiking levels slightly from

the 500-1000 ppb range to the approximate 300 ppb observed for acetone, the most concentrated volatile found in Hanford wastes sampled thusfar<sup>2</sup>.

The OLI model, which was successfully used earlier to predict evaporator operating conditions and bulk saturation, was also used to predict the relative partitioning of each target organic compound between condensate, concentrate and off-gas streams (Table 5). This work was a major effort that exhausted model input capacity with 21 organic salts (e.g., Na<sub>2</sub>H<sub>2</sub>EDTA), 45 inorganic salts, and 15 organic species (14 target organic compounds + acetone solvent). The model was built on an equilibrium speciation of 17 vapor species, 50 undissociated aqueous species, 90 ionic species, and 24 solid species, requiring a simultaneous solution of 132 nonlinear equilibrium relationships in addition to the usual mass and charge conservation equations. Both the OLI software and in-house databases were employed in this work. The relative distributions of the 14 target organic compounds, fed at an assumed 1 ppm, generally match well with the experimental results, with the exception of pentachlorophenol, pyrene and Aldrin (Table 5). Aforementioned analytical issues for pentachlorophenol quantification account for this discrepancy.

The model predicted a separate organic phase in all aqueous streams rich in Aldrin, BEHP, pyrene and naphthalene, which appears contrary to experimental results. A minute organic phase rich in Aldrin, BEHP, pyrene, naphthalene and 1,2,4-trichlorobenzene was predicted for the feed stream, but was not experimentally observed in the PVF bags of spiked feed simulant or in the evaporator. A possible reason for the predicted separate organic phase is that the OLI model was unable to account for the secondary interaction between water and acetone which would assist dissolution of the heavier semivolatiles. However, other possibilies not accounted for include interactions of the semi-volatile target compounds with the lighter relatively more soluble volatile species and/or the organic complexants present in the AN-107 waste simulant. To determine the OLI model accuracy with respect to the predicted organic phase, benchtop experiments using vials with 20 mL simulant spiked with the following solutions were performed: 1) 14 target organic spiking solution in acetone with 1 wt% dye, 2) same dyed spiking solution with an additional 0.2 mL bis(2-ethylhexyl)phthalate, and 3) 1 wt% dye in acetone. Sudan Red 7B was used due to its high selectivity for the organic phase as

demonstrated in tests with benzene in simulated Savannah River Site waste<sup>18</sup>. A simulant solution containing the dyed spiking solution and an additional 0.2 mL BEHP showed a very strong red organic layer atop the simulant, demonstrating a negative test result, while the simulant sample with only dyed acetone yielded a simulant with specks of crystallized dye. Tiny globules of a dyed phase floating near the top of the vial was observed in the simulant spiked with the dyed spiking solution, suggesting the presence of an organic liquid phase as predicted by the OLI model. When this solution was heated in a water bath to 50-55°C, the dyed globules were observed to rapidly dissolve into the simulant. As the spiked feed was withdrawn from the top of headspace-less PVF bags, these post-experimental tests strongly suggest that the separate organic phase entered the experimental system, and dissolved in the 50°C evaporator pot before partitioning into the various evaporator effluent streams. While addition of these organic phase components was not as uniform throughout the 75 hour run as planned, the approximately 40 PVF bags of spiked feed used did distribute the addition of these compounds adequately as demonstrated by the nearly identical target component material balances obtained during both the volatile and semi-volatile organic off-gas sampling periods. While the impact on the concentrate and off-gas streams caused by the presence of an organic phase was likely minimal, the quantities of Aldrin, BEHP and pyrene observed in the condensate phase may be low as the condensate was withdrawn from the condensate tank from the bottom and the second phase was not observed to disappear at 40°C. The lack of an observed accumulated second phase after 75 hours of operation is inconclusive. Interestingly, the material balance for naphthalene is good despite the OLI model prediction as a major component in the organic phase.

To put the OLI model results into context and examine other possible sources for discrepancies between the model predictions and experimental data, theoretical vapor-liquid equilibrium calculations were performed using Henry's Law and an idealized Raoult's Law. Henry's Law was selected for its common use as an empirical model at low organic concentrations in aqueous systems, such as in organic-contaminated groundwater modeling. An idealized Raoult's Law, assuming an ideal solution in both the liquid and vapor phases, was selected as a baseline to understand the effect of vapor pressure on organic partitioning. As has been used previously for many non-ideal systems, the Henry's Law constant was calculated using the following expression obtained in the literature<sup>19,20</sup>:

$$H = \frac{C_{gas}[g/L]}{C_{liquid}[g/L]} = \frac{P^{vp}M_w}{RTS}$$
(Eq. 1)

where H is the dimensionless Henry's Law constant, C<sub>gas</sub> and C<sub>liquid</sub> are the concentrations of the compound of interest in the gas and liquid phases, T is absolute temperature, R is the Universal Gas Constant, and  $P^{vp}$ ,  $M_w$  and S are the pure organic compound vapor pressure, molecular weight and aqueous solubility, respectively. The Henry's Law constant defined as the ratio of the gas and liquid concentrations assumes ideal gas behavior and that the solute concentration in the liquid phase is very dilute, both reasonable assumptions for the experimental evaporator system. The accuracy of eq 1 has been verified at SRTC for benzene in caustic salt solutions<sup>21</sup> through experimental measurement of both aqueous and gas phase concentrations. Equation 1 has also been used at SRTC for estimating Henry's Law constants for 1-butanol in caustic salt solutions<sup>22</sup> and benzene in sodium tetraphenylborate solutions<sup>23,24</sup> where experimentally measured solubility data were combined with pure compound vapor pressure data from the literature. In the calculations for this study, pure compound vapor pressure for the 14 target organic analytes were also taken from the technical literature. Aqueous solubility data were used as no solubility data were available for these target organic compounds in Hanford waste salt solutions. As a first approximation, competition between the "salting out" effect of the high ionic strength aqueous phase and the expected increase in organic solubility due to the high organic complexant concentrations in the AN-107 aqueous waste was thought to permit the replacement of experiment-derived waste solubility data with aqueous solubility data.

These empirical models were applied to the vapor-liquid equilibria in the evaporator pot and the condenser. The vapor-liquid equilibrium concentrations were calculated at 60 mm Hg absolute pressure (-27.6 in Hg vacuum), with evaporator and condenser operating temperatures of 50°C and 40°C, respectively. The partitioning of each organic species was calculated by simple mass balance combining design feed (9.6 mL/min), condensate (3.0 mL/min), and air in-leakage (11.5 mL/min) rates with experimentally measured organic input quantities. For example, actual target analyte input rates were calculated dividing the total analyte mass fed in Table 3 with the estimated total sampling time (4050 min). The concentrate flow rate was expected to be 6.6 mL/min, and the total vapor flow rate was the sum of the air in-leakage and 3.0 mL/min water

vapor. Application of Henry's Law or the idealized Raoult's Law reduces the equation to a single unknown, permitting simple algebraic calculation of the vapor and liquid phase target organic compound concentrations. A similar material balance was then performed for the evaporator condenser using the calculated vapor concentrations as the material input. Mole fraction conversions to mass concentrations utilized the ideal gas mixture assumption, a measured average concentrate density, and an average concentrated salt solution molecular weight of 23.1 g/mole calculated by the OLI model.

The calculation results relative to the experimental data are shown in Figures 2 and 3, where individual target organic species distribution between the concentrate, condensate and evaporator off-gas streams is expressed as a percentage of the analyte fed into the evaporator.

In Figure 2, Raoult's Law is shown to overpredict the retention of volatiles and light-semivolatile species in the condensate and concentrate, resulting in minimal off-gas emissions in contrast to the experimental data. The Raoult's Law expected trend of increasing organics retention with increasing target analyte boiling point led to only a slight overprediction of some heavier semivolatiles retention in the concentrate. In contrast, Henry's Law applied using eq 1 compared well with experimental data for the volatile species (Figure 3). Henry's Law correctly predicted the majority of volatile and light semi-volatile analytes to leave the evaporator through the condensor vent. Higher concentration of volatile and light semi-volatile species in the evaporator condensate relative to the concentrate also compares well with the experimental data, except for the chlorinated species 1,2,4-trichlorobenzene and 1,2,3-trichloropropane. Chemical degradation of trichloropropane on the sampling sorbents prior to analysis prevented comparison to predicted off-gas emission. Significant quantities of heavier semi-volatiles were calculated to exit in the evaporator condensate as predicted by the OLI model which is contrary to the experimental data. Significant off-gas emissions of pyrene are likely due to a relatively high vapor pressure used in the calculations. Similarly the extremely low aqueous solubilities assumed appear to lead to the hexachlorobenzene and Aldrin results. Additional calculations revealed that the combination of high solubility and very low vapor pressure can lead to target organic compound retention in the concentrate, and that high aqueous solubility alone can lead to preferential carryover into the condensate. Similar results are obtained if the van der Waals

interactions of the larger semi-volatile species with the large complexing species like EDTA, HEDTA, citrate, gluconate and glycolate in the waste lead to very large increases in organic aqueous solubility (e.g., ~50-100X or more). Interestingly, Henry's Law constants for groundwater remediation obtained from reference literature<sup>25</sup> were found to yield very similar organic distribution results to the calculated Henry's Law Constants results (Figure 4) and the OLI model.

Last, other potentially useful and unusual experimental results for this particular simulated waste will be mentioned, although detailed discussion and calculations can be found in Reference 13. The overall volume balance data indicated that the feed was concentrated by a factor of 1.42, assuming ideal mixing and that the condensate was pure water. Combining this concentration factor with the evaporator feed data, predicted species concentrations in the concentrate were calculated. Given the estimated 10% random error in the analytical data, actual and predicted concentrate metals and total solids concentrations matched very well, being within 12% for the majority of analytes except Si and Zr. Most major anionic analytes including formate and nitrate also compared well with predicted concentrations within 7% of the experimentally-derived quantities. However, the concentration of nitrite, another abundant anion, was overestimated by 25%. Minor anionic species such as phosphate, sulfate, oxalate, and halides were not considered as these could easily precipitate in various salt forms whose concentrations are too low to be detected by X-ray diffraction analysis of insoluble solid samples. Overall, the bulk of the analytical data indicates that the AN-107 Envelope C simulant generally behaves like an ideal mixture in the 5.5-8 M Na concentration range, within measurement error. A similar analysis with concentrate samples taken after a "final" boildown to a "saturated" solution near 10.1 M Na yielded similar results. Good comparison of simulant composition after steady state evaporation with expected Hanford waste concentrations was also found by Fiskum et al.<sup>26</sup> Finally during the "final" boildown of an aliquot of ~8.3 M Na concentrate, evaporator contents within a 1-2 minute period transitioned from a green semi-translucent liquid to a very viscous greenish-white gel at a calculated 10.1 M Na, corresponding to bulk saturation at 48.6 wt% total solids (94.6 g TS per 100 g water) at 50°C. This sudden transition was not observed previously with other Hanford waste simulants for Tanks 241-AN-105 and 241-AZ-102.

#### CONCLUSIONS

A bench-scale evaporation demonstration was successfully performed with the Hanford Tank AN-107 (Envelope C) simulated waste feed spiked with 14 volatile, semi-volatile and pesticide target compounds at 1.03 ppm each. Based on the results of the regulatory off-gas sampling and modeling studies, the following conclusions can be made: 1) the EPA SW-846 Methods were adaptable to bench-scale caustic waste evaporation studies, 2) volatiles and light semi-volatiles (1,2,4-trichlorobenzene and naphthalene) with <220°C BP and >~1 mm Hg vapor pressure almost completely exit through the evaporator condenser vent, 3) heavier semi-volatiles and pesticides generally appear to remain in the evaporator concentrate although slight carryover to the condensate was observed, 4) the OLI Environmental Simulation Program model can successfully predict evaporator operating conditions and complex waste saturation points, and describe distribution for many of the target organic compound, and 5) Henry's Law can be used to predict volatile and light semi-volatile organic compound distributions into the evaporator streams, but further refinement of relevant solubility data may be required to increase the predictive capability for the heavier semi-volatile compounds studied.

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## **Table 1.** Experimental Mass and Volume Balance Results: Overall and by Sampling Event.

		Condensate Concentrate		Mass Balance
Sampling Period/Event	Mass Fed (g)	Generated (g)	Generated (g)	Closure (%)
Volatiles Off-gas	24704	6475	19343	4.5
Semi-volatiles/Pesticide	24881	6107	18531	1.0
Off-gas				
Total	49585	12582	37874	1.7

	Volume Fed	Condensate	Condensate Concentrate	
Sampling Period/Event	(mL)	Generated (mL)	Generated (mL)	Closure (%)
Volatiles Off-gas	19361	6475	13816	4.8
Semi-volatiles/Pesticide	19499	6107	13236	0.8
Off-gas				
Total	38860	12582	27052	2.0
Assumed density	1.276	1	1.4	

**Table 2.** Experimental Decontamination Factors.

Analyte	Feed		Condensate	Calculated DF
Cs (mg/L)	9.24		0.000019	1 E 5
	(AA)		(ICP-MS)	
Sr (mg/L)	80	73	<0.0004	1 E 5
Free OH (M)	0.553	0.561	2.51 E –6	1 E 5
			(pH = 8.4)	
Na (mg/L)	125000	131000	<2	> 1 E 4
Ca (mg/L)	160	143	<0.008	> 1 E 4
Ni (mg/L)	315	283	<0.014	> 1 E 4
Nitrate (mg/L)	145000	138000	<10	> 1 E 4

		Boiling	Average	Std.
Chemical	CAS Number	Point (°C)	Concentration (µg/L)	Dev. (µg/L)
Benzene	71-43-2	80	1430	71
4-methyl-2-pentanone (MIBK)	108-10-1	117	2572	233
Toluene	108-88-3	111	1065	64
1,2-dibromoethane	106-93-4	131	73	9
Chlorobenzene	108-90-7	132	1175	148
1,2,3-trichloropropane	96-18-4	157	990*	
1,2,4-trichlorobenzene	87-61-6	214	590	
Naphthalene	91-20-3	218	567	35
Hexachlorobenzene	118-74-1	322#	813	269
Pentachlorophenol	608-93-5	310	60	29
Pyrene	129-00-0	393	930	0
Bis(ethylhexyl)phthalate (BEHP)	117-81-7	231+	1035	7
Benzo[a]pyrene (BaP)	50-32-8	495	1460	202
Aldrin	309-00-2	242	1037	21

**Table 3.** Measured Average Concentrations of 14 Target Organic Compounds in the Spiked

 Feed

\*predicted from previous spiking tests, \*sublimes, \*at 5 mm Hg

<b>Table 4.</b> Overall Mass Balance for Each	Target Organic Compound During AN-107 Simulan
Regulatory Run	

			Mass (µg) Recovered in						
		Mass			Sorbent	Pump	Off-gas		Mass
	Chemical	Fed (µg)	Condensate	Concentrate	Tube	Traps	Line Rinse	TOTAL	Closure (%)
	Benzene	55550	405	174*	49896	15*	0	50491	9.11
	Std. Dev	2748		111				111	4.50
	4-methyl-2-pentanone (MIBK)	99928	2063*	1833*	66401	373*	0	70670	29.28
	Std. Dev	9068	1644	1099				1977	6.72
	Toluene	41386	326	235*	22736	10*	0	23307	43.68
tiles	Std. Dev	2473		83				83	3.37
'ola	1,2-dibromoethane	2821	523	55*	9335	24*	0	9938	-252.25
1	Std. Dev	346		50				50	43.27
	Chlorobenzene	45660	554	166*	17811	11*	0	18542	59.39
	Std. Dev	5770		27				27	5.13
	1,2,3-trichloropropane	38471	2139*	6222*	0	34*	0	8395	78.18
	Std. Dev		448	3085				3117	8.10
	1,2,4-trichlorobenzene	22927*	1000	1508*	19599	130	0	22238	3.01
	Std. Dev		476	443		35		651	2.84
	Naphthalene	22021*	3712	683*	17024	448	0	21867	0.69
	Std. Dev	1365	1623	461		47		1688	9.83
	Hexachlorobenzene	31574	22	22522*	0	0*	940	23483	25.62
ŝ	Std. Dev	10443	26	3847				3847	27.45
atile	Pentachlorophenol	2332	0	4058	0	0*	0	4058	-74.04
Po-	Std. Dev	1124		716				716	89.36
emi	Pyrene	36140*	1699	20425*	0	28*	719	22870	36.72
Ň	Std. Dev	0	417	2353				2390	6.61
	Bis(ethylhexyl)phthalate	40220	38	24618*	0	0	0	24656	38.70
	(BEHP)								
	Std. Dev	275	75	2231				2232	5.57
	Benzo[a]pyrene (BaP)	56735*	0	31449*	0	0*	0	31449	44.57
	Std. Dev	7859		4975				4975	11.66
Pest-	Aldrin	40285*	315	31449*	0	18*	0	31782	21.11
icide	Std. Dev	809	142	4975				4977	12.46
	Theoretical (each)	50518					*from S	RTC Ana	lytical Result

Table 5.	Experimental and	OLI Model Predicted	Organics Distribution as a
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Percentage of Each Species Fed.

		% of total feed						
		EXPER	RIMENTAL DA	TA	OLI N	Condensor		
	Target Organic	Condensate	Concentrate	Off-gas	Condensate	Concentrate	Off-gas	Vent
								(ug/g)
	Benzene	0.7	0.3 <sup>s</sup>	89.8	0.4	0.0	99.5	723
	4-methyl-2-pentanone (MIBK)	2.1 <sup>s</sup>	1.8 <sup>s</sup>	66.8	11.9	0.2	87.9	963
atile	Toluene	0.8	0.6 <sup>s</sup>	55.0	0.4	0.0	99.6	330
Vola	1,2-dibromoethane	18.6	2.0 <sup>s</sup>	331.7	3.5	0.1	96.4	135
	Chlorobenzene	1.2	0.4 <sup>s</sup>	39.0	0.9	0.0	99.1	258
	1,2,3-trichloropropane	5.6 <sup>s</sup>	16.2 <sup>s</sup>	0.1	4.9	0.1	95.1	0
	1,2,4-trichlorobenzene	4.4	6.6 <sup>s</sup>	86.1	0.9	0.0	99.0	315
	Naphthalene	16.9	3.1 <sup>s</sup>	79.3	2.8	0.0	97.2	274
atile	Hexachlorobenzene	0.1	71.3 <sup>s</sup>	3.0	0.0	100.0	0.0	0
-10	Pentachlorophenol	0.0	174.0	0.0	77.8	19.4	2.8	0
Semi	Pyrene	4.7	56.5 <sup>s</sup>	2.1	88.3	6.0	5.6	0
0)	Bis(ethylhexyl)phthalate (BEHP)	0.1	61.2 <sup>s</sup>	0.0	12.6	87.4	0.0	0
	Benzo(a)pyrene	0.0	55.4 <sup>s</sup>	0.0	0.0	100.0	0.0	0
Pest-	Aldrin	0.8	78.1 <sup>s</sup>	0.0	67.7	31.3	1.0	0
icide								
	<sup>s</sup> from SRTC Analytical Result							



## Figure 1. Evaporator System Schematic



**Figure 2.** Target organic compound distribution from experimental data and Idealized Raoult's Law (RL) calculation

**Figure 3.** Target organic compound distribution from experimental data and Henry's Law calculation (CHL)





**Figure 4.** Target organic compound distribution from experimental data and literature Henry's Law (LHL) calculation

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