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Analysis of antifoam agent degradation products in an evaporator

Fernando Fondeur, Stephen Crump, and Thomas White

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Analysis of antifoam agent degradation products in an evaporator

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ABSTRACT

A wetting agent used to control foaming in the Chemical Processing Cell at the Defense Waste Processing Facility degrades to form compounds that could volatilize to form vapor exceeding the lower flammability limit. Three identified components of concern were hexamethyl disiloxane, trimethyl silanol, and propanal. Analytical methods were developed and implemented on a real waste sample to monitor degradation products. Using standards, an extraction method with dichloromethane and analysis by gas chromatography-mass spectrometry and hydrogen nuclear magnetic resonance was developed. Both methods had detection limits less than 1 mg/L for the analytes.

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Introduction

The Savannah River Site (SRS) currently stores approximately 36 million gallons (Mgal) of high-level radioactive waste (33.4 Mgal of supernate and saltcake, and 2.6 Mgal of sludge) in 43 tanks (8 other tanks are permanently filled with grout). Several evaporators are deployed to reduce the excess water in the tanks and at the Defense Waste Processing Facility (DWPF); a waste immobilization facility where radioactive sludge, radioactive supernate, and glass frit are combined to form molten glass. The molten glass is placed into steel canisters that are temporarily stored at SRS until another storage site is identified. The bulk of the water entering the tank farms comes from operations at DWPF. Antifoam agents are added to the liquid waste to reduce the liquid height in the evaporator and to reduce the concentration of trapped air that may affect the rheology of the liquid waste at the evaporator. The practical usefulness of the antifoam is limited by the harsh conditions in the evaporator.

In a recent study,[1,2] the decomposition of the antifoam solutions (antifoam 747 and Dow Corning Q2-3183A) that are part of the operation of the sludge receipt and adjustment tank (SRAT) and the slurry mix evaporator (SME) was investigated. Preparation of the radioactive sludge and supernate for the addition of glass-forming chemicals occurs in the SRAT while the frit glass is added to the prepared radioactive liquid waste in the SME. In that study, three compounds (see Fig. 1) were identified with chemical and physical properties that may pose risks to the safe operation. In particular, hexamethyl disiloxane (HMDSO), trimethyl silanol (TMSOH), and propanal were identified as volatile components (see Table 1) that can pose a flammability issue and favor the formation of toxic organo-mercury compounds.[3–12]

This work identified three different analytical methods of detecting HMDSO, TMSOH, and propanal. These are (1) purging the supernate with an inert gas, trapping the gas with activated carbon, and desorbing gas into a gas chromatograph-mass spectrometer (GC-MS); (2) extracting the supernate with dichloromethane (DCM) followed by analysis of the DCM with a hyphenated GC-MS tandem (this is the backup method of choice); or finally (3) analyzing the DCM extract by hydrogen nuclear magnetic resonance (^{1}H-NMR) (this is the standby method of choice). The purge and trapping method was only pursued with non-radioactive samples.

This work pursued extracting the supernate with DCM. Extraction efficiencies with chloroform were approximately the same as extracting with DCM. Extracting with DCM involves fewer processing operations and the team was more familiar with this method from previous applications.

Experimental procedure

Standard addition method introduction

The standard addition technique involves adding known amounts (or volumes) of standard solutions to one or more aliquots of the processed sample solution, compensating for a sample constituent that enhances or depresses the analyte signal.[13] When matrix effects are to be expected and/or

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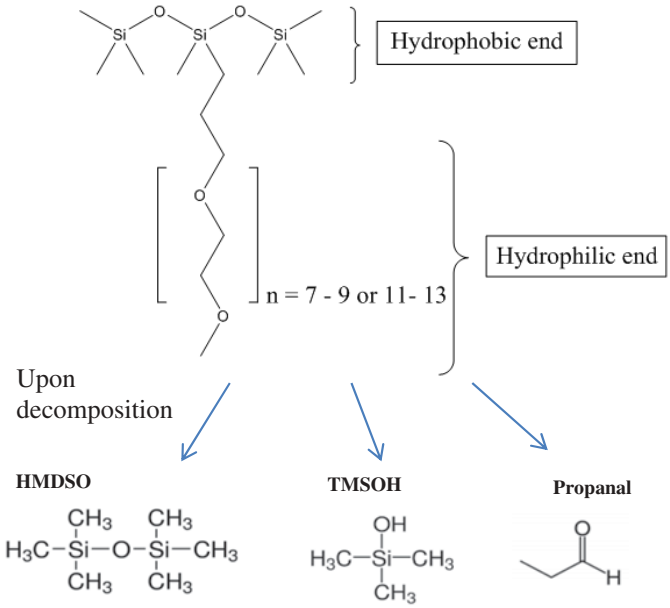


Q4 **Figure 1.** Three byproducts of concern from the decomposition of the antifoam used at DWPF.[1]

matrix-matched calibration samples are not available, standard addition method (SAM) is the method of choice.

In SAM, known aliquots of the analyte are added to the sample (the sample contains an unknown, x_o, concentration of the analyte to be determined). Typically, these aliquots should include approximately 50%, 100%, and 150% of the analyte concentration of the sample (x_o). The instrument response due to the analyte is plotted (or regressed) against the volume of aliquots added (or the final analyte concentration in the sample). The obtained line is extrapolated until it hits the x-axis (or $y = 0$ or zero signal) and from there the x-value is read. The ratio of the intercept to the slope is subtracted from the read x-value to obtain the analyte concentration in the sample. In the majority of the cases, there is no offset in the measurements ($b = 0$) and the point of interception of the abscissa is the actual concentration of the analyte in the sample.[13]

$$y = mx + b \Rightarrow m(x + x_o) + b$$
$$= mx + (mx_o + b) \Rightarrow \boxed{x = -x_o - b/m} \quad (1)$$

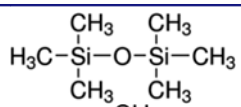
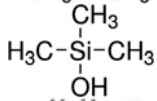
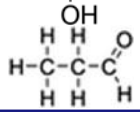
A limitation to this method is that the slope of the standard addition plot should be less than 20% different from a calibration line built with known concentrations of the analyte. The coefficient of determination (the square of the correlation coefficient or r^2) of the fitted line has to be at least 0.995 or better. Interferences (if any) should not vary as the ratio of analyte concentration to sample matrix changes, nor should they be additive as that may cause the baseline to shift. The method is labor intensive and inaccuracies in preparing the spiked samples can change the slope of the line.

Sample preparation

Water samples were first acidified to a pH value of 6.0 using nitric acid. The acidic conditions helped preserve and stabilize the chemicals from decomposition. Recoveries from the acidified water samples ranged from 62% to 75% (with relative standard deviation values ranging from 3% to 5%). Samples were acidified to ensure a complete extraction of TMSOH (prevent hydrolysis of TMSOH). Exact knowledge of the recoveries is not needed to calculate concentrations when calibration lines are built from the SAM method. In the case of the Tank 22H sample, the supernate was neutralized with 3 M nitric acid to a pH value of 6.

HMDSO, TMSOH, and propanal each have a very low solubility in water. To ensure the correct amount of analyte was added to the acidified water, an appropriate amount of each component was first spiked into 1 mL of DCM. The DCM was then added to approximately 4 mL of water (water volume large enough to keep the DCM soluble) and mixed, after mixing, no secondary phase was observed. However, we expected the insoluble analytes to separate from water. All samples were processed for about the same length of time and treated the same way to minimize

Table 1. Physical properties of TMSOH, HMDSO, and propanal.

Compound	Formula	Structure	Molar mass (g/mol)	Solubility in water	Lower flammability limit (vol %)	Boling point (°C)
Hexamethyl disiloxane (HMDSO)	$C_6H_{18}OSi_2$		162.38	0.933 at 23°C (4, 5)	0.8 (6)	100
Trimethyl silanol (TMSOH)	$C_3H_{10}OSi$		90.20	35 g/L at 25°C (6)	1.45 (5)	99
Propanal	C_3H_6O		58.08	310 g/L at 25°C (7,8)	2.6 (6,9)–2.9 (10, 11,12)	46–50

evaporation. Water samples containing 10, 20, 40, and 100 mg/L of HMDSO, TMSOH, and propanal were then contacted with DCM at a 1:1 and 2:1 water-to-DCM ratio (by volume). The DCM extracted from the 1:1 samples was analyzed by semi-volatile organic analysis (SVOA). The DCM extracted from the 2:1 samples was analyzed by ^{1}H-NMR.

Three check samples were prepared to check the SVOA and ^{1}H-NMR analytical methods. Check set #1 included a water sample that was spiked with 20 mg/L of HMDSO and TMSOH in DCM. Three additional check set #1 samples were prepared by spiking the source sample with 5, 10, and 20 mg/L TMSOH and HMDSO to yield a total of four check set 1 samples.

Similarly, but with different levels of TMSOH and HMDSO, check set #2 included a water sample spiked with 15 mg/L TMSOH and 1.5 mg/L HMDSO. Three additional check set #2 samples were prepared and they were spiked with 0.5, 1, and 2 mg/L of TMSOH and HMDSO to make a total of four check set #2 samples.

In the case of the ^{1}H-NMR measurements, a third check sample containing 15 mg/L each of TMSOH, HMDSO, and propanal was prepared. Three additional samples from check set 3 were made and spiked with 10, 30, and 40 mg/L of TMSOH, HMDSO, and propanal, respectively.

For the GC-MS measurements, a 25-m, 0.33-µm capillary column (silica based) was used. For the ^{1}H-NMR experiments, the samples were put in a 7 Tesla magnet where they were pulsed for 2.6 µs (30° pulse) with 10-s delays between the pulses. Time domain and sampling rate were set for quantitation.[14]

Linearity and limit of detection

A typical SVOA chromatogram of TMSOH is shown in Fig. 2. Figure 2 also shows the ^{1}H-NMR spectra of TMSOH (0.122 ppm), HMDSO (0.6 ppm), and the hydrogen in the carbonyl group of propanal (9.75 ppm). All reported ppm shifts are relative to DCM. These peaks were integrated and correlated with the analyte concentrations in the standard samples, as shown in Figs 3 and 4.

As observed from Figs 3 and 4, both the SVOA and ^{1}H-NMR methods are linear in all three components of concern (TMSOH, HMDSO, and propanal) over the range of interest (0–100 mg/L). In the case of the SVOA method, regression was nearly perfect (R^2 = 0.999). In the case of the ^{1}H-NMR method, the fitting was forced to go through the origin (the preferred case for the SAM method). In the ^{1}H-NMR spectra, two spectral features (peaks) were associated with propanal: the HC=O peak at 9.75 ppm, and the CH_3 triplet at 1.06 ppm relative to the magnetic resonance frequency of TMSOH (tetramethyl silane). The signal from the hydrogen adjacent to the carbonyl group (HC=O) was used for quantification. The CH_3 signal (triplet) required J-decoupling and was not further pursued. The wider confidence interval observed in the ^{1}H-NMR method (Fig. 4) compared to the SVOA method (Fig. 3) is possibly due to a

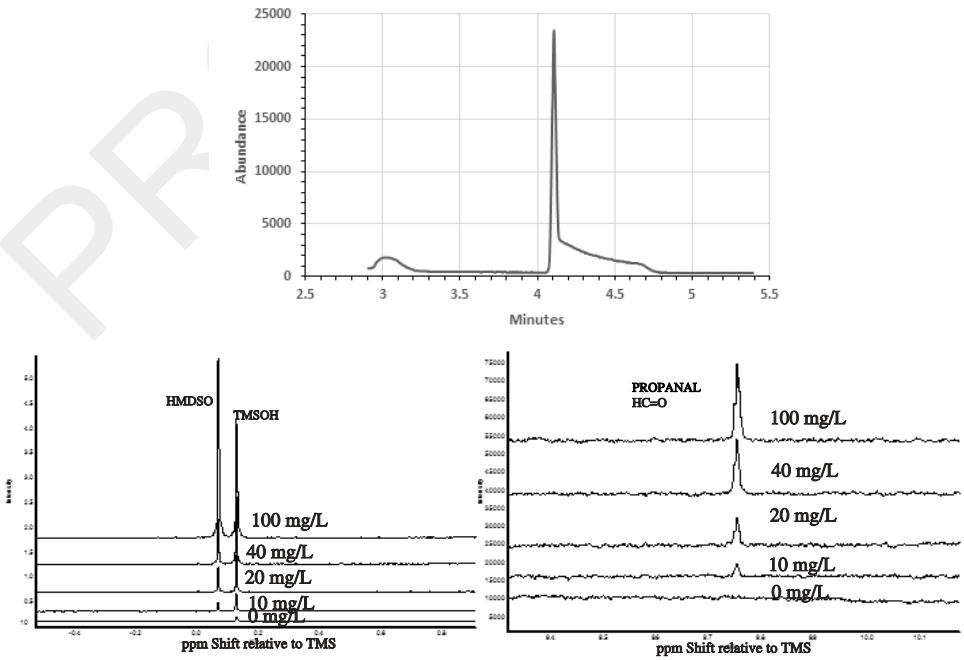


Figure 2. The SVOA chromatograph of TMSOH (top figure). Also shown the ^{1}H-NMR spectra of HMDSO, TMSOH, and propanal in the bottom two figures (TMS: tetramethyl silane).

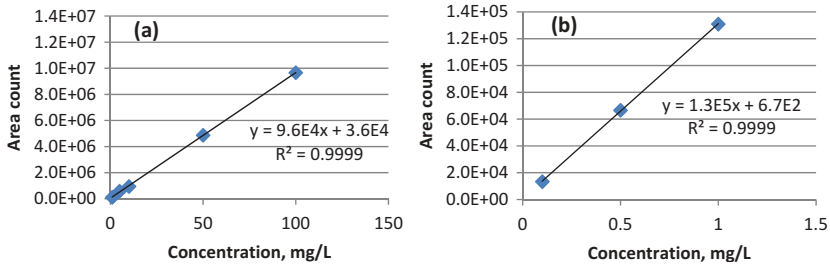


Figure 3. Calibration line obtained from the SVOA method for (a) TMSOH and (b) HMDSO.

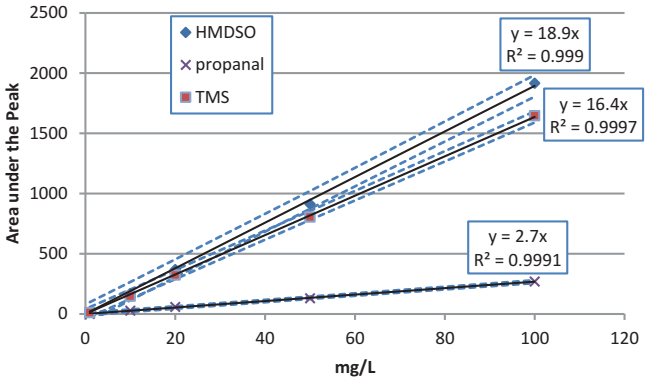


Figure 4. Linearity check of the ^{1}H-NMR for HMDSO, TMSOH and propanal. Broken lines represent the 95% prediction interval.

Table 2. Estimated limit of detection (LOD) for SVOA and ^{1}H-NMR.

Component	SVOA (ppm)	^{1}H-NMR (ppm)[b]
TMSOH	<0.25	0.1
HMDSO	<0.10	0.2
Propanal	NM[c]	0.8[a]

[a]Using the HC=O peak of the propanal spectrum.
[b]LOD was estimated from 3 × σ (or SD)/slope (from Figs 3 and 4). For ^{1}H-NMR, the standard of deviation equals the RMS.
[c]Propanal peak comes out at the same time as the solvent (DCM) peak.
NM: not measured.

larger noise in the NMR signal (mostly heat generated in the NMR probe due to electronics). The linear response observed in both methods indicated that the SAM can be applied to analyze these analytes for an unknown sample. Furthermore, the linearity also suggested that the level of analyte recovery from extraction of water with DCM did not matter.

Based on multiple blank runs in the SVOA method and the "noise level" root mean square (RMS) variation of the spectra in Fig. 4, the limit of detection (LOD = 3σ/slope in the calibration line in Figs 3 and 4) was calculated and reported in Table 2. A similar calculation was conducted with the ^{1}H-NMR data on the "noisy" regions of the spectrum on the left and right of the C=O, TMSOH, and HMDSO peaks.

As noted in Table 2, both methods have LOD less than 1 ppm for all three components of concern. A more rigorous determination of the LOD[15] in Fig. 4 indicates that the LOD is greater than 1 ppm for the ^{1}H-NMR method. Limit of quantitation (= 3.33 × LOD) can be said to range between 1 and 3 ppm for all species. When considering all the sources of noise including sample preparation and sample measurement, the LOD is much larger for the ^{1}H-NMR method and it is approximately 4 ppm for HMDSO, about 2 ppm for TMSOH, and about 5 ppm for propanal (based on the C=O group).

Results and discussion

After establishing linearity and an acceptable LOD of TMSOH, HMDSO, and propanal with both the SVOA and ^{1}H-NMR, we then ran check samples on both methods to verify their performance.

The results from analyzing the check samples are shown in Figs 5 and 6. The data in Figs 5 and 6 reconfirmed the linear behavior previously observed for TMSOH, HMDSO, and propanal in both methods. Given the success with the check samples, the team then measured two samples (duplicates) from Tank 22H.

Samples HTF-22-15-34 and HTF-22-15-35 were first run with SVOA. Sample HTF-22-15-34 was then measured by ^{1}H-NMR. Once agreement was achieved (with the backup method ^{1}H-NMR), the team felt additional ^{1}H-NMR measurements was not needed. The results from the Tank 22H measurements are shown in Fig. 7 and tabulated in Table 3.

As can be seen in Table 3, both methods gave the same results. The noise is larger in the ^{1}H-NMR measurements because a larger range of spiked material was used (up to 40 mg/L) and sample heating occurs during the analysis. Note that no HMDSO and propanal were detected. These components are more susceptible to hydrolysis (in a neutral or caustic environment), radiolysis, and expected to be practically insoluble in water. Detecting these components under harsh conditions

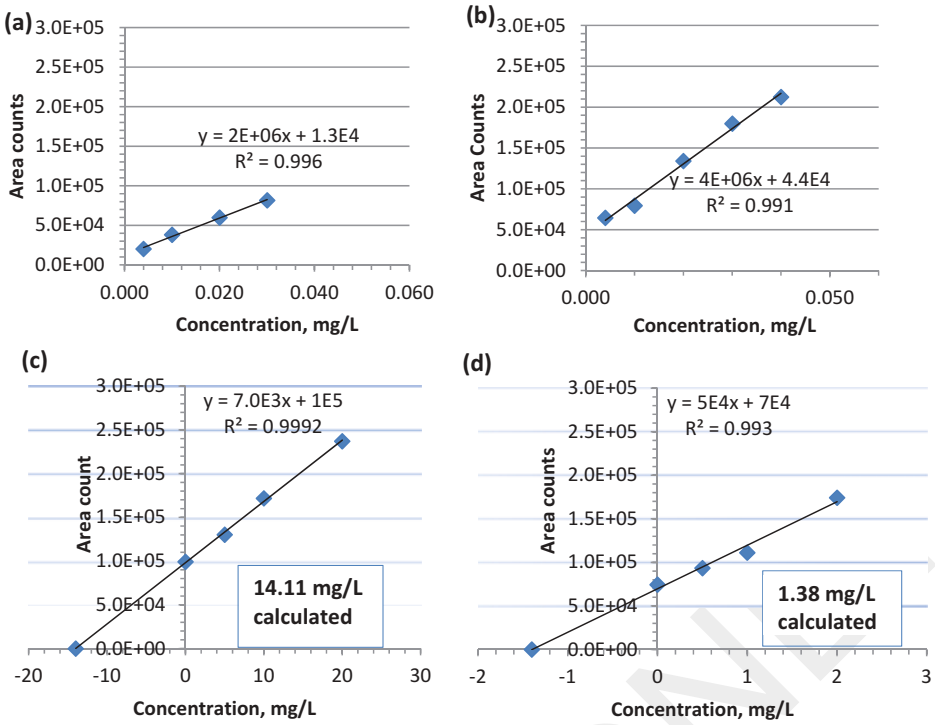


Figure 5. Linearity test and check samples analysis of TMSOH-HMDSO spiked solutions from SVOA: (a) TMSOH, (b) HMDSO, (c) 15 mg/L TMSOH check sample, and (d) 1.5 mg/L HMSO check sample.

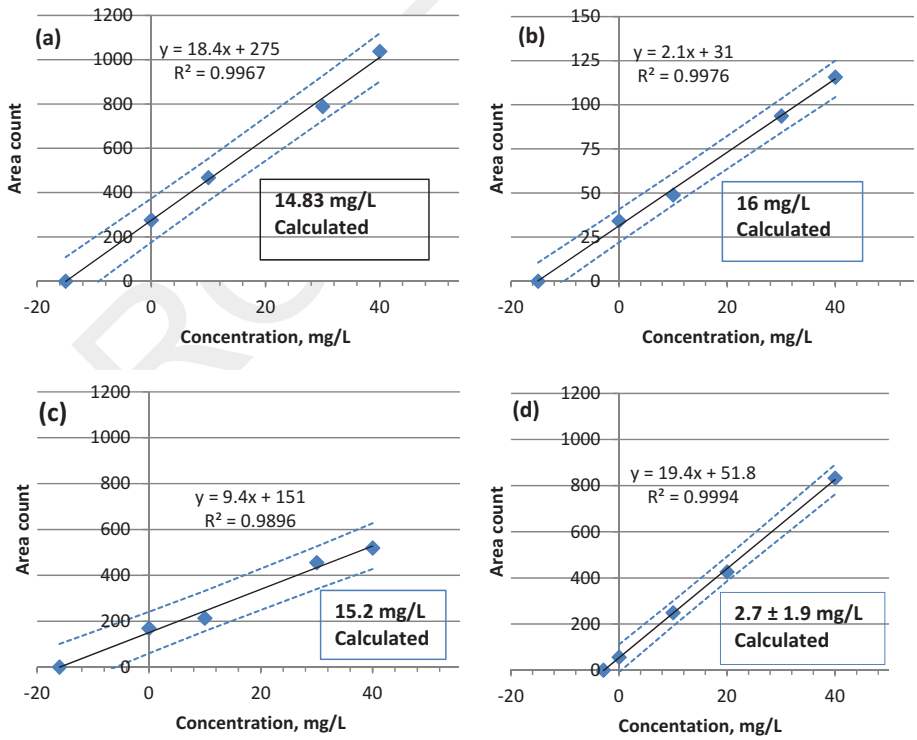


Figure 6. Linearity test (SAM method) of ^{1}H-NMR analysis of 15 mg/L spiked samples of (a) TMSOH, (b) HMDSO, and (c) propanal in water. Also shown in (d), the H-NMR measurement of HTF-22-15-34 (Tank 22H sample) where TMSOH was found. Broken lines represent 95% prediction intervals.

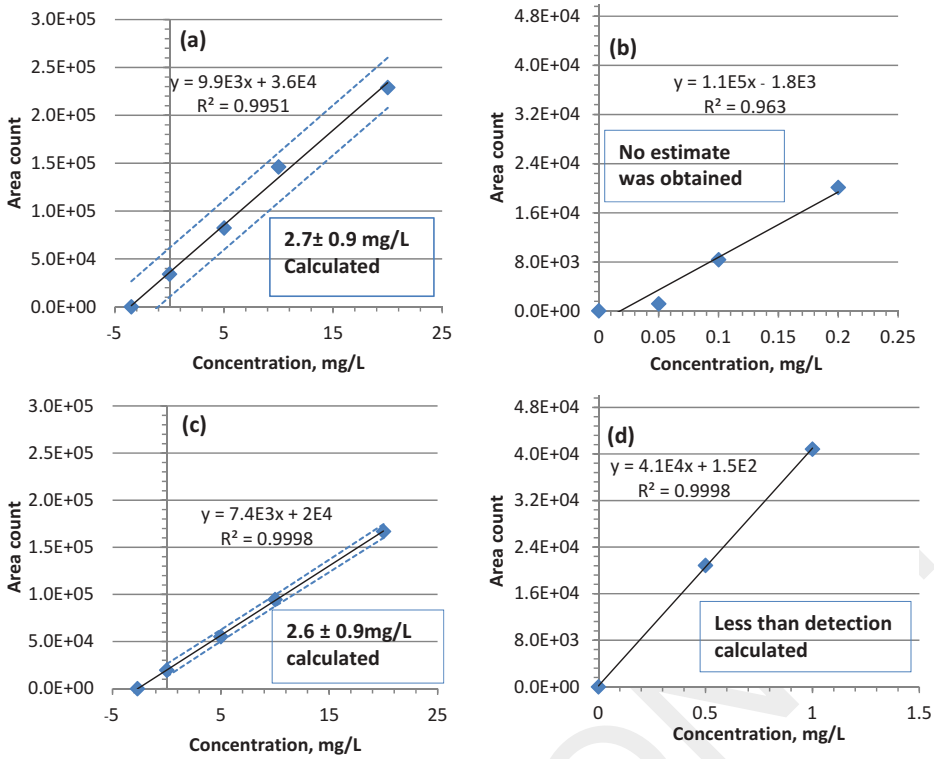


Figure 7. HMDSO and TMSOH concentration in Tank 22H samples by SVOA: (a) TMSOH in sample HTF-22-15-34, (b) HMDSO in sample HTF-22-15-34, (c) MSOH in sample HTF-22-15-34, and (d) HMSDO in sample HTF-22-15-35. Broken lines represent the 95% prediction interval.

Table 3. Measured concentration of TMSOH, HMDSO, and propanal.

Component	Check set (mg/L)	Check set measured by SVOA (mg/L)	Check set measured by ^{1}H-NMR (mg/L)	HTF-22-15-34 measured by SVOA (mg/L)	HTF-22-15-35 measured by SVOA (mg/L)	HTF-22-15-34 measured by ^{1}H-NMR (mg/L)
TMSOH	15	14.1	14.8	2.6 ± 0.9	2.70 ± 0.9	2.7 ± 1.9
HMDSO	15	NM	16.00	<LOD	<LOD	<LOD
HMDSO	1.5	1.38	NM	<LOD	<LOD	NM
Propanal	15	NM	15.16	<LOD	<LOD	<LOD

NM: not measured; LOD: limit of detection.

with routine analytical methods is a challenge. Based on these encouraging results, it is recommended that future analysis of these components should at least include extraction with DCM and analysis of the extraction by either or both SVOA and ^{1}H-NMR.

Conclusions

Evaporators are used to reduce the radioactive liquid waste inventory at the SRS. Antifoam agents are added to the radioactive supernate before evaporation. Given the harsh conditions, the breakdown products from the antifoam agents are volatile and they can react with mercury to form organo-mercury compounds. Understanding the impact of these breakdown by-products requires measuring their concentrations.

The by-products from the antifoam agent degradation at the SRAT and SME evaporator unit operations demanded accurate analytical measurement methods for these degradation products in radioactive aqueous solutions. The three components of concern were HMDSO, TMSOH, and propanal. Using standards, the Savannah River National Laboratory (SRNL) developed an extraction method with DCM and the extractions were analyzed by GC-MS tandem and a ^{1}H-NMR spectrometer. Both GC-MS and ^{1}H-NMR had detection limits less than 1 mg/L for HMDSO, TMSOH, and propanal.

SRNL received two supernate samples (duplicates) from Tank 22H. Using the extraction method, both GC-MS and ^{1}H-NMR provided the same results. The GC-MS reported approximately 2.6 and 2.7 ± 0.9 mg/L TMSOH in Tank 22H supernate and no HDMSO and propanal was detected. The ^{1}H-NMR reported a concentration of

2.7 ± 1.9 mg/L TMSOH and no HDMSO and propanal was detected. The higher noise in the ^{1}H-NMR is possibly due to heat transfer from the NMR probe to the sample during pulsing. The team demonstrated that the SAM was applied successfully in this case where only a few samples were available. In the case of the ^{1}H-NMR, a more precise measurement can be obtained by simply spiking the sample with a soluble NMR tracer (whose magnetic resonance does not overlap with that of the analytes) and without the need of making additional samples (as required in the SAM method).

Based on these results, it is recommended that future analysis of these components (TMSOH, HMDSO, and propanal) or other similar materials should include the method developed in this work. Both GC-MS and ^{1}H-NMR can detect and measure mixtures of samples as long as the components of these mixtures are separated in time as in the case of GC-MS or in resonance frequency as in the case of the ^{1}H-NMR measurement.

Future testing should evaluate the quantitative accuracy and precision of the purge-and-trap method that was not pursued in this work.

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