MRI

Method Evaluation for the Analysis of Linear Alkylbenzene Sulfonates (LAS) in Sediment by Liquid Chromatography/Mass Spectrometry (LC/MS)

Final Report

For
Mr. Alvaro J. DeCarvalho
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MRI Project No. 310220

August 13, 2001

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Subject: MRI Report "Method Evaluation for the Analysis of Linear Alkylbenzene Sulfonates (LAS) in Sediment by Liquid Chromatography/Mass Spectrometry (LC/MS)"

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Dear Mr. DeCarvalho and Members of the Sediment Task Force Committee:

The purpose of this study was to determine if LAS is detectable by LC/MS using the same general instrument operating parameters as those used for the alkyl sulfates/alkyl ethoxysulfates (AS/AES). This limited study was also used to determine if freeze-dried sediment may be extracted with methanol and analyzed without extensive matrix cleanup for both LAS and AS/AES at the same time. If successful, this would eliminate the need for separate extraction and analysis of sediment for LAS, potentially improve sensitivity, provide chemical confirmation through mass spectrometry, and simplify field-sampling activities. The results reported herein are based on the MRI Proposal 811054-R1, dated March 28, 2001.

Summary of Results

Based on this limited study, it was demonstrated that both the LAS and (representative) AS/AES homologues can be detected using the same instrument operating conditions from earlier AS/AES method validation studies. Although not all chromatographically separated, the concentrations of individual chemicals or homologues are calculated by measuring the response in the appropriate ion channel. The C10 through C14 LAS homologues exhibited retention times of ~ 13 to 21 minutes on a C8 Phenomenex Prodigy column, eluted with a gradient mixed mobile phase of buffered water/acetonitrile at a flow rate of 0.2 mL/min. Representative AS/AES chemicals eluted under the same conditions at retention times ranging from ~ 13 to 24 minutes into the run. Chromatographic precision was good for all compounds at +/- 0.2% relative standard deviation from the average retention time over a range of standard concentrations.

Linearity of the C10 through C14 LAS homologues exhibited correlation coefficients of 0.995 or better (3-point curves) at concentrations ranging from 0.068 to 19.2 µg/mL (dependent on individual homologue in the formulated reference standard). Analysis of independent standard reference materials for C13 and C14 LAS indicated accuracy of 51% and 60% (estimated), respectively.

Sediment samples from 3 different sources were freeze-dried, extracted, and analyzed by this method. The analysis results exhibited total LAS concentrations ranging from 0.325 µg/g (East Fork Little Miami), 0.578 µg/g (Winton Woods), and 9.89 µg/g (Glendale) on a dry-weight basis. Precision of triplicate analysis for the Little Miami sample was 0.325 +/- 0.164 (s) µg total LAS /g sediment, on a dry weight basis. A reagent blank sample, analyzed at the same time as the sediment samples, showed trace level LAS; however the background levels were significantly below the sediment samples and were not measurable by the linear regression method.

Limits of detection (LOD) and limits of quantitation (LOQ), defined as 3 and 10 times the instrumental signal-to-noise, were estimated by spiking sediment extracts with a LAS standard solution. The LOD estimated values ranged from 0.12 to 0.28 µg/g total LAS and the estimated LOQ values ranged from 0.43 to 0.92 µg/g total LAS (based on an assumed 20-g sediment sample weight), as determined by this technique.

The scope-of-work and experimental design are reviewed in Section 1, sample results are presented in Section 2, calibration data are summarized in Section 3, and the study results are discussed in Section 4.

1.0 Scope of Work

1.1 Experimental Design

This study evaluated the chromatography of LAS standard solutions using the LC/MS instrument operating parameters developed for the AS/AES chemicals. An AS/AES mixed standard was also analyzed to assure that these surfactants can be chromatographically separated within the same operational and mass scan ranges of the instrument. The LAS standards were prepared at various concentrations to demonstrate linearity of response, assess retention time variance with concentration, calculate LAS concentrations in samples, and evaluate limits of detection (LOD) / limits of quantitation (LOQ).

In addition, portions of the three sediment samples received for the AE method validation study (MRI Project 310208) were freeze-dried and methanol-extracted using the AS/AES procedure to measure residual LAS concentrations. The methanol extraction method is consistent with published methods for separation of LAS from sediment. One of the three sediment samples was prepared, extracted, and analyzed in triplicate to measure overall precision and reproducibility.

One extract from each of the 3 sediment samples was spiked with an LAS standard solution at a target concentration equivalent to 10 times the signal-to-noise or a minimum of 2 times the residual LAS concentrations found in each sediment sample. These data were used to estimate the limits of detection and quantitation (LOD/LOQ) for the three sediment samples.

The data objectives for this study were:

- Determine if LAS homologues can be detected by LC/MS using the same operating conditions developed for AS/AES method.
- Calculate residual LAS concentrations and/or matrix interference on 3 different sediment samples.
- Determine the precision of LAS measurement by analyzing one of the 3 sediments in triplicate.
- Estimate the Limits of Detection (LOD) for LAS from the analysis of standard solutions and the instrument signal-to-noise (S/N).
- Evaluate the Limits of Quantitation (LOQ) for LAS by post-spiking extracted sediment samples.

Results are presented in Section 2.

1.2 Extraction Procedure for LAS & AS/AES in Sediment

The following extraction procedure was based on the AS/AES draft method[1]. This extraction procedure is comparable to several published methods for the extraction of LAS from sediment. Minor changes were made (e.g., retaining an archive portion of the extract) for the purposes of this investigation.

1. Decontaminate all labware for surfactants using the procedure described in the AS/AES draft SOP dated 3/2/01. [Note: The cleanup procedure was subsequently enhanced to include an organic solvent rinse (methanol:ethyl acetate:water, 78:20:2, v/v/v) and oven heating at 110°C for 1 hour to reduce background LAS levels.]
2. Freeze-dry ~20-30-g wet weight (overlay water removed) of preserved sediment as described in the AS/AES draft method.
3. Prepare a reagent-only method blank to process with the sediment samples.
4. Add 50 mL of methanol to the dry sediment sample and method blank.
5. Extract by wrist-action shaker (30 min).
6. Extract by sonication (10 min).
7. Centrifuge at ~ 870 G for 5 min.
8. Decant methanol from sediment.
9. Repeat methanol extraction steps and combine extract solution.
10. Adjust to a fixed volume (e.g., 100-mL) with additional methanol. Remove one-half of the extract store at ~ 2-6°C as an archive.
11. Evaporate the remaining extract solution at ~ 40°C to dryness under nitrogen. Isopropyl alcohol (0.5 mL) is added to the extract prior to this evaporation step to act as a "keeper" for the LAS compounds, minimizing loss of chemical due to volatility.
12. Reconstitute the dry residue in 1-mL of the initial HPLC mobile phase at the initial solvent ratio. [This is a modification of the referenced AS/AES procedure and is intended to reduce retention time shifts by matching the final sample extract solution with the mobile phase.]
13. Dilute the samples as needed to adjust for variances in LAS/AS/AES residual levels in environmental investigation samples. [Note: Each of the sediment sample extracts in this study were diluted and analyzed separately; however, the diluted extract results were inconclusive due to background LAS levels.]
14. Spike with 100 µL AS/AES internal standard (~20 µg/mL of deuterated sodium dodecyl-d_{25} sulfate) and 100 µL of LAS internal standard (~20 µg/mL of deuterated d_4-C_{12}-LAS)
15. Sonicate solution for 2 minutes to ensure dissolution.
16. Filter the solutions (0.45 micron or smaller) to remove particulate matter.
17. Transfer liquid to an autosampler vial for analysis.

[1] "Extraction and Analysis of Alkyl Sulfate/Alkyl Ethoxylate Sulfates in Environmental Sediments," D. Robaugh, draft copy received March 3, 2001.

1.3 Combined Analysis Method for LAS and AS/AES

The following analyses were performed to demonstrate that LAS and AS/AES could be analyzed by LC/MS using the same general operating conditions. The instrument operating conditions were based on the referenced AS/AES draft method.

1. LAS standard solutions were prepared at concentrations of 0.068 to 19.2 µg/mL based on the individual homologue concentrations in the formulated reference standard. The standard solutions were prepared in 50/50 methanol:water (v/v) and spiked with 100 µL of LAS internal standard (~20 µg/mL of deuterated d_4-C_{12}-LAS). [Note: The LAS concentrations are originally based on a reported 6 ng/mL LOD for total C_{12}LAS at a 3:1 S/N.]
2. AS/AES standard solutions were prepared at ~ 30 µg/mL in methanol/water. A 1-mL aliquot was spiked with 100 µL AS/AES internal standard (~20 µg/mL of deuterated sodium dodecyl-d_{25} sulfate).
3. LC/MS operating conditions were set up as shown in Figure 1. These general parameters were used for the AS/AES draft method.
4. A high concentration LAS standard was injected to check chromatography and establish retention times.
5. An AS/AES standard was injected to check chromatography and establish retention times.
6. The chromatography and/or operating conditions were adjusted as needed and the standards were re-analyzed if the operating conditions were changed.
7. A standard blank was analyzed to check for any background surfactants present.
8. Multiple concentration LAS standards were injected to evaluate linearity of responses.
9. The extracted sediment samples and method blank were analyzed to determine residual LAS concentrations and any matrix interference. [Note: Diluted sediment extracts were also analyzed later, but the results were inconclusive due to background LAS.]
10. One each of the three sediment extracts was spiked with LAS standard at about 2 times the residual LAS concentration or 10 times signal-to-noise, whichever was higher. The internal standard concentrations were adjusted, and the spiked extracts were re-analyzed to evaluate Limits of Quantitation (LOQ) and Limits of Detection (LOD).

Figure 1. Instrument Operating Conditions for the Combined Analysis of LAS and AS/AES Surfactants

The following general operating parameters were used for the LAS study. These general operating conditions were taken from an earlier AS/AES method validation study.

PARAMETER	OPERATING CONDITIONS
INSTRUMENT	HP 1090
COLUMN	C8 Phenomenex Prodigy
DIMENSIONS	5 micron, 250 x 2.1 mm
SOLVENT A	80% water with 10 mM ammonium acetate / 20% AcN, (v/v)
SOLVENT B	20% water with 10 mM ammonium acetate / 80% AcN, (v/v)
FLOW RATE	0.2 mL/min
VOLUME INJECTION	20 µL
APPROX. RETENTION TIMES	LAS: To be determined. AS/AES homologues: Elute within first 40 minutes.
PROGRAM	*PERCENTAGE A/B FOLLOWS:*
0 min	70/30
30 min	25/75 in 30 min
30.1min to 40 min	0 / 100 after 30 min, hold until 40 min mark.
40 to 60 min	20 min post-equilibration time at starting conditions.
INSTRUMENT	Micromass Quattro Tandem Triple Quadrupole MS
MS PARAMETERS	With atmospheric pressure ionization interface.
	(The column eluent is flowed directly to the ESP probe of the MS without splitting.)
OPERATING MODE	Full-scan, single-quadrupole detection mode.
IONIZATION METHOD	Negative ion electrospray
SCAN RANGE	258 =< m/z <=700
SCAN TIME	2 sec.
TOTAL ACQUISITION TIME	40 min (plus 20 min equilibration time).
MASS SCALE CALIBRATION	Sodium iodide clusters, generated by direct infusion of a 1 mg/mL mixture of sodium iodide in 50/50 AcN:water
SOURCE TEMPERATURE	150°C
DWELL TIME	Not specified in AS/AES method (0.5 seconds suggested)
NITROGEN PRESSURE	100 psig
NEBULIZER FLOW RATE	14 L/min
DRYING GAS FLOW RATE	400 L/min
CONE VOLATAGE	25 Volts
LAS IONS MONITORED	IS (deuterated d_4-C_{12}-LAS) = 329
	C10 LAS = 297
	C11 LAS = 311
	C12 LAS = 325
	C13 LAS = 339
	C14 LAS = 353
AS/AES IONS MONITORED	As specified for the 36 chemicals and internal standard listed in the draft AS/AES Validation Report. Representative subset reported.

2.0 Results

2.1 Chromatographic Retention Times

One of the objectives of this limited method evaluation study was to demonstrate that both the AS/AES compounds and the LAS homologues are measurable within a single analysis run. Methanol-extracted samples and standard solutions were analyzed using the same or similar instrument operating conditions as those listed in the Standard Operating Procedure "Extraction and Analysis of AS/AES in Environmental Sediments."

The chromatographic results show good separation and response for these compounds. Retention times for representative AS/AES components (C12-C15, EO=0, 2, 4, 8) and for the LAS homologues C10, C11, C12, C13, and C14 chain lengths are summarized in Table 1. Trace level LAS were found in both the standard reagent blank and in the AES standard series; AS/AES was not detected in the reagent blank or in the LAS standards.

Table 1. AS/AES & LAS Standard Retention Time Summary

		RETENTION TIME IN MINUTES										
STANDARD ID (total LAS or AS/AES)	m/z	Std. Blk. (0 µg/mL)	LAS 10 (~ 5.7 µg/mL)	LAS 50 (~ 28 µg/mL)	LAS 100 (~ 57 µg/mL)	AES 100 (~ 130 µg/mL)	AES 200 (~ 260 µg/mL)	AES 25 (~ 32 µg/mL)	AES 25 (~ 32 µg/mL)	AES 2.5 (~ 3.2 µg/mL)	**AVG. (min)**	**RSD (%)**
LAS IS	329	17.6 a/	17.5	17.5	17.5	17.8 a/	17.8 a/	nd b/	nd /b	17.6 a/	**17.6**	**0.1**
C10 LAS	297	13.1 a/	13.1	13.1	13.1	13.4 a/	13.4 a/	13.4 a/	13.1 a/	13.2 a/	**13.1**	**0.0**
C11 LAS	311	15.2 a/	15.2	15.0	15.0	15.5 a/	15.5 a/	15.4 a/	15.1 a/	15.3 a/	**15.1**	**0.1**
C12 LAS	325	17.3 a/	17.1	17.1	17.0	17.5 a/	17.5 a/	17.5 a/	17.1 a/	17.3 a/	**17.1**	**0.1**
C13 LAS	339	19.3 a/	19.3	19.2	19.2	19.6 a/	19.6 a/	19.5 a/	19.2 a/	19.4 a/	**19.3**	**0.0**
C14 LAS	353	nd	21.3	21.3	21.3	nd	nd	Nd	nd	nd	**21.3**	**0.0**
AES IS	290	12.9	12.9	12.9	12.9	13.2	13.2	13.2	12.9	13	**13.0**	**0.1**
C12 EO=0	265	nd	nd	nd	nd	13.5	13.5	13.5	13.3	13.3	**13.4**	**0.1**
C13 EO=0	279	nd	nd	nd	nd	15.6	15.5	15.5	15.3	15.4	**15.5**	**0.1**
C14 EO=0	293	nd	nd	nd	nd	17.7	17.6	17.6	17.3	17.5	**17.5**	**0.2**
C15 EO=0	307	nd	nd	nd	nd	19.8	19.6	19.7	19.4	19.5	**19.6**	**0.2**
C12 EO=2	353	nd	nd	nd	nd	16.6	16.4	16.5	16.2	nd	**16.4**	**0.2**
C13 EO=2	367	nd	nd	nd	nd	18.7	18.5	18.6	18.3	nd	**18.5**	**0.2**
C14 EO=2	381	nd	nd	nd	nd	20.8	20.6	20.7	20.4	nd	**20.6**	**0.2**
C15 EO=2	395	nd	nd	nd	nd	22.9	22.7	22.8	22.5	nd	**22.7**	**0.2**
C12 EO=4	441	nd	nd	nd	nd	17.4	17.2	17.3	17	nd	**17.2**	**0.2**
C13 EO=4	455	nd	nd	nd	nd	19.5	19.4	19.4	19	nd	**19.3**	**0.2**
C14 EO=4	469	nd	nd	nd	nd	21.5	21.4	21.5	21.2	nd	**21.4**	**0.1**
C15 EO=4	483	nd	nd	nd	nd	23.8	23.5	23.7	23.3	nd	**23.6**	**0.2**
C12 EO=8	617	nd	nd	nd	nd	17.8	17.8	17.8	17.5	nd	**17.7**	**0.1**
C13 EO=8	631	nd	nd	nd	nd	19.9	19.8	19.9	19.6	nd	**19.8**	**0.1**
C14 EO=8	645	nd	nd	nd	nd	nd	21.9	22	21.6	nd	**21.8**	**0.2**
C15 EO=8	659	nd	nd	nd	nd	nd	24.1	24.2	23.8	nd	**24.0**	**0.2**

a/ Trace level LAS detected.

b/ The LAS internal standard was not added to this standard.

nd = Not detected.

2.2 Estimated LOD/LOQ Values for LAS

The LOD/LOQ values presented below were estimated by spiking sediment extracts with a LAS standard solution. The retention times and chromatographic peaks were examined and the LOD was calculated by multiplying the actual concentration by three times the estimated signal-to-noise response. The LOQ value was also calculated by this technique at 10 times the estimated signal-to-noise.

These values should be considered as estimates because of the significant variation in homologue concentrations within the formulated standard and the variable low background LAS concentrations observed in the reagent and method blanks.

Table 2. LOD / LOQ Estimated Values (Assumed 20-g dry weight)

SAMPLE ID	C10 LAS	C11 LAS	C12 LAS	C13 LAS	C14 LAS	**TOTAL LAS**
Units:	µg/g, dry	µg/g, dry	µg/g, dry	µg/g, dry	µg/g, dry	**µg/g, dry**
Glendale LOD	0.02	0.04	0.04	0.01	0.01	**0.12**
Glendale LOQ	0.06	0.15	0.15	0.04	0.03	**0.43**
Winton Woods LOD	0.06	0.07	0.07	0.04	0.04	**0.28**
Winton Woods LOQ	0.18	0.24	0.24	0.12	0.14	**0.92**
E. Fork Little Miami LOD	0.03	0.07	0.07	0.03	0.02	**0.22**
E. Fork Little Miami LOQ	0.09	0.24	0.24	0.08	0.06	**0.71**

2.3 Sediment Analysis Results

Residual total homologue concentrations (C10-C14) for LAS were determined for 3 different types of sediment samples. Multiple peaks were observed for the homologues and the combined peaks were summed as the total homologue value. Concentrations of individual isomers were not calculated.

These values should be considered estimated concentrations due to the wide range of sample concentrations, some of which exceed the limited 3-point calibration range of the standards. Concentrations are based on the relative response (LAS homologue area vs. internal standard area) compared to separate analysis of the calibration standards.

One of the 3 sediment samples (East Fork Little Miami) was extracted in triplicate to demonstrate precision. The total LAS sample results were all above the estimated total LOD values but below the estimated LOQ values for the Little Miami and Winton Woods samples. Total LAS concentration in the Glendale sample was significantly higher than the other 2 sediments.

Complete LAS results for the sediment samples are presented in Table 3 and the identification and physical characteristics of the sediment samples is presented in Table 4.

Table 3. Sediment Analysis Results

SAMPLE ID Units:	Dry Sample Wt. grams	C10 LAS µg/g, dry	C11 LAS µg/g, dry	C12 LAS µg/g, dry	C13 LAS µg/g, dry	C14 LAS µg/g, dry	**TOTAL LAS** **µg/g, dry**
Reagent Blank	20 g (assumed)	<LOQ	< LOQ	<LOQ	<LOQ	<LOQ	**<LOQ**
Glendale	29.33	0.328	1.620	3.960	3.400	0.577	**9.890**
% Distribution =		3	16	40	34	6	
Winton Woods	19.52	0.106	0.129	0.209	0.119	0.015	**0.578**
% Distribution =		18	22	36	21	3	
East Fork Little Miami	33.13	0.097	0.165	0.163	0.071	0.018	**0.514**
East Fork Little Miami	34.86	0.038	0.061	0.079	0.056	0.010	**0.244**
East Fork Little Miami	33.34	0.045	0.052	0.068	0.045	0.008	**0.218**
East Fork Little Miami	Average =	0.060	0.093	0.103	0.057	0.012	**0.325**
East Fork Little Miami	Std. Dev. =	0.032	0.063	0.052	0.013	0.005	**0.164**
% Distribution =		18	29	32	18	4	

Table 4. Sediment Characterization Results

LABEL DESCRIPTION:	East Fork Little Miami Sediment (13-Mar-01)	Glendale Sediment (13-Mar-01)	Winton Woods Sediment (13-Mar-01)
REFERENCE NO.:	MVT-536-49-1	MVT-536-49-2	MVT-536-49-3
PARAMETER			
Moisture (%)	24.2	22.1	42.6
Organic carbon (%)	0.47	0.91	2.41
Cation exchange capacity (meq/100 g)	2.8	5.4	13.9
Texture	Sand	Loamy sand	Loam
% Sand	91	89	35
% Silt	0	0	46
% Clay	9	11	19
% Interstitial Water*	2.4% (+/- 82% RSD)	6.0% (+/- 39% RSD)	20.7% (+/- 3% RSD)

* The percent interstitial water is the average of duplicate measurements, gravimetrically determined by centrifugation at 3000 rpm for 5 minutes. The calculated Relative Centrifugal Force (RCF) was 874 G.

3.0 Calibration Data

3.1 Linearity

The following table summarizes the concentrations and linear regression calibration results for the LAS standards. The reference material used for calibration was provided by the client and identified as follows:

Industry Blend Low MW LAS Slurry
Sample VO 146-105-1
Oil: 0.83-0.85%
Sodium sulfate: 0.63%
Active: 36.54%
Homologue distribution:
C10 = 10.78
C11 = 38.90
C12 = 38.74
C13 = 6.30
C14 = 1.28

The standard concentrations were corrected for activity and % homologue distribution.

Table 5. LAS Standard Calibration Summary

Standard ID Units:	X (Conc'n) (µg/mL)	Y (Response) (Area LAS/ Area IS)		
C10-10	0.7903	1.1464	CORR =	0.99999
C10-50	3.8077	4.8453	SLOPE =	1.21749
C10-100	7.2840	9.0536	INT =	0.19305
C11-10	2.0799	2.8288	CORR =	0.99691
C11-50	10.0216	12.3955	SLOPE =	1.04720
C11-100	19.1700	20.7830	INT =	1.08660
C12-10	2.0714	2.6804	CORR =	0.99726
C12-50	9.9803	11.9784	SLOPE =	1.02985
C12-100	19.0920	20.2621	INT =	0.94920
C13-10	0.3369	0.3619	CORR =	0.99759
C13-50	1.6230	1.9746	SLOPE =	1.10710
C13-100	3.1050	3.4352	INT =	0.05480
C14-10	0.0684	0.1051	CORR =	0.99993
C14-50	0.3298	0.4148	SLOPE =	1.21164
C14-100	0.6310	0.7864	INT =	0.01976

3.2 Analysis of Check Standards

In addition to the calibration standards, individual LAS homologue standards, provided by the client, were analyzed for C13 and C14. These results, corrected for theoretical activity and an assumed 100% purity, are shown in Table 5.

The percent accuracy for the two standards was 51% for the C13 and 60% for the C14 reference materials compared to the calibration data. These values should be considered estimated because the concentrations were significantly above the calibration standards and the number of individual compounds within the homologue series may be different from the reference material. These independent check standards were primarily used to verify chromatographic retention times for the C13 and C14 homologue series.

Table 6. Analysis of Check Standards for LAS C13 and LAS C14 Homologues

Standard ID	Theoretical Active Conc'n µg/mL	Conc'n Found a/ µg/mL	Accuracy (%)
C13 LAS HOMOLOG V1086-149-1 92.61% ACTIVE	20.39	10.39	51
C14 LAS HOMOLOG V1086-149-2 92.90% ACTIVE	24.47	14.63	60

a/ Extrapolated results compared to Industry Blend Low MW LAS Slurry Standard listed in Section 3.1.

4.0 Discussion

This limited study demonstrates that both LAS and AS/AES surfactants can be extracted from sediment and analyzed at the same time and that the method is capable of measuring LAS concentrations in 3 different types of sediments. Spiked sediment and reagent samples were analyzed with the test samples; but the recovery data were inconclusive due to low LAS spike levels (~1% relative to the residual LAS sediment concentrations) and the trace-level background concentrations of LAS observed in reagent and method blanks. However, the LAS homologue distribution pattern for the Glendale sample is consistent with published reports using HPLC and recovery of LAS in sediment is reported in to be 87% using similar extraction techniques ("Determination of LAS," E. Matthijs, et. al., Tenside Surfactants Detergents 24 (1987) 4, p. 197.).

Based on these initial results, it is recommended that additional chemical recovery experiments be performed at higher LAS spiked sediment concentrations consistent with residual LAS levels and high enough to minimize potential LAS background levels. Different spiked concentrations are also necessary because of the ~30-fold difference in homologue concentrations within the formulated commercial mixture used as the reference standard material for this study. A limited stability study may be appropriate to determine the interaction and fate of different surfactants within an environmental sample over time.

More accurate analysis of test samples could be accomplished by analysis of one or more dilutions of the extracts or extension of the calibration ranges to bracket actual found concentrations in real samples. A tiered approach to spike recovery and sample analysis determinations would be based on residual LAS concentrations for environmental samples that vary with the source and type of sediment.

Further study and refinement of the estimated LOD/LOQ values may be needed to demonstrate lower concentrations for use as risk assessment data. Although the decontamination procedures employed in this study successfully remove AS/AES background, more rigorous decontamination procedures are needed to further reduce both field and laboratory background LAS levels.

For technical questions regarding this report, please contact Mr. Dennis Hooton at 816-753-7600, ext. 1198.

Sincerely,

Dennis Hooton
Senior Chemist

Approved:

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