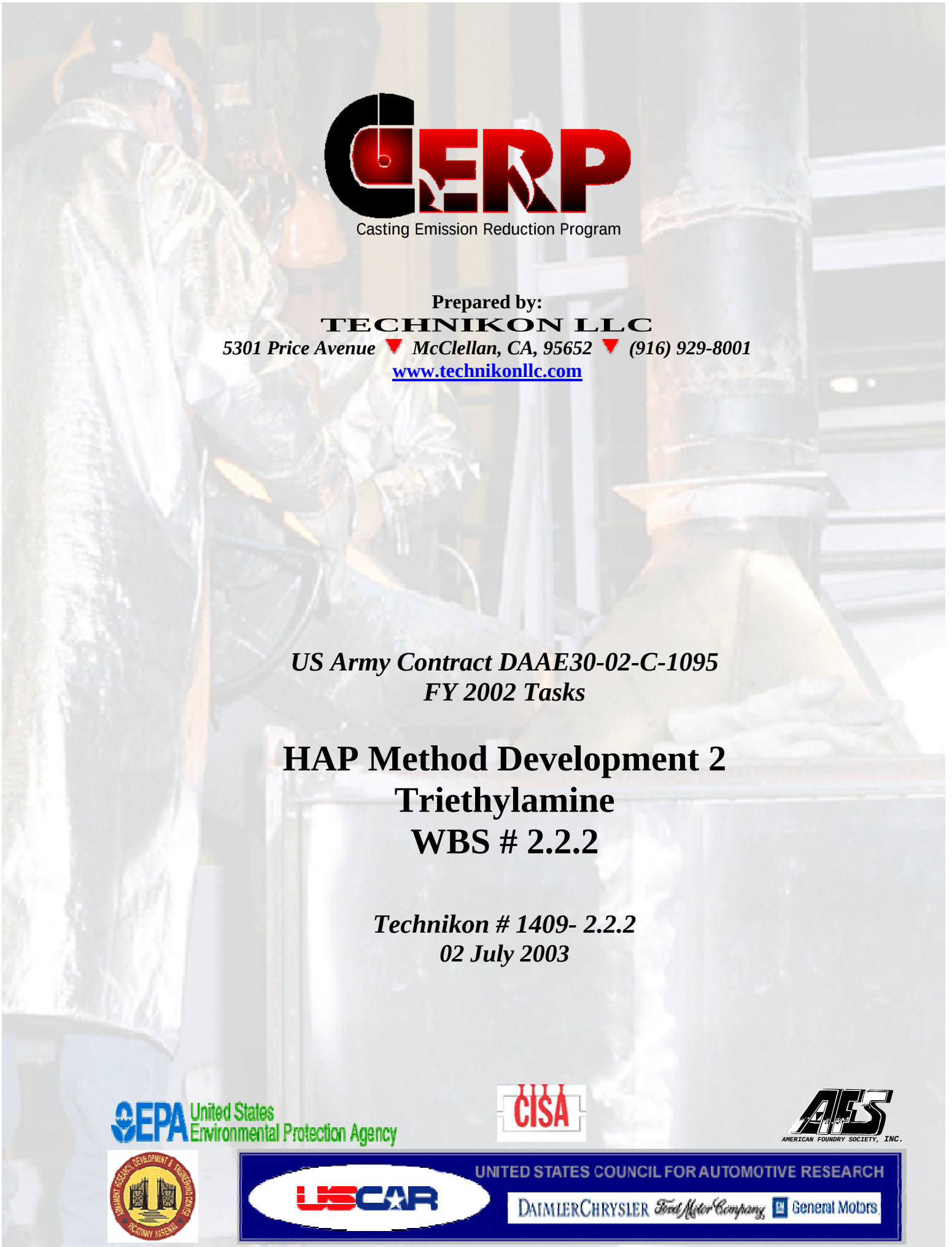

CERP
Casting Emission Reduction Program

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HAP Method Development 2
Triethylamine
WBS # 2.2.2

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02 July 2003

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CISA
AFS AMERICAN FOUNDRY SOCIETY, INC.
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Application Method

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HAP Method Development 2
Triethylamine

WBS # 2.2.2

1. **PURPOSE**

This method may be used to determine the concentration(s) of the listed analytes (see Table 1) in ambient air, workplace air, and process/facility emissions.

2. **SCOPE**

This procedure applies to the compounds listed in Table 1.

TABLE 1
Analytes

	Boiling Point (°C)	Density (g/mL)	MW (g/mole)	Range (ug)
Triethylamine	88.9	0.728	101.2	800-6000

3. **DEFINITIONS**

mg = milligram
L = liter
ml = milliliter
µg = microgram
m^3 = cubic meter
°F = degrees Fahrenheit

4. **APPARATUS AND REAGENTS**

4.4 Gas chromatograph equipped with a nitrogen-phosphorous ionization detector
4.4 Column - see instrument parameters
4.3 Syringes
4.4 Methanol - reagent (AR) grade
4.5 Target Analyte(s) - reagent (AR) grade
4.6 Standard solution - 25% MeOH
4.7 Desorbing solution – 0.2N H_2SO_4 (aq) in 10% MeOH
4.8 Neutralizing solution – 0.3N KOH (aq.)
4.9 Vials - screw cap with Teflon™ cap liners
4.10 Assorted pipets and volumetric flasks
4.9 Balance, sensitive to 0.1 mg

5. CALIBRATION

5.1 Prepare, in the standard solvent, a stock solution or solutions containing the target analyte(s), each at a concentration convenient for further dilution to levels approximating the levels expected in the field samples.

5.1.1 For liquids, the volume of pure analyte(s) needed for the stock solution(s) may be calculated using Equation 1 (see section 8.1).

5.1.2 For solids, use Equation 1 without "d". "V_a" then becomes the analyte weight in milligrams.

5.1.3 For "V_s" in Equation 1, use the mean air volume expected to be sampled in the field.

5.1.4 The following procedure has been found to provide accurate calibration standards, however, other procedures may be used at the discretion of the analyst.

5.1.4.1 Weigh the approximate calculated amount of each analyte into a volumetric flask of the appropriate volume and record the weight(s) to nearest 0.1 mg.

5.1.4.2 Fill the volumetric flask to the mark with the standard solvent and mix thoroughly.

5.1.4.3 Calculate the concentrations obtained with this stock solution and the dilutions necessary to achieve the target concentrations for each of the analytes. Use concentrations in units of mass/volume, e.g., mg/mL.

5.1.5 Perform dilutions, recording all volumes used, and clearly label both in a bound notebook and on the flasks containing the solutions. Each label should also include the solution disposal date and the analyst's initials. The labels should be made as indelible as possible, keeping in mind the environment in which the solutions will be stored.

5.2 Inject a known reproducible volume, using solvent flush techniques, of each standard into the gas chromatograph such that the lowest calibration standard response is greater than five (5) times the background noise level (see Section 7, Instrument Parameters).

5.2.1 When an autosampler is being used, its control parameters must be set to assure consistently accurate sample transfer and complete syringe rinsing between injected solutions.

5.3 Analyze each standard in triplicate, record and average the peak area(s).

5.4 Prepare a calibration curve by plotting the weight of analyte in each standard versus the mean peak area(s) for each standard.

5.5 The calibration curve shall have a correlation coefficient greater than 0.98 for the curve fit used. If the coefficient of variation is less than 0.98, the cause of the problem must be identified and corrected prior to sample analysis.

6. ANALYSIS OF SAMPLES

6.1 Remove samples from storage and allow to warm to room temperature.

6.2 Transfer each section of solid sorbent to an appropriately labeled vial.

6.3 Pipet an appropriate volume (1.0 mL for 100 mg/50 mg tubes) of the desorbing solvent into each vial and cap immediately.

6.4 Allow to desorb for four (4) hours using an ultrasonic bath.

6.5 Pipette 0.5 mL into a clean vial. Neutralize with 0.5 mL KOH solution.

6.5 Inject a known volume (same as used in part 5.2) of the solution, using solvent flush techniques, into the gas chromatograph (see Section 7, Instrument Parameters).

6.6 Record the peak area(s) of the analyte(s) present.

6.7 Calculate the concentration of analyte in the sampled environment (equations 2-7).

6.8 Report the weight, in µg, for each analyte.

6.9 Laboratory blanks, spikes, and sample duplicates will be analyzed at a minimum frequency of 5% or one (1) each per batch for batches containing fewer than twenty (20) samples.

7. INSTRUMENT PARAMETERS

7.1 Instrument parameters may vary significantly with changes in sample matrix, instrument make and model, and column condition. Appendix A contains instrument parameters that have been used to successfully determine each analyte. These parameters should be considered a starting point only and optimized for each set of samples.

8. CALCULATIONS

8.1 The volume of analyte needed to prepare appropriate standards may be calculated using the following equation:

$$V_a = 20 \; X \; \frac{(TLV) \;\; (V_s)}{1000 \; X \; d} \; X \; V_{Sol} \qquad 1$$

. . . where:

V_a is the volume of analyte needed to prepare the standard, µL

20 is a scaling factor to give a V_a that is conveniently measurable and a resulting stock solution concentration that is readily diluted to useful concentrations

TLV is the expected concentration of the analyte in the sampled gas, mg/m^3

V_s is the volume of air sampled in the field, L

d is the density of the analyte of interest, g/mL

V_{Sol} is the volume of the desorbing solvent used for the stock solution, mL

8.2 Using a computer application (e.g., a chromatography data system or Excel) or calculator, calculate the coefficients (m_i, b_i) of the linear regression:

$$Area_i = m_i * Conc_i + b_i \qquad 2$$

where:

- $Area_i$ is the area of the analyte peak "i" when the standard containing it is analyzed
- $Conc_i$ is the concentration of analyte "i" in the standard, e.g., mg/L
- m_i is the slope of the linear regression between the area and the concentration
- b_i is the y-intercept of the linear regression between the area and the concentration

If the y-intercept equals 0, then the slope is equivalent to the classical definition of the response factor. For EPA applications, the agency may require the linear regression to be calculated with the regression through the origin, i.e., the y-intercept (b_i) must be equal to 0.

8.3 Calculate the weight of analyte "i" in a sample as follows:

$$Wt_{Bf} = DV * (Area_{Bf} - b)/m \qquad Wt_{Bb} = DV * (Area_{Bb} - b)/m \qquad 3$$

$$Wt_{Sf} = DV * (Area_{Sf} - b)/m \qquad Wt_{Sb} = DV * (Area_{Sb} - b)/m \qquad 4$$

$$Crtd\ Wt_i = (Wt_{Sf} - Wt_{Bf}) + (Wt_{Sb} - Wt_{Bb}) * 2\ (df) \qquad 5$$

. . . where:

- Wt_{Bf} is the weight of the analyte of interest found on the front section of the blank solid sorbent tube, mg
- $Area_{Bf}$ is the area of the analyte peak of interest from the chromatographic run of the blank solid sorbent tube front section, mV-sec
- Wt_{Bb} is the weight of the analyte of interest found on the back section of the blank solid sorbent tube, mg
- $Area_{Bb}$ is the area of the analyte peak of interest from the chromatographic run of the blank solid sorbent tube back section, mV-sec
- Wt_{Sf} is the weight of the analyte of interest found on the front section of the solid sorbent tube on which the sample was collected, mg

$Area_{Sf}$ is the area of the analyte peak of interest from the chromatographic run of the sample solid sorbent tube front section, mV-sec

Wt_{Sb} is the weight of the analyte of interest found on the back section of the solid sorbent tube on which the sample was collected, mg

$Area_{Sb}$ is the area of the analyte peak of interest from the chromatographic run of the sample solid sorbent tube back section, mV-sec

DV is the volume of solvent use to desorb the sorbent media, mL

Crtd Wt_i is the total weight of analyte "i" corrected for any amounts found on the blank solid sorbent tube, mg

NOTE: If the corrected weight of analyte i found on the back section of the sample tube (Wt_{Sb}-Wt_{Bb}) is equal to or greater than 10% of the total amount of analyte present on the sample tube, then "breakthrough" has occurred. Breakthrough results should be reported, but clearly identified as such. These are to be considered ***minimum*** amounts present in the air sampled.

8.4 Calculate the concentration of analyte in the sampled air as follows:

$$C_i \ (\frac{mg}{m^3}) = \frac{Crtd\ Wt_i\ X\ 1000}{(V_S)\ (DE_i)} \qquad 6$$

. . . where:

C_i is the concentration of analyte i in the sampled air, mg/m^3

Crtd Wt_i is the corrected weight of analyte i in the sample, mg

1000 is the number of liters in a cubic meter, L/m^3

V_s is the volume of air sampled, L

DE_i is the desorption efficiency of the analyte

8.5 Calculate the concentration of analyte(s) in the sampled air in parts per million (ppm) using the following equation:

$$C_i\ (ppm) = \frac{C_i\ (\frac{mg}{m^3})\ X\ 24.45}{MW_i} \qquad 7$$

. . . where:

C_i (ppm)	is the concentration of analyte i in parts per million
C_i (mg/m^3)	is the concentration of analyte i in milligrams per cubic meter
24.45	is the molar volume of a gas at 70°F and standard pressure, mL/mmole
MW_i	is the molecular weight of analyte i, mg/mmole

9. REFERENCES

9.1

Analyte	Literature Reference
Triethylamine	NIOSH 2010

INSTRUMENT PARAMETERS

Capillary Columns

Analyte	Triethylamine
Column:	
Dimensions:	60 m x 0.32mm i.d. x 1.8 μm film thickness
Type:	RTX-624 or equivalent.
Material:	Fused Silica
Temperature Profile	
Initial Temp:	60 °C
Final Temp.:	150 °C
Post Run Hold:	3 min
Program Rate:	20°C/min to 150°C
Injector Profile:	
Temperature:	180°C
Mode:	Split
Split Flow:	100 mL/min
Pressure:	17.38
Detection:	
Type:	NPD
Detector Temperature:	325 °C
Carrier Gas:	
Type:	He
Initial Flow Rate:	2 mL/min
Mode:	Constant Pressure
Sample:	
Injection Volume:	1.0 μl
Solvent:	H_2SO_4/KOH/CH_3OH/H_2O

Triethylamine Method Development Average Results

Desorption Efficiency

Average Mass, ug	Average Spike Amount, ug	DE (%)
5407	5804	93
2643	2709	98
741	832	89

Storage Stability

Sample Number	Average Mass Found, ug	Average Mass Spiked, ug	Mass Recovered (DE Applied), ug
immediate	4745	5804	6430
one week	4417	5794	5923
two weeks	4417	5828	5985
four weeks	4238	5732	5743

Discussion

The target analyte method verified with triethylamine included analyte analysis, storage of the samples, and analyte recovery. A series of seventy-three (73) samples were prepared at three spike levels. The samples were divided into groups to be analyzed immediately after collection, and after one (1), two (2), and four (4) weeks. Storage was evaluated at both room temperature and freezer temperature.

Samples were also analyzed to determine the desorption efficiency of triethylamine. The average percent (%) desorption efficiency for triethylamine was found to be 93%.

Detailed results for all analyses are shown in the following tables. At levels lower than approximately 800 ug, recoveries for triethylamine were found to be unacceptable. The results are shown for reference purposes only.

Triethylamine Method Development Detailed Results

Sample Number	Mass Found (Corrected), ug	Mass Spiked, ug	Storage Type	Storage Conditions
SS-1	4946	5804	immediate	NA
SS-2	5258	5804	immediate	NA
SS-3	NA	5804	immediate	NA
SS-64	4524	5789	one week	Rm. Temp
SS-65	4791	5789	one week	Rm. Temp
SS-66	4692	5804	one week	Rm. Temp
SS-73	4824	5789	one week	Freezer
SS-74	4852	5804	one week	Freezer
SS-75	4813	5789	one week	Freezer
SS-28	4871	5804	two weeks	Rm. Temp
SS-29	5118	5804	two weeks	Rm. Temp
SS-30	4860	5804	two weeks	Rm. Temp
SS-37	4527	5804	two weeks	Freezer
SS-38	4419	5804	two weeks	Freezer
SS-39	4699	5949	two weeks	Freezer
SS-46	4914	5514	four weeks	Rm. Temp
SS-47	4731	5804	four weeks	Rm. Temp
SS-48	4409	5659	four weeks	Rm. Temp
SS-55	4516	5804	four weeks	Freezer
SS-56	4527	5804	four weeks	Freezer
SS-57	4247	5804	four weeks	Freezer

Triethylamine Method Development Detailed Results

Sample Number	Mass Found (Corrected), ug	Mass Spiked, ug	Storage Type	Storage Conditions
SS-4	324	595	immediate	NA
SS-5	401	609	immediate	NA
SS-6	416	579	immediate	NA
SS-67	276	551	one week	Rm. Temp
SS-68	272	551	one week	Rm. Temp
SS-69	215	580	one week	Rm. Temp
SS-76	294	580	one week	Freezer
SS-77	272	580	one week	Freezer
SS-78	265	580	one week	Freezer
SS-31	402	579	two weeks	Rm. Temp
SS-32	363	579	two weeks	Rm. Temp
SS-33	378	551	two weeks	Rm. Temp
SS-40	NA	551	two weeks	Freezer
SS-41	332	579	two weeks	Freezer
SS-42	309	579	two weeks	Freezer
SS-49	248	579	four weeks	Rm. Temp
SS-50	268	609	four weeks	Rm. Temp
SS-51	224	579	four weeks	Rm. Temp
SS-58	220	579	four weeks	Freezer
SS-59	208	579	four weeks	Freezer
SS-60	219	579	four weeks	Freezer

Triethylamine Method Development Detailed Results

Sample Number	Mass Found (Corrected), ug	Mass Spiked, ug	Storage Type	Storage Conditions
SS-7	29	58	immediate	NA
SS-8	28	58	immediate	NA
SS-9	23	58	immediate	NA
SS-70	25	57	one week	Rm. Temp
SS-71	13	57	one week	Rm. Temp
SS-72	25	56	one week	Rm. Temp
SS-79	12	57	one week	Freezer
SS-80	19	57	one week	Freezer
SS-81	15	57	one week	Freezer
SS-34	33	58	two weeks	Rm. Temp
SS-35	25	58	two weeks	Rm. Temp
SS-36	42	58	two weeks	Rm. Temp
SS-43	20	59	two weeks	Freezer
SS-44	25	58	two weeks	Freezer
SS-45	19	58	two weeks	Freezer
SS-52	26	58	four weeks	Rm. Temp
SS-53	16	59	four weeks	Rm. Temp
SS-54	21	55	four weeks	Rm. Temp
SS-61	45	58	four weeks	Freezer
SS-62	42	58	four weeks	Freezer
SS-63	34	58	four weeks	Freezer

Desorption Efficiency

Sample Number	Mass, ug	Mass Spiked, ug	DE (%)
DE-37	5380	5804	93
DE-38	5520	5805	95
DE-39	5320	5804	92
DE-40	2640	2757	96
DE-41	2840	2757	103
DE-42	2450	2612	94
DE-43	740	842	88
DE-44	756	813	93
DE-45	728	842	86
		Average	**93**