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Analytical Methods Development in Support of the Caustic Side Solvent Extraction System

April 2001

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Analytical Methods Development in Support of the Caustic Side Solvent Extraction System

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Executive Summary

The goal of the project reported herein was to develop and apply methods for the analysis of the major components of the solvent system used in the Caustic-Side Solvent Extraction Process (CSSX). These include the calix(4)arene, the modifier, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol and tri-n-octylamine. In addition, it was an objective to develop methods that would allow visualization of other components under process conditions. These analyses would include quantitative laboratory methods for each of the components, quantitative analysis of expected breakdown products (4-*sec*-butylphenol and di-n-octylamine), and qualitative investigations of possible additional breakdown products under a variety of process extremes. These methods would also provide a framework for process analysis should a pilot facility be developed.

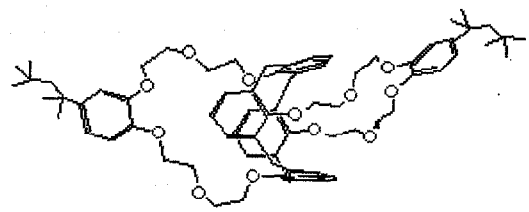
Two methods were implemented for sample preparation of aqueous phases. The first involves solid-phase extraction and produces quantitative recovery of the solvent components and degradation products from the various aqueous streams. This method can be automated and is suitable for use in radiation shielded facilities. The second is a variation of an established EPA liquid-liquid extraction procedure. This method is also quantitative and results in a final extract amenable to virtually any instrumental analysis.

Two HPLC methods were developed for quantitative analysis. The first is a reverse-phase system with variable wavelength UV detection. This method is excellent from a quantitative point of view. The second method is a size-exclusion method coupled with dual UV and evaporative light scattering detectors. This method is much faster than the reverse-phase method and allows for qualitative analysis of other components of the waste. For tri-n-octylamine and other degradation products, a GC method was developed and subsequently extended to GC/MS. All methods have precision better than 5%. The combination of these methods allows both quantitative analysis of the major solvent components and visualization of any minor components, including breakdown products.

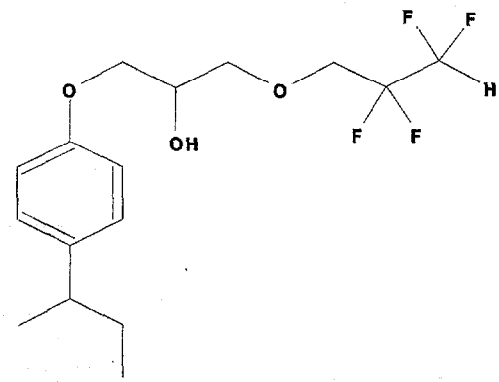
1. Introduction

One of the separation processes under investigation by the DOE Tank Focus Area is a calix[4]arene based solvent system developed at Oak Ridge National Laboratory for the removal of cesium from highly alkaline radioactive waste. The final product stream is a highly concentrated, weakly acidic cesium solution suitable for encapsulation in glass (vitrification). There are four components in the solvent system:

- Calix[4]arene-bis(*t*-octylbenzo-crown-6); "BOBCalixC6"; 11,500 mg/L, 0.01 molar,



- 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol; "Modifier"; 186,000 mg/L, 0.5 molar,



- Tri-n-octylamine; TOA; 354 mg/L, 0.001 molar, and

- ISOPAR® L diluent.

The goal of the project reported herein was to develop and apply methods for the analysis of these and other components (excluding the ISOPAR® L) under process conditions. These analyses would include quantitative laboratory methods for each of the components, quantitative analysis of expected breakdown products (4-*sec*-butylphenol and dioctylamine), and qualitative investigations of possible additional breakdown products under a variety of process extremes. These methods would also provide a framework for process analysis should a pilot process facility be developed.

The analytical methods necessary for attaining project goals fell into two categories. First, it was necessary to develop methods for precise and accurate quantitative measurement of the three main components of the solvent: the calixarene, the modifier, and the TOA. Second, it was necessary to develop methods for the identification and

semi-quantitative analysis of a range of potential decomposition by-products in the solvent. In addition, there was a need to be able to examine, at least qualitatively, the samples for minor components entering the process though the simulant and/or the real waste feed. Three matrices were involved, the solvent, the simulant, and the strip/scrub solutions. The strip solution is a dilute nitric acid solution (0.001M). These solutions are an integral part of the process cycle. In addition, consideration was given to the future needs for analysis of radioactive samples including process analysis in the proposed plant. While recognizing that the real waste may involve a changing matrix, the reported methods were developed with matrices matched as closely as possible to the expected waste streams.

2. Materials

All solvents used were HPLC grade or better (isopropanol, water, chloroform). Analytical standards were prepared gravimetrically in the appropriate solvent and further diluted prior to use. All pure compounds were acquired from the Chemical Separations Group, Chemical & Analytical Sciences Division, Oak Ridge National Laboratory and used as received. For all gas chromatographic analyses, the carrier gas was ultra-high-purity helium.

3. Sample preparation

The primary sample matrices were the solvent itself and the aqueous samples resulting from the process. Sample preparation of the solvent samples involved a simple dilution with isopropanol. Isopropanol and chloroform were considered as diluents. Isopropanol was selected based on its more limited volatility, excellent solubility properties relative to the main components, and applicability to a range of instrumental analyses. Further, this solvent is relatively benign environmentally, and will not generate a mixed waste. When solvent samples, which had been in contact with acidic aqueous streams were analyzed for tri-n-octylamine, 1% triethylamine was added to the diluent. This was done to neutralize any residual acid in the solvent. Residual acid was found to decrease the response factor for tri-n-octylamine in the final measurement. Excess triethylamine has the capability to make the instrumental system basic, preventing non-specific adsorption of organic bases (tri-n-octylamine, dioctylamine)

Preparation of the various aqueous samples (simulant, scrub, and strip solutions) was carried out using Oasis solid phase extraction cartridges (Waters Associates, Milford Ma.). A known volume of aqueous sample is applied to the cartridge, which is capable of extracting a broad range of organic compounds. The cartridge is then eluted with isopropanol, and the extract is suitable for further characterization. The apparatus used for this method is shown in Figure 1. These cartridges are convenient, require no pretreatment, and minimize exposure to radioactive samples. Recovery of the components of the pristine solvent system was quantitative using this methodology.

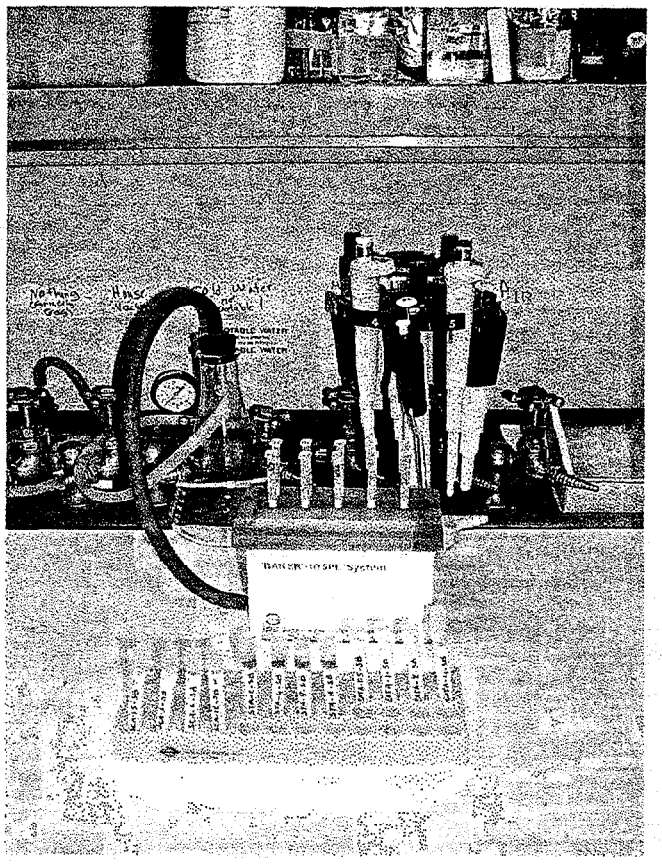


Figure 1. Apparatus used for the extraction of aqueous samples.

A slight vacuum is used to facilitate flow through the cartridges, which are shown inserted into a Baker extraction manifold. In normal operation, a 5-10 mL sample is passed through the cartridge, and then eluted with 1-2 mL isopropanol.

Preparation of aqueous samples resulting from partition studies was carried out using a variation of EPA Method 1310. This is a liquid/liquid extraction method carried out in a separatory funnel. For these experiments, the pH was adjusted to assure that the target analytes would be in the neutral form, and the extraction was carried out three times using methylene chloride as the solvent. The methylene chloride was evaporated down in a modified Kuderna-Danish evaporator, and the residue redissolved in isopropanol prior to analysis. Recovery of the target analytes was quantitative using this methodology.

4. Analytical methods for solvent components

4.1. Reverse-Phase HPLC

For the purpose of solvent constituent analysis, specifically the calixarene and the modifier, two HPLC methods were developed and employed. Both used a Hewlett-Packard Model 1090 HPLC equipped with an autosampler and a diode array detector (UV absorbance). The first was an adaptation of an existing method from Savannah River Technology Center (SRTC)[1], which employed a highly loaded reverse phase (RP) column with an isopropanol/water mobile phase. As implemented at ORNL, the method used a 250 mm Chemcosorb-5ODS UH column, 3.2 mm diameter (Phenomenex). The solvents were A: 99/1 water/isopropanol and B: isopropanol. The initial mobile phase was 69.7 % B and 30.3 % A with a flow rate of 0.25 mL/min. The total run time was 35 min with a post-run equilibration time of 7 min. Temperature was 45 °C. Under these conditions, good separation was achieved between the calixarene, modifier, and 4-*sec*-butylphenol, which was expected to be a by-product of modifier degradation. An example of the chromatography of authentic standards is shown in Figure 2. The retention time of 4-*sec*-butylphenol is 7.491 minutes, that of the modifier is 8.626 minutes, and the calixarene 30.995 minutes. In this case, detection was by UV absorbance at 226 nm.

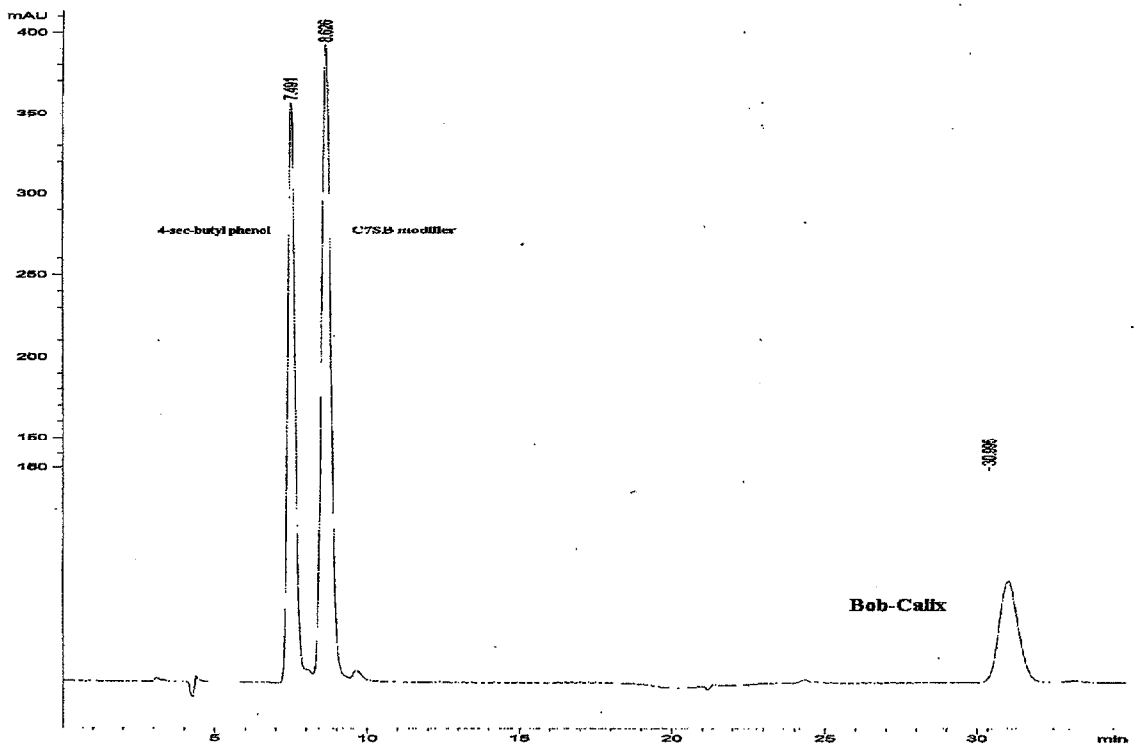


Figure 2. Reverse phase liquid chromatogram of standard components (50 mg/L).

Advantages of this method include the ability to elute a broad range of organic compounds, good sensitivity for the target analytes, and excellent quantitative properties. Disadvantages include the inability to detect non-UV-absorbing compounds (e.g., TOA), and relatively long analysis time, perhaps making this method unsuitable for process analysis. An example of the analysis of the pristine solvent system at three wavelengths is in Figure 3. This method was found to be very sound for quantitative analysis as well. Example calibration curves for the method at various wavelengths are shown in Figure 4 through Figure 11.

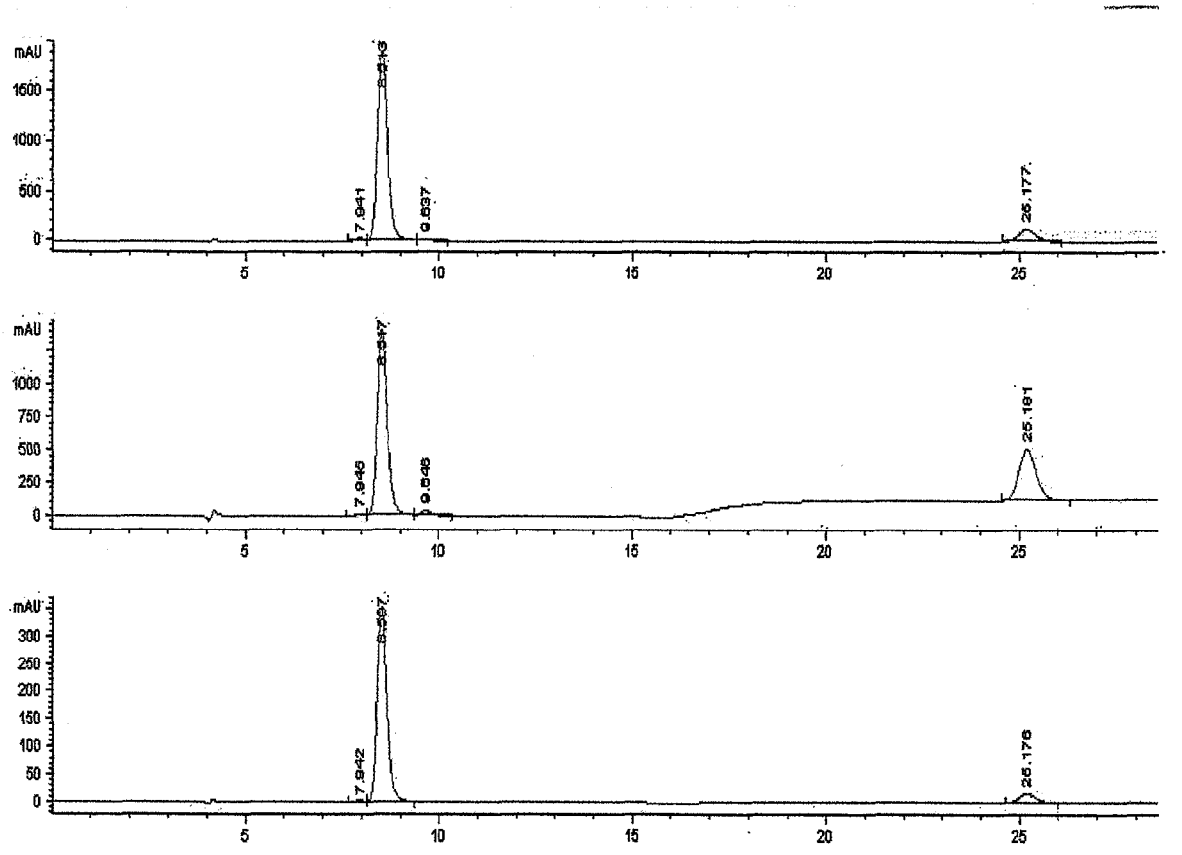


Figure 3. Multi-wavelength analysis of pristine solvent system.

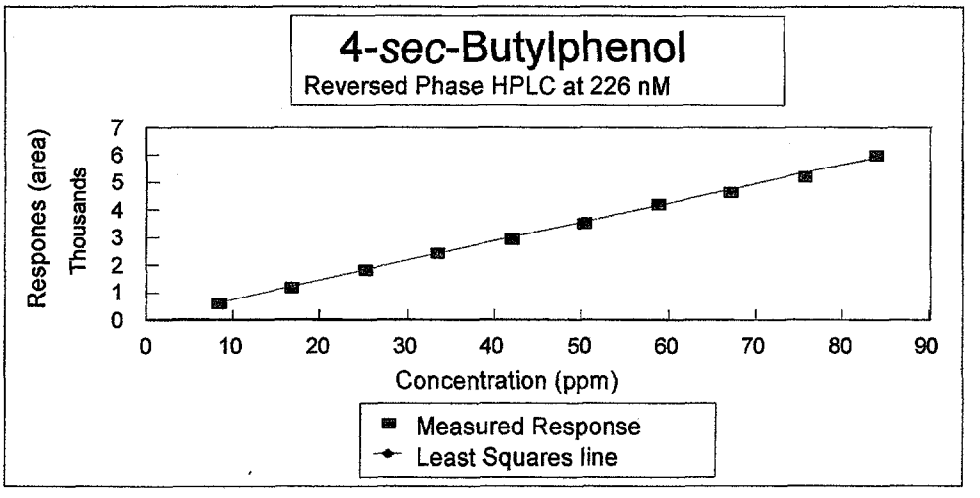


Figure 4. Calibration curve for 4-*sec*-butylphenol at 226 nm.

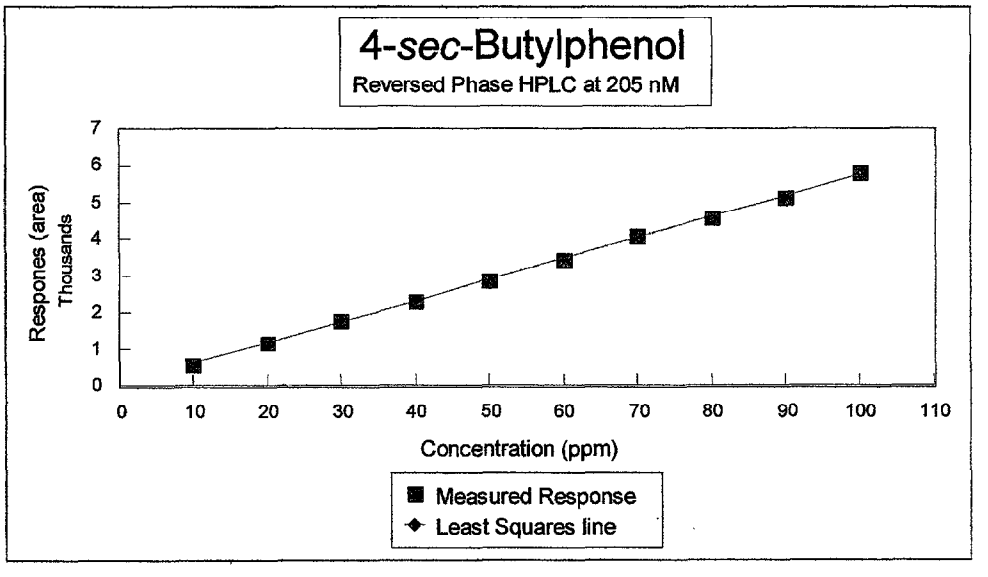


Figure 5. Calibration curve for 4-*sec*-butylphenol at 205 nm.

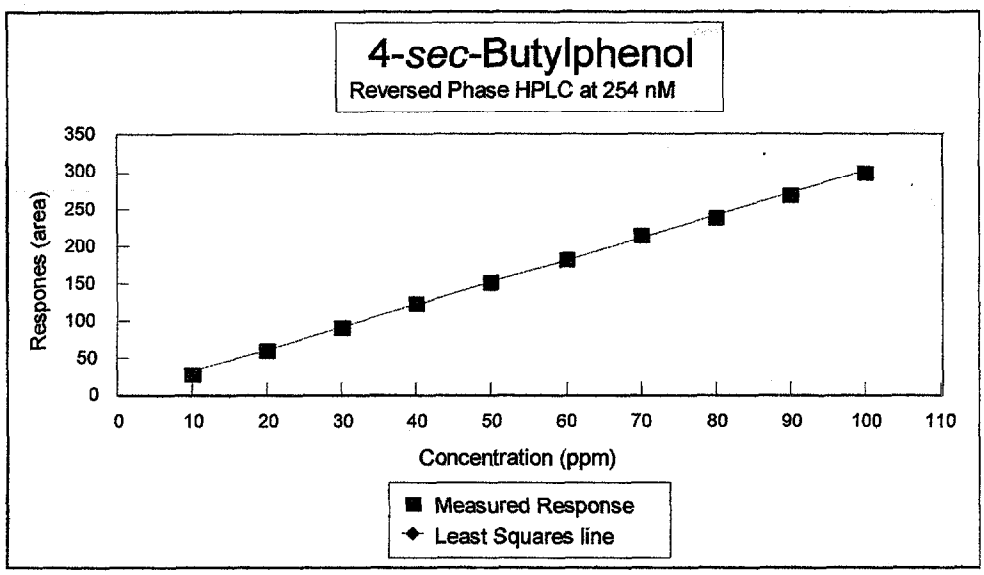


Figure 6. Calibration curve for 4-*sec*-butylphenol at 254 nm.

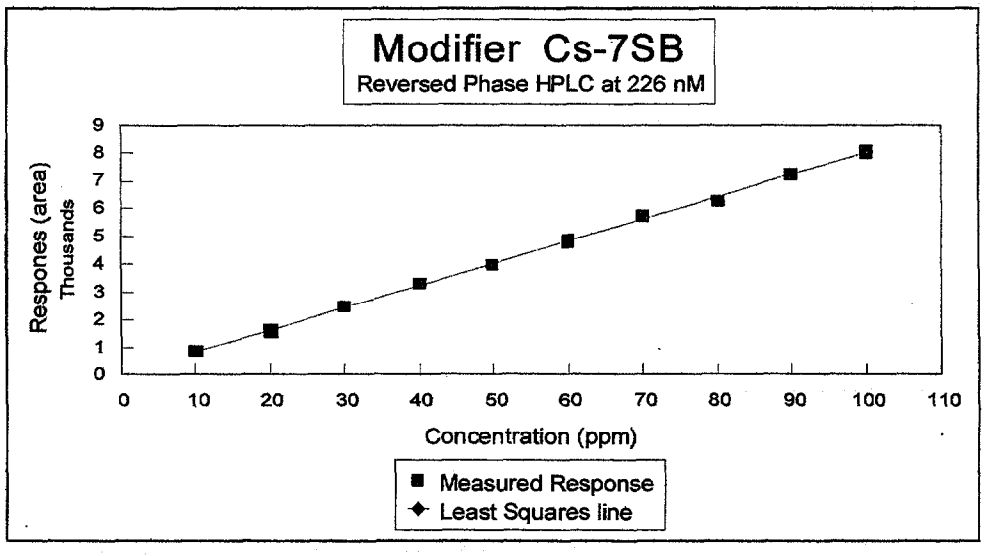


Figure 7. Calibration curve for Cs-7SB at 226 nm.

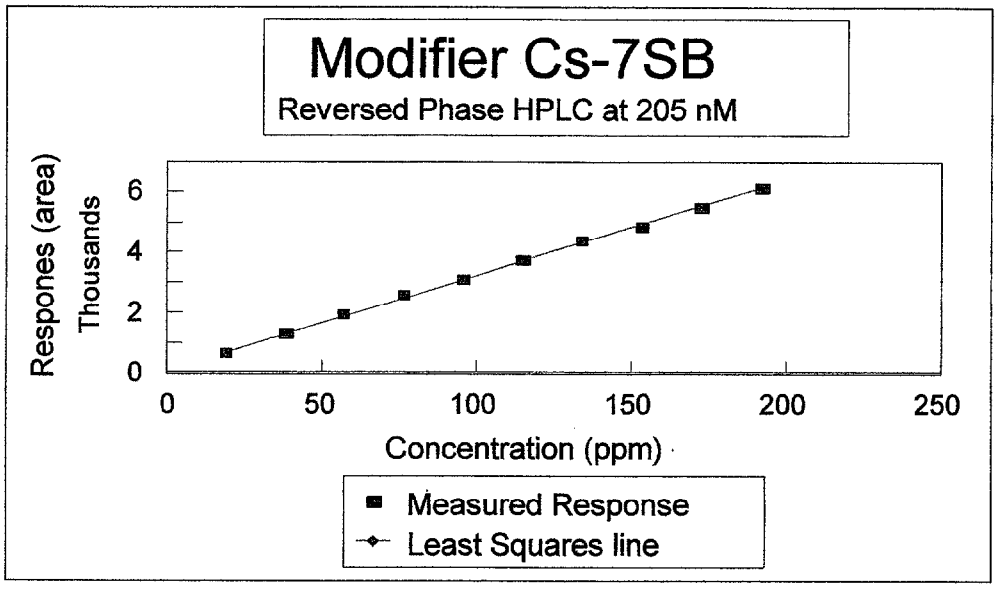


Figure 8. Calibration curve for Cs-7SB at 205 nm.

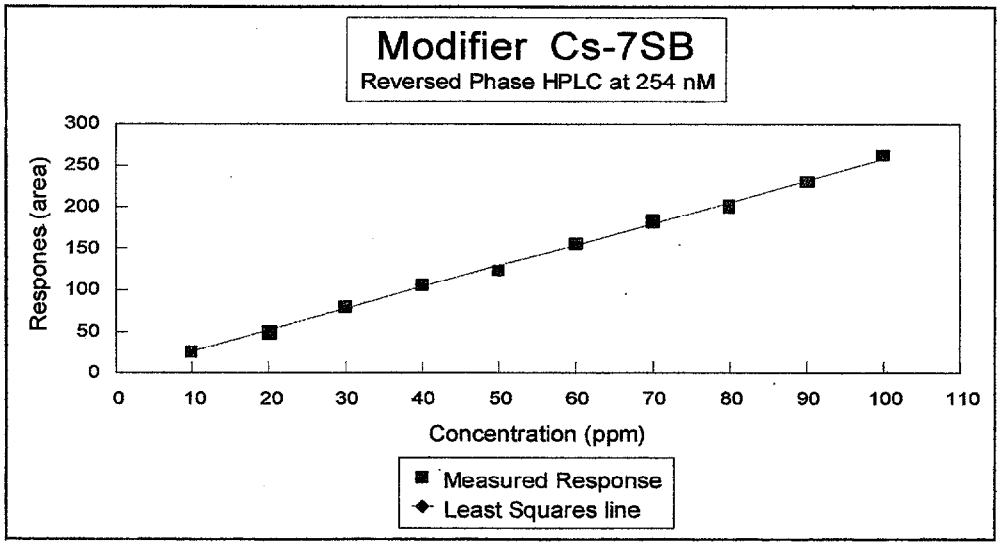


Figure 9. Calibration curve for Cs-7SB at 254 nm.

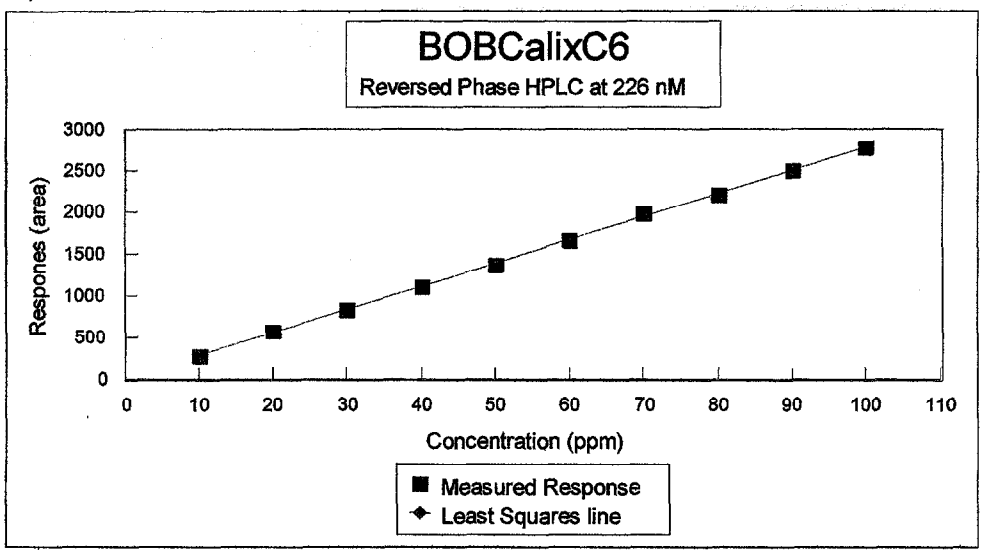


Figure 10. Calibration curve for BOBCalixC6 at 226 nm.

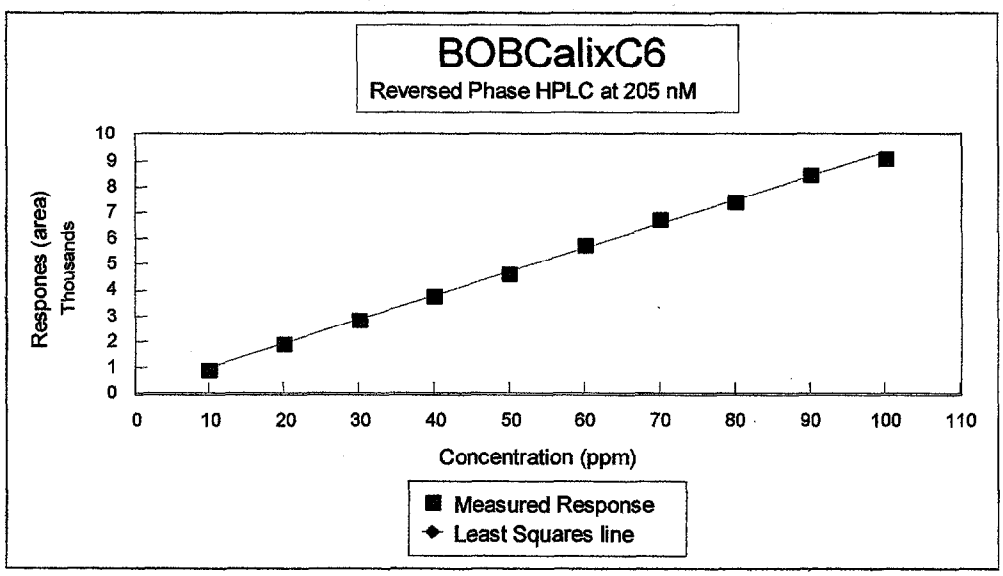


Figure 11. Calibration curve for BOBCalixC6 at 205 nm.

The linearity and fit are excellent in all of these plots. All raw data, including calculations, is given in Appendix 1. Unless otherwise noted, all quantitative data contained in this report for these three compounds was generated using this method. The variety of wavelengths improves the accuracy of the analysis by allowing for multiple response factors and minimizing the possibility of interferences. Day to day accuracy and precision data are given in Table 1.

Table 1. Intra-day accuracy and precision

Analyte	Known Conc. (mg/L)	Measured Conc. (mg/L)	% RSD
4-*sec*-butylphenol			
	6.012	6.014 ± 0.141	2.62
	5.010	4.999 ± 0.141	3.15
	4.008	4.033 ± 0.339	8.79
	3.006	2.984 ± 0.217	7.82
	1.002	1.007 ± 0.084	9.93
Cs-7SB			
	1690	1682 ± 92	0.76
	1521	1518 ± 93	0.79
	1352	1367 ± 96	0.66
	845	839 ± 95	1.18
BOBCalixC6			
	126.4	125.5 ± 3.4	1.17
	114.9	116.1 ± 4.7	0.17
	103.4	103.3 ± 4.2	0.65
	91.9	91.9 ± 3.9	1.00
	57.5	57.3 ± 4.2	1.04

4.2. Gel Permeation Chromatography method for quantitative and qualitative analysis

Because of the limitations of the reverse-phase method discussed above, a second, complementary method was developed at ORNL and subsequently applied at SRTC. This method involves a high performance gel permeation chromatography column (GPC). Thus, the separation is based on molecular weight rather than specific interaction with the stationary phase. The column, a Shodex 801, is a non-aqueous size-exclusion material with an exclusion limit of molecular weight approximately 1500. The mobile phase is chloroform. Flow rate is set at 1 mL/min. The column temperature is 40 °C. Under these conditions, all analytes elute within 10 minutes.

In addition, the method features the use of two detectors in series. The first detector is an absorbance detector, identical to that used in the reverse phase method described above, while the second is an evaporative light scattering detector (ELD). The ELD operates by evaporating the mobile phase in an optical cell and measuring the light scattering caused by the resulting particles of analyte. Since the light scattering is

independent of the absorbance, compounds which cannot be detected due to optical transparency do give a response, providing they are sufficiently non-volatile. TOA, for example, is detectable using the ELD, although we found the quantitative aspects of the TOA analysis to be somewhat non-linear.

The method has the following advantages. Due to the use of the GPC column, all potential analytes, both expected and unknown, providing they are soluble in the mobile phase, elute from the column and are detected. This is in contrast to the reverse-phase system, where very polar organics will elute as unretained peaks, and very non-polar organics may not elute at all. Second, all of the peaks are eluted in 10 minutes, providing a significant increase in sample throughput. Third, the method allows for the collection of sample fractions in a volatile solvent. These fractions can be subjected to further instrumental analysis. Finally, by virtue of the elution of materials in order of decreasing molecular weight, the retention time of unknown peaks can be used to assess approximate molecular weight, providing additional qualitative information. The chromatograms shown in Figure 12 illustrate the separation of the calixarene and the modifier using this system and method. The top chromatogram is from the ELD, the bottom from the UV. The signals are recorded simultaneously, although there is a slight time delay due to the solution transport time from the UV detector to the ELD.

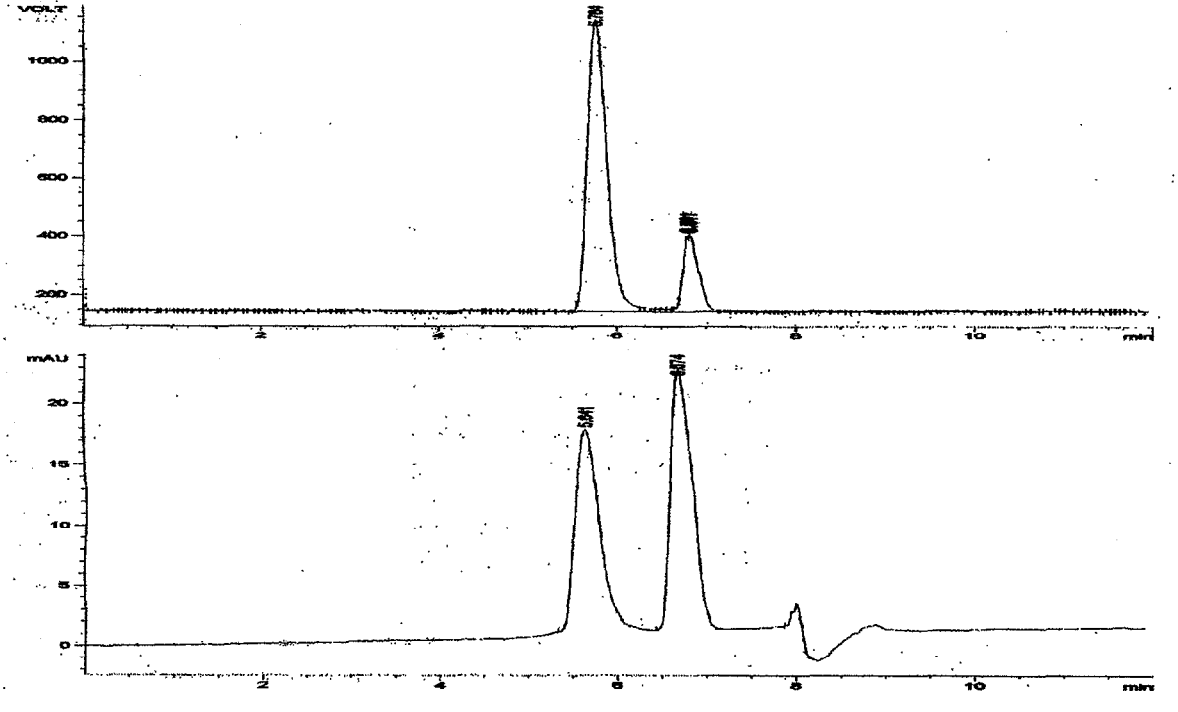


Figure 12. GPC analysis of the solvent system. Top chromatogram is from the ELD. Bottom chromatogram is from the UV absorbance detector. The peak at 5.6 minutes is BOBCalixC6, and the peak at 6.7 minutes is the modifier.

The two HPLC methods are complementary, in that they can be used in parallel or in series (via collection of the GPC effluent and analysis of the fraction by reverse-phase-HPLC). The GPC method can also provide an estimate of molecular weight for unknown peaks, as shown in Figure 13. This plot illustrates the relationship between molecular weight and elution volume. Because the flow rate is 1mL/min., the elution volume is the same as the retention time. In the case of unknown compounds, the plot can be used to approximate molecular weight.

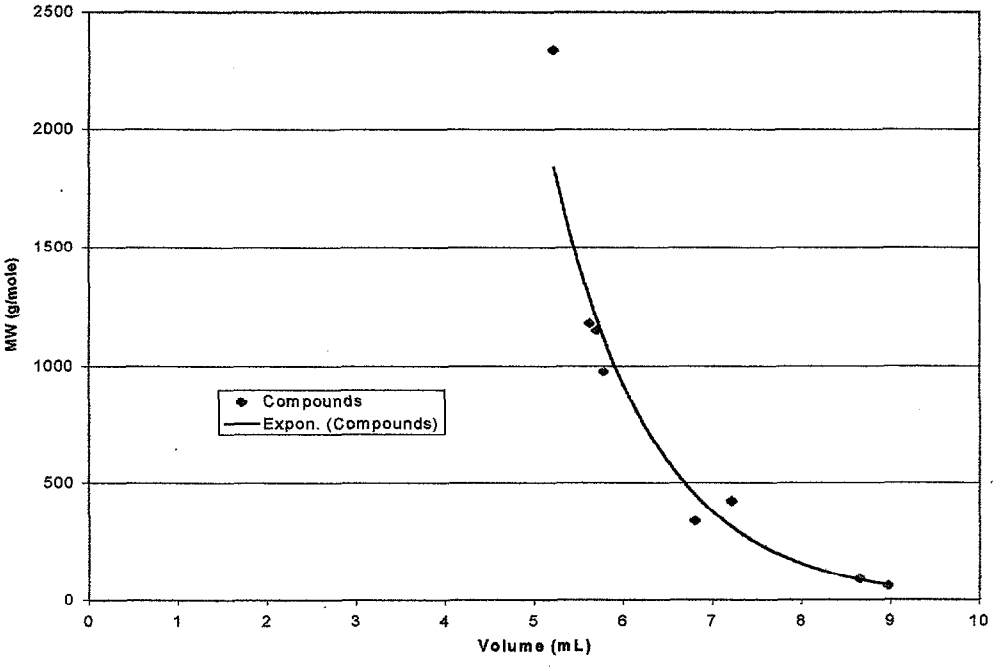


Figure 13. Plot of molecular weight of polystyrene standards versus elution volume The high molecular weight compounds elute earlier.

The quantitative aspects of this method are similar to the reverse-phase method as far as UV detection, although the use of chloroform as the mobile phase restricts the choice of wavelength. The detector response to the analytes was determined to be linear on the diode array detector (observation wavelength of 280 nm) over the concentration ranges present in the solvent after a 1:100 dilution. The linear relationships between peak area and concentration of Cs-7SB and BOBCalixC6 are summarized in Table 2. The % RSD for the slopes of Cs-7SB and BOBCalixC6 is about 2%. Calibration curves for the BOBCalixC6, the Cs-7SB, and the 4-*sec*-butylphenol are shown in Figure 14 through Figure 16.

Table 2. Linearity of the GPC method for the test compounds

Analyte	Conc. Range (mg/L)	Slope	Intercept	Correlation Coefficient
Cs-7SB	850 - 1700	2.9821	-12.5	1.0
BOBCalixC5	60 - 125	3.5822	-22.0	0.999

With respect to the evaporative light scattering detector, the calibration curves were linear over about one order of magnitude. This narrow range is not really a limitation in this application, as the target concentration is known. However, there was still an advantage in terms of precision and linearity for the UV detector at 280 nm.

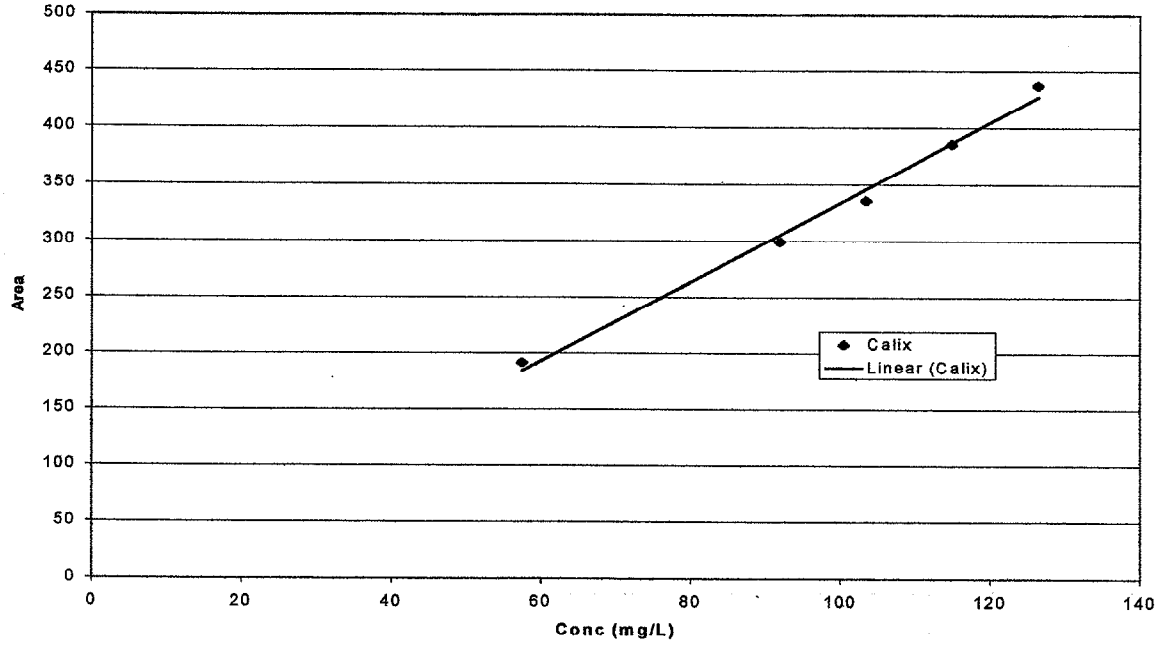


Figure 14. Calibration curve for BOBCalixC6 at 280 nm.

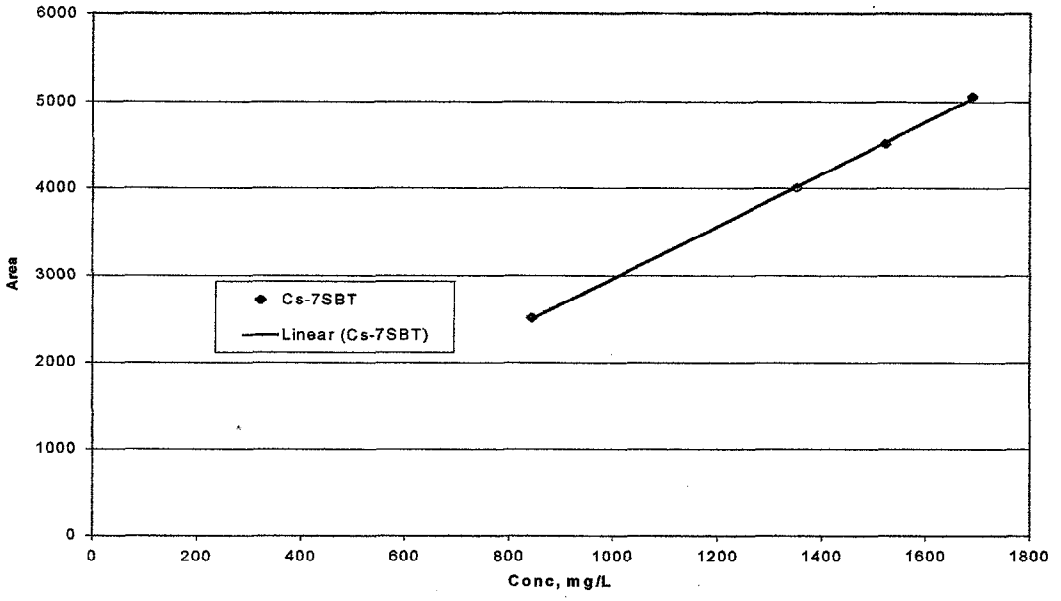


Figure 15. Calibration curve for Cs-7SB at 280 nm.

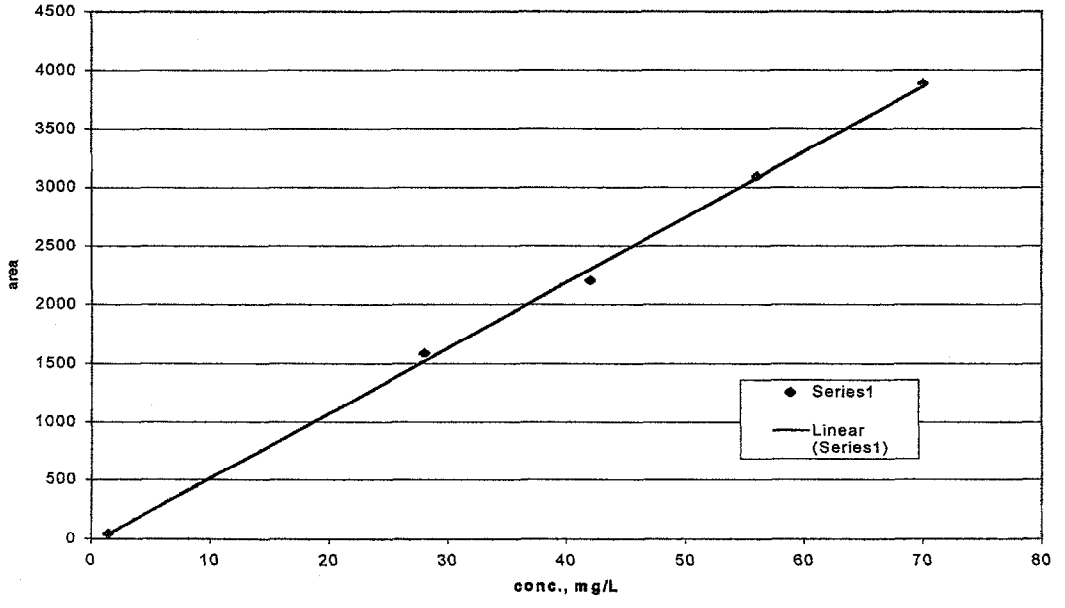


Figure 16. Calibration curve for 4-*sec*-butylphenol at 280 nm.

4.3. Analytical method for tri-n-octylamine (TOA)

Although the analysis of TOA could be carried out by GPC, it was found that analysis using gas chromatography yielded better results. The advantages include better detection limits (tri-n-octylamine is UV transparent), multiple detector capability, and superior resolution from the modifier, which is in large excess.

The gas chromatography was carried out on a Varian Model 3400 GC equipped with an autosampler and a flame ionization detector (FID). The column was a 30M 3 0.32 mm DB-5, 1.0uM film thickness. The temperature profile for the analysis was an initial oven temperature of 70 °C for 2 minutes, 5 °C/min. to 150 °C, 10 °C/min. to 250 °C, and a 5 minute hold. Under these conditions, TOA elutes at approximately 25.5 minutes as a symmetrical peak free of interference from the modifier, which elutes at about 22 minutes; a typical chromatogram is shown in Figure 17.

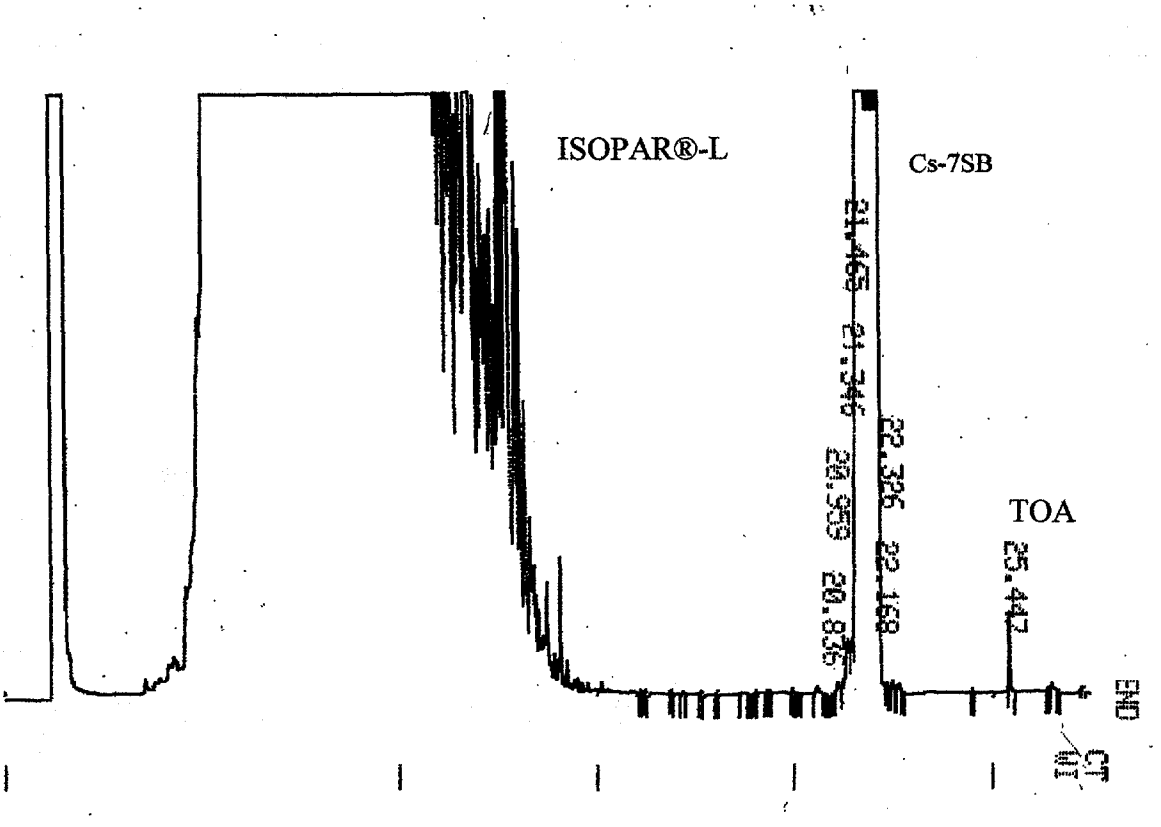


Figure 17. Gas chromatographic analysis of pristine solvent system for tri-n-octylamine (retention time of 25.447 minutes).

Calibration is by external standardization at or near the target concentration. The method is stable and reproducible (replicate injections consistently less than 2% RSD).

Standard addition was performed on one of the samples from the internal irradiation experiment,[2] and the results are shown in Figure 18.

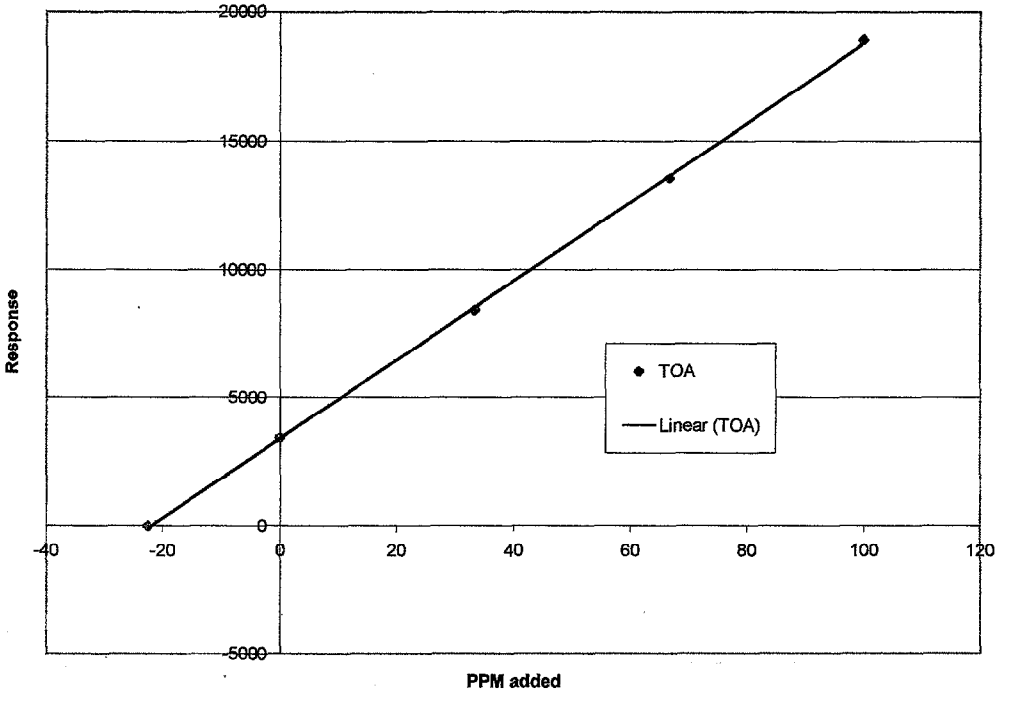


Figure 18. Results of standard addition of tri-n-octylamine to pristine solvent sample.

It should be noted that these conditions are similar to the conditions commonly used for semivolatile organics by GC/MS in EPA methods.[3] Therefore there is a substantial body of information on the retention time of organic compounds available that can aid the assessment of unknown peaks. Although a portion of the chromatogram is completely obscured by the ISOPAR® L diluent, which is the major component in the solvent, there is still the possibility of detecting breakdown products with elution times longer than the ISOPAR® L, as well as the possibility of detecting tributyl phosphate and possibly other materials introduced into the solvent by contact with the simulant or real waste. In addition, the possibility exists to use a mass spectrometer as the detector rather than an FID. A method based on GC/MS was developed at ORNL and also at SRTC. The method is similar in performance to the FID method, although for the long term, GC/MS may be preferable for reasons noted below with respect to solvent breakdown products and the retention of components from the waste stream.

4.4. Extension of the analytical methods to possible breakdown products

As mentioned earlier, it was considered necessary to develop methods which would allow at least the possibility of detecting breakdown products of the components of the solvent system. Through the course of this work, two major breakdown products were identified: 4-*sec*-butylphenol and dioctylamine. The 4-*sec*-butylphenol is a result of breakdown of the modifier and the dioctylamine results from breakdown of the tri-n-octylamine . Furthermore, with respect to analysis of the solvent system under operating conditions, it would be preferable to use methods which would offer the possibility of providing qualitative information on minor components from the real waste, particularly those with the potential for affecting the efficiency of the CSSX process. These factors led to an investigation of the possibility of using GC/MS rather than GC/FID or reverse-phase HPLC for the analysis of 4-*sec*-butylphenol, di-n-octylamine, and tri-n-octylamine. The details of the analysis of tri-n-octylamine were worked out largely at SRTC, due to the fact that a GC/MS was available. This method uses single ion monitoring to quantitatively measure the tri-n-octylamine and 4-*sec*-butylphenol. Analytical separations were carried out on a Hewlett Packard 6890 gas chromatograph, equipped with a 30 m DB-5 column, with 0.25 mm diameter and 0.25 um film thickness. Quantitation was performed using a Hewlett Packard 5973 mass selective detector. Selected ion monitoring, ion 254 for TOA and ion 121 for 4-*sec*-butylphenol, was used to obtain the chromatogram shown in Figure 19. This method also proved useful for quantitative analysis. Relative standard deviations for replicate sample analysis were typically <3%.

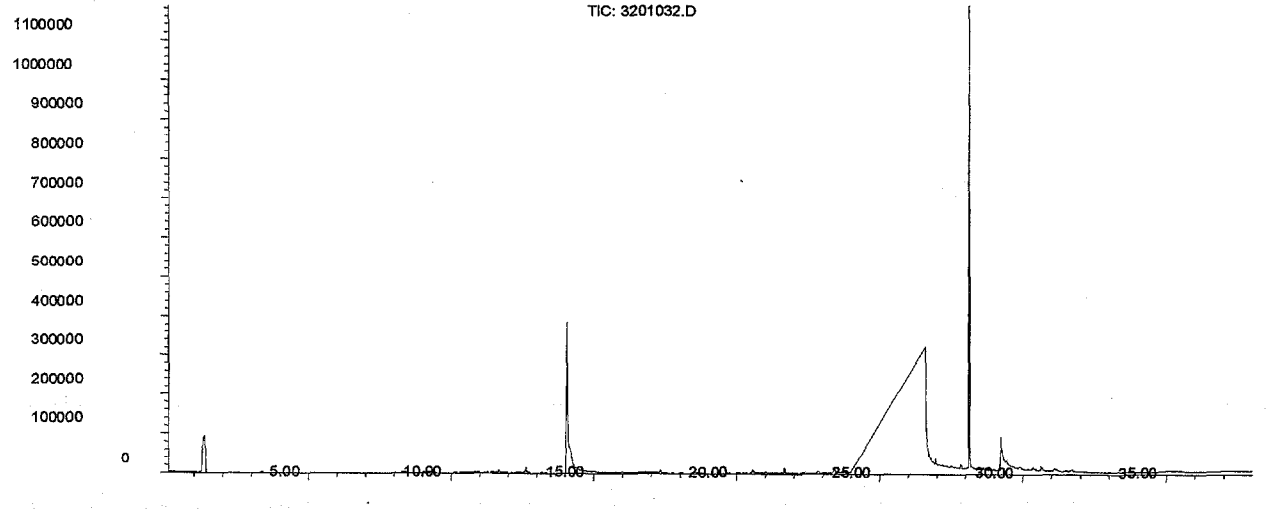


Figure 19. Mass chromatogram of 4-*sec*-butylphenol (15 minutes), and tri-n-octylamine (28 minutes).

One additional approach was investigated for the analysis of di-n-octylamine and tri-n-octylamine. During the thermal stability experiment (3) pristine solvent samples were stored at elevated temperatures over the various aqueous phases. It was noticed that there was degradation of tri-n-octylamine at elevated temperature in solvent over the scrub solution (0.05M nitrate). Initially, di-n-octylamine was formed. However, as time progressed, the di-n-octylamine also appeared to be degrading. A logical assumption would be that the di-n-octylamine was degrading to octylamine. However, octylamine elutes in the portion of the chromatogram obscured by the ISOPAR® L. Therefore, a gas chromatographic method similar to the above method in terms of GC conditions but employing an alkali flame ionization detector (NPD) was used to visualize the nitrogen-containing species in the sample. A chromatogram of standard solutions of the three major expected components is shown in Figure 20.

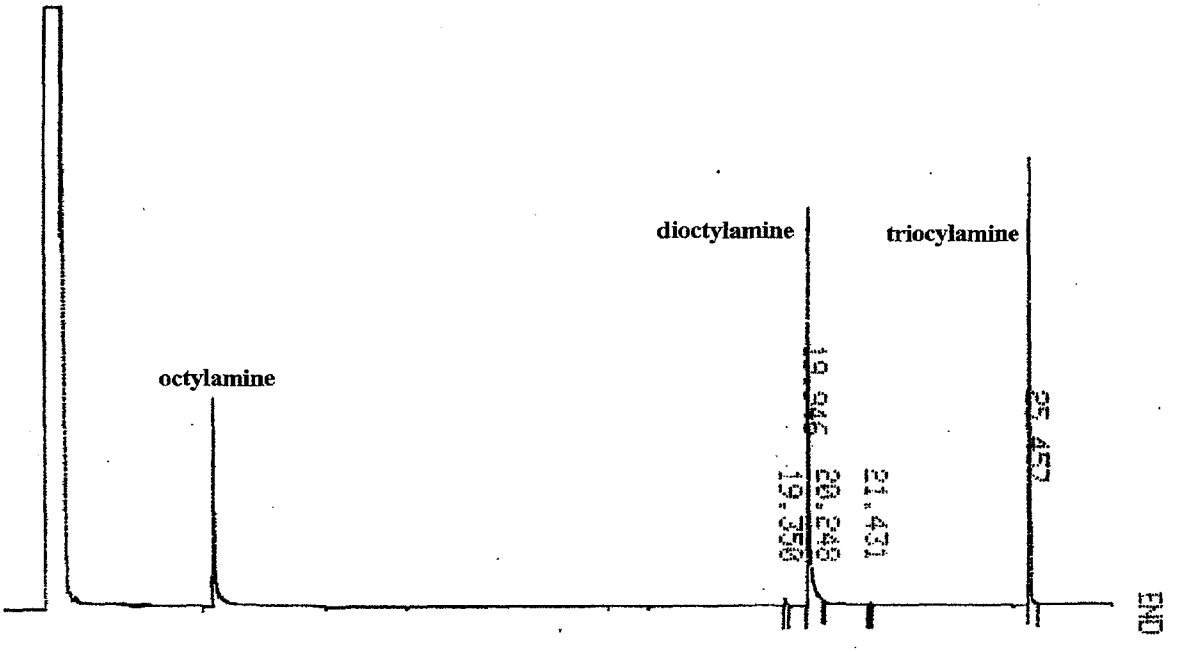


Figure 20. Chromatogram of the expected thermal breakdown products of tri-n-octylamine.

Analysis of the solvent system prior to thermal treatment using the NPD is shown in Figure 21. Note the minimal interference from the ISOPAR® L, which elutes in the range of 10-16 minutes. The asymmetric peak at 26 minutes is due to the extrmely high concentration of Cs-7SB. Nevertheless, if there were nitrogen-containing species coeluting with the Cs-7SB, it is likely that they would be detected here. The retention time of the TOA is slightly longer than in earlier chromatograms due to the fact that the column film thickness is greater (1.0 uM vs. 0.25 uM).

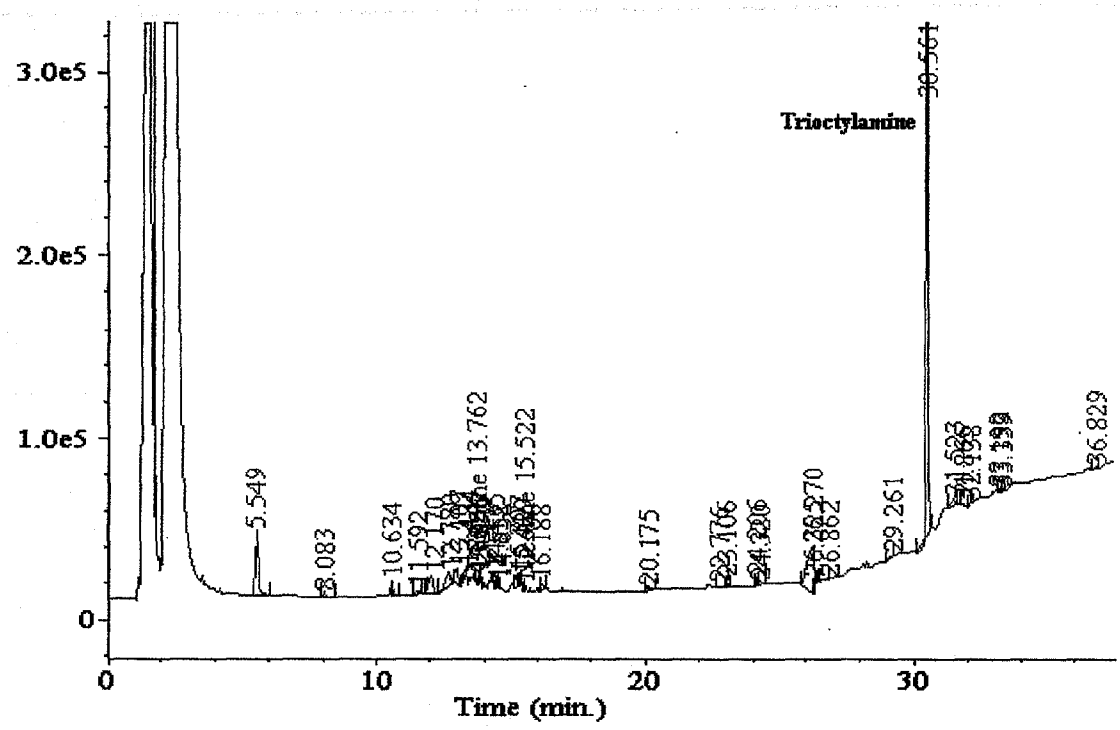


Figure 21. Analysis of the solvent system prior to thermal treatment using a nitrogen-selective detector.

An chromatogram of a degraded sample from the thermal stability experiment is shown in Figure 22. No octylamine was seen, but there are several small peaks eluting between the dioctylamine and the tri-n-octylamine. An attempt was made to identify these components via GC/MS, but their concentration was too low to acquire a reasonable mass spectrum. However, from this analysis it can be concluded that no major nitrogen containing compounds will be present in the solvent as a result of degradation of the tri-n-octylamine. Thus, the use of similar GC conditions combined with multiple detectors offers the possibility of enhanced characterization of the solvent system. This capability may prove extremely useful during plant operation with real waste components.

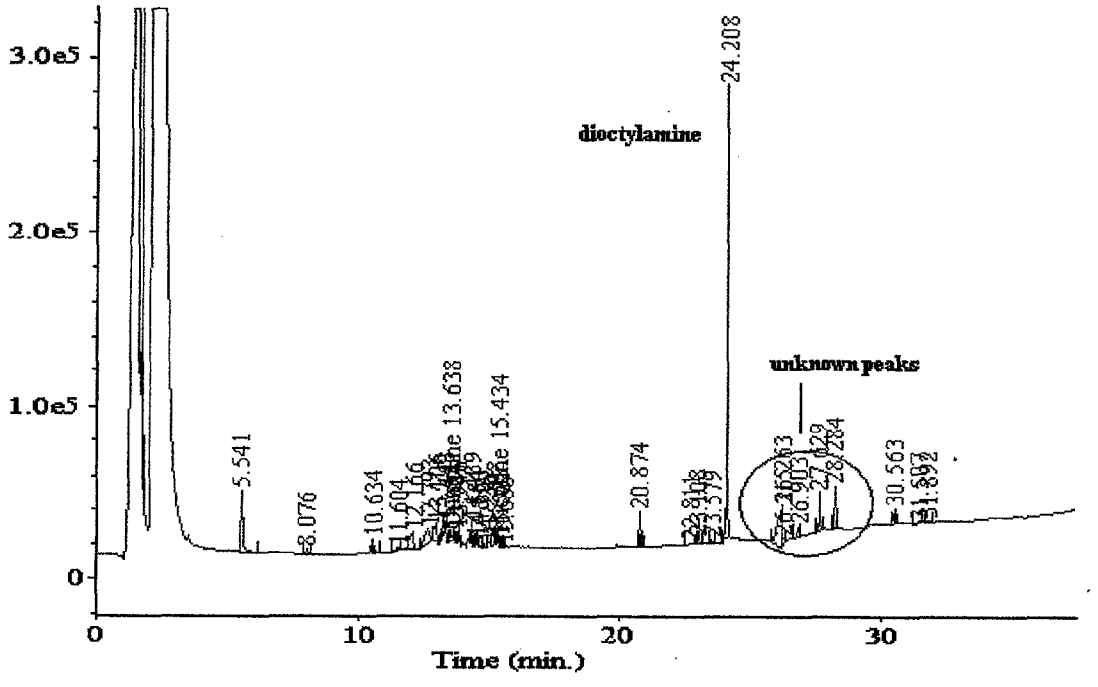


Figure 22. Analysis of thermally degraded sample.

5. Recommendations for process analysis.

An additional objective of this work was to make recommendations as to the type and frequency of analyses to be carried out in the plant setting. Some of these issues are resolved by examination of the behavior of the solvent system when subjected to extreme conditions. After external irradiation, internal irradiation, multiple process cycling, and thermal treatment well beyond that expected in process operation, it is clear that the calixarene and modifier are quite stable.[4] Therefore, there appears to be no real need for continuous monitoring of these components during plant operation. This would seem to offer the opportunity for operational cost savings. However, an off-line analytical capability still needs to be established. This capability might consist of analysis by either HPLC method. Since the number of samples to be analyzed will likely be low, and turn-around time requirements not terribly important, a case could be made for the use of the reverse phase method, based on the fact that the method does not produce a mixed waste. However, for the purpose of examining samples in the case of process upset, the qualitative advantages of the dual-detector GPC method will be useful. Therefore, the recommendation is for the use of reverse-phase HPLC for routine process analysis and

quality assurance of the solvent system, and for the use of the dual-detector GPC system for unusual circumstances.

Studies[4] indicated that there was a lower degree of stability in the tri-n-octylamine concentration during treatment at extremes, and that furthermore there is some matrix specificity in the response (hence the addition of triethylamine during dilution). Thus, there may be a reason to conduct more frequent analysis for this solvent component. In addition, by using GC/MS, the tri-n-octylamine can be analyzed coincidentally with 4-*sec*-butylphenol. The acquisition and use of isotopically labeled tri-n-octylamine and 4-*sec*-butyl phenol would allow precise and accurate measurement of these two compounds regardless of matrix, and regular analysis of 4-*sec*-butylphenol would provide an early indication of modifier breakdown. Furthermore, GC/MS would provide qualitative information on any additional components entering the system from the real waste (e.g., tributylphosphate). Thus, it is recommended that regular analysis of tri-n-octylamine and 4-*sec*-butylphenol be conducted by GC/MS, using extracted ion current profiling rather than SIM (in order to preserve the qualitative information), and using stable isotopes for quantitative analysis.

Perhaps the most important analysis from a process point of view is the composition of the incoming waste. This will be true regardless of the nature of the separation process. However, the nature of the solvent extraction process is that a limited number of possible waste constituents have the potential for causing major upsets in process operation. Plant operation experience will define which parameters will need to be monitored, and at what frequency. As experience is gained on the variability of the waste feed, an adequate process control plan will be developed.

6. Summary

In summary, two HPLC methods and one GC method have been developed and implemented for the analysis of samples related to this project. In addition, a solid phase extraction system has been applied to the separation of organic compounds from aqueous materials which come in contact with the solvent. The combination of these methods allows both quantitative analysis of the major components of the solvent, and visualization of any minor components, including breakdown products.

7. References

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8. Acknowledgements

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9. Appendix 1. Calibration data for reverse-phase HPLC method.

All concentrations in mg/L.

DETECTION LIMITS ACCORDING TO HUBAUX AND VOS

*-*TITLE: **BOBCalixC6 calibration on RP HPLC @ 226 nm**

INPUTS 1. CALIBRATION POINTS STARTING AT X11 AND Y11

NEEDED: 2. t FOR UPPER CURVE 1.8600 95.0000 %CONFID

3. t FOR LOWER CURVE 1.8600 95.0000 %CONFID

4. REGRESSION OUTPUT TO J1.

CROSSES? YES Area at Quant Limit 77.6

DET LIM	**0.634**
QUANT LM	**1.266**
Intercept, a	**12.074**
St Dev a	**16.187**
Slope, b	**51.725**
St Dev b	**0.135**
R Squared	**0.99995**

CALIBRATION POINTS		ERROR LIMIT CURVES			INCREMENTS		
CONC-X	RESP-Y	CALC Y	UPPER Y	LOWER Y	UP INC	LOW INC	conc/resp
1.15	70.5	71.6	104	39	33	33	0.01631
2.88	166.0	161.0	194	128	33	33	0.01735
5.75	314.0	309.5	342	277	32	32	0.01831
11.5	600.0	606.9	639	575	32	32	0.01917
23	1191.0	1201.7	1234	1170	32	32	0.01931
46	2379.0	2391	2423	2360	32	32	0.01934
69	3617.0	3581	3614	3548	33	33	0.01908
92	4770.0	4771	4806	4736	35	35	0.01929
115	5947.0	5960	5998	5923	38	38	0.01934

DETECTION LIMITS ACCORDING TO HUBAUX AND VOS

						DET LIM	**1.679**
*-*TITLE:	**BOBCalixC6 calibration on RP HPLC @ 205 nm**					**QUANT LM**	**3.368**
INPUTS	1. CALIBRATION POINTS STARTING AT X11 AND Y11					**Intercept, a**	**121.867**
NEEDED:	2. t FOR UPPER CURVE	1.86	95.00	%CONFID		**St Dev a**	**134.689**
	3. t FOR LOWER CURVE	1.86	95.00	%CONFID		**Slope, b**	**176.163**
	4. REGRESSION OUTPUT TO J1.					**St Dev b**	**2.835**
CROSSES?	YES	Area at Quant Limit		715.3		**R Squared**	**0.99793**

CALIBRATION POINTS		ERROR LIMIT CURVES			INCREMENTS		
CONC-X	RESP-Y	CALC Y	UPPER Y	LOWER Y	UP INC	LOW INC	conc/resp
5E+00	959.0	1043.2	1328	759	284	284	0.00545
1E+01	1959.0	1964.5	2240	1689	275	275	0.00534
2E+01	2900.0	2885.9	3154	2618	268	268	0.00541
2E+01	3771.0	3807.2	4071	3543	264	264	0.00555
3E+01	4670.0	4728.5	4991	4466	263	263	0.00560
3E+01	5792.0	5650	5914	5386	264	264	0.00542
4E+01	6789.0	6571	6840	6303	268	268	0.00539
4E+01	7441.0	7493	7768	7217	275	275	0.00562
5E+01	8508.0	8414	8698	8130	284	284	0.00553
5E+01	9103.0	9335	9631	9039	296	296	0.00575

DETECTION LIMITS ACCORDING TO HUBAUX AND VOS

*-*TITLE: **BOBCalixC6 calibration on RP HPLC @ 254 nm**

INPUTS 1. CALIBRATION POINTS STARTING AT X11 AND Y11
NEEDED: 2. t FOR UPPER CURVE 1.86 95.00 %CONFID
3. t FOR LOWER CURVE 1.86 95.00 %CONFID
4. REGRESSION OUTPUT TO J1.

CROSSES? YES Area at Quant Limit 100.8

DET LIM	**0.836**
QUANT LM	**1.673**
Intercept, a	**12.000**
St Dev a	**20.214**
Slope, b	**53.071**
St Dev b	**0.426**
R Squared	**0.99949**

CALIBRATION POINTS		ERROR LIMIT CURVES			INCREMENTS		
CONC-X	RESP-Y	CALC Y	UPPER Y	LOWER Y	UP INC	LOW INC	conc/resp
5E+00	284.0	289.6	332	247	43	43	0.01842
1E+01	584.0	567.1	608	526	41	41	0.01791
2E+01	835.0	844.7	885	804	40	40	0.01879
2E+01	1124.0	1122.3	1162	1083	40	40	0.01861
3E+01	1377.0	1399.8	1439	1360	39	39	0.01899
3E+01	1677.0	1677	1717	1638	40	40	0.01871
4E+01	1999.0	1955	1995	1915	40	40	0.01831
4E+01	2214.0	2233	2274	2191	41	41	0.01890
5E+01	2503.0	2510	2553	2467	43	43	0.01881
5E+01	2789.0	2788	2832	2743	44	44	0.01875

DETECTION LIMITS ACCORDING TO HUBAUX AND VOS

						DET LIM	**3.145**
*-*TITLE:	**Modifier Cs-7SB calibration on RP HPLC @ 205 nm**					**QUANT LM**	**6.505**
INPUTS	1. CALIBRATION POINTS STARTING AT X11 AND Y11					**Intercept, a**	**108.867**
NEEDED:	2. t FOR UPPER CURVE	1.86	95.00	%CONFID		**St Dev a**	**44.897**
	3. t FOR LOWER CURVE	1.86	95.00	%CONFID		**Slope, b**	**31.354**
	4. REGRESSION OUTPUT TO J1.					**St Dev b**	**0.257**
CROSSES?	YES	Area at Quant Limit		312.8		**R Squared**	**0.99946**

CALIBRATION POINTS			ERROR LIMIT CURVES		INCREMENTS		
CONC-X	RESP-Y	CALC Y	UPPER Y	LOWER Y	UP INC	LOW INC	conc/resp
2E+01	647.0	710.9	806	616	95	95	0.02968
4E+01	1313.0	1312.8	1405	1221	92	92	0.02925
6E+01	1943.0	1914.8	2004	1825	89	89	0.02964
8E+01	2570.0	2516.8	2605	2429	88	88	0.02988
1E+02	3119.0	3118.8	3206	3031	88	88	0.03078
1E+02	3738.0	3721	3809	3633	88	88	0.03082
1E+02	4372.0	4323	4412	4233	89	89	0.03074
2E+02	4850.0	4925	5016	4833	92	92	0.03167
2E+02	5516.0	5527	5622	5432	95	95	0.03133
2E+02	6130.0	6129	6227	6030	99	99	0.03132

DETECTION LIMITS ACCORDING TO HUBAUX AND VOS

							DET LIM	**4.300**
*-*TITLE:	**Modifier Cs-7SB calibration on RP HPLC @ 226 nm**						**QUANT LM**	**8.639**
INPUTS	1. CALIBRATION POINTS STARTING AT X11 AND Y11						**Intercept, a**	**64.467**
NEEDED:	2. t FOR UPPER CURVE	1.86	95.00	%CONFID			**St Dev a**	**81.141**
	3. t FOR LOWER CURVE	1.86	95.00	%CONFID			**Slope, b**	**41.439**
	4. REGRESSION OUTPUT TO J1.						**St Dev b**	**0.465**
CROSSES?	YES	Area at Quant Limit		422.5			**R Squared**	**0.99899**

CALIBRATION POINTS			ERROR LIMIT CURVES		INCREMENTS		
CONC-X	RESP-Y	CALC Y	UPPER Y	LOWER Y	UP INC	LOW INC	conc/resp
2E+01	849.0	860.1	1031	689	171	171	0.02261
4E+01	1652.0	1655.7	1821	1490	166	166	0.02324
6E+01	2481.0	2451.3	2613	2290	162	162	0.02322
8E+01	3288.0	3247.0	3406	3088	159	159	0.02336
1E+02	3956.0	4042.6	4201	3884	158	158	0.02427
1E+02	4869.0	4838	4997	4679	159	159	0.02366
1E+02	5738.0	5634	5795	5472	162	162	0.02342
2E+02	6264.0	6429	6595	6264	166	166	0.02452
2E+02	7229.0	7225	7396	7054	171	171	0.02390
2E+02	8078.0	8021	8199	7843	178	178	0.02377

DETECTION LIMITS ACCORDING TO HUBAUX AND VOS

						DET LIM	**6.493**
*-*TITLE:	**Modifier Cs-7SB calibration on RP HPLC @ 254 nm**					**QUANT LM**	**12.772**
INPUTS	1. CALIBRATION POINTS STARTING AT X11 AND Y11					**Intercept, a**	**0.333**
NEEDED:	2. t FOR UPPER CURVE	1.86	95.00	%CONFID		**St Dev a**	**3.983**
	3. t FOR LOWER CURVE	1.86	95.00	%CONFID		**Slope, b**	**1.347**
	4. REGRESSION OUTPUT TO J1.					**St Dev b**	**0.023**
CROSSES?	YES	Area at Quant Limit		17.5		**R Squared**	**0.99771**

CALIBRATION POINTS			ERROR LIMIT CURVES		INCREMENTS		
CONC-X	RESP-Y	CALC Y	UPPER Y	LOWER Y	UP INC	LOW INC	conc/resp
2E+01	27.0	26.2	35	18	8	8	0.71111
4E+01	51.0	52.1	60	44	8	8	0.75294
6E+01	80.0	77.9	86	70	8	8	0.72000
8E+01	107.0	103.8	112	96	8	8	0.71776
1E+02	123.0	129.7	137	122	8	8	0.78049
1E+02	157.0	156	163	148	8	8	0.73376
1E+02	184.0	181	189	173	8	8	0.73043
2E+02	202.0	207	215	199	8	8	0.76040
2E+02	231.0	233	242	225	8	8	0.74805
2E+02	264.0	259	268	250	9	9	0.72727

DETECTION LIMITS ACCORDING TO HUBAUX AND VOS

						DET LIM	**1.378**
*-*TITLE:	**4-*sec*-butylphenol calibration on RP HPLC @ 205 nm**					**QUANT LM**	**2.789**
INPUTS	1. CALIBRATION POINTS STARTING AT X11 AND Y11					**Intercept, a**	**41.267**
NEEDED:	2. t FOR UPPER CURVE	1.86	95.00	%CONFID		**St Dev a**	**42.631**
	3. t FOR LOWER CURVE	1.86	95.00	%CONFID		**Slope, b**	**67.962**
	4. REGRESSION OUTPUT TO J1.					**St Dev b**	**0.559**
CROSSES?	YES	Area at Quant Limit		230.8		**R Squared**	**0.99946**

CALIBRATION POINTS		ERROR LIMIT CURVES			INCREMENTS		
CONC-X	RESP-Y	CALC Y	UPPER Y	LOWER Y	UP INC	LOW INC	conc/resp
8E+00	593.0	612.1	702	522	90	90	0.01417
2E+01	1204.0	1183.0	1270	1096	87	87	0.01395
3E+01	1782.0	1753.9	1839	1669	85	85	0.01414
3E+01	2319.0	2324.8	2408	2241	84	84	0.01449
4E+01	2879.0	2895.7	2979	2812	83	83	0.01459
5E+01	3451.0	3467	3550	3383	84	84	0.01460
6E+01	4089.0	4037	4122	3952	85	85	0.01438
7E+01	4548.0	4608	4695	4521	87	87	0.01478
8E+01	5133.0	5179	5269	5089	90	90	0.01473
8E+01	5813.0	5750	5844	5656	94	94	0.01445

DETECTION LIMITS ACCORDING TO HUBAUX AND VOS

						DET LIM	**2.329**
*-*TITLE:	**4-*sec*-butylphenol calibration on RP HPLC @ 226 nm**					**QUANT LM**	**4.656**
INPUTS	1. CALIBRATION POINTS STARTING AT X11 AND Y11					**Intercept, a**	**51.467**
NEEDED:	2. t FOR UPPER CURVE	1.86	95.00	%CONFID		**St Dev a**	**73.760**
	3. t FOR LOWER CURVE	1.86	95.00	%CONFID		**Slope, b**	**69.542**
	4. REGRESSION OUTPUT TO J1.					**St Dev b**	**0.967**
CROSSES?	YES	Area at Quant Limit		375.3		**R Squared**	**0.99846**

CALIBRATION POINTS			ERROR LIMIT CURVES		INCREMENTS		
CONC-X	RESP-Y	CALC Y	UPPER Y	LOWER Y	UP INC	LOW INC	conc/resp
8E+00	616.0	635.6	791	480	156	156	0.01364
2E+01	1200.0	1219.8	1370	1069	151	151	0.01400
3E+01	1832.0	1803.9	1951	1657	147	147	0.01376
3E+01	2420.0	2388.1	2533	2243	145	145	0.01388
4E+01	2964.0	2972.2	3116	2828	144	144	0.01417
5E+01	3545.0	3556	3701	3412	145	145	0.01422
6E+01	4240.0	4141	4287	3994	147	147	0.01387
7E+01	4657.0	4725	4875	4574	151	151	0.01443
8E+01	5179.0	5309	5465	5153	156	156	0.01460
8E+01	5990.0	5893	6055	5731	162	162	0.01402

DETECTION LIMITS ACCORDING TO HUBAUX AND VOS

*-*TITLE: **4-*sec*-butylphenol calibration on RP HPLC @ 254 nm**

INPUTS 1. CALIBRATION POINTS STARTING AT X11 AND Y11

NEEDED: 2. t FOR UPPER CURVE 1.860 95.000 %CONFID

3. t FOR LOWER CURVE 1.860 95.000 %CONFID

4. REGRESSION OUTPUT TO J1.

CROSSES? YES Area at Quant Limit 12.7

DET LIM	**1.398**
QUANT LM	**2.843**
Intercept, a	**2.667**
St Dev a	**2.258**
Slope, b	**3.546**
St Dev b	**0.030**
R Squared	**0.99944**

CALIBRATION POINTS			ERROR LIMIT CURVES		INCREMENTS		
CONC-X	RESP-Y	CALC Y	UPPER Y	LOWER Y	UP INC	LOW INC	conc/resp
8E+00	30.0	32.5	37	28	5	5	0.28000
2E+01	61.0	62.2	67	58	5	5	0.27541
3E+01	92.0	92.0	97	88	4	4	0.27391
3E+01	124.0	121.8	126	117	4	4	0.27097
4E+01	153.0	151.6	156	147	4	4	0.27451
5E+01	183.0	181	186	177	4	4	0.27541
6E+01	215.0	211	216	207	4	4	0.27349
7E+01	239.0	241	246	236	5	5	0.28117
8E+01	269.0	271	276	266	5	5	0.28104
8E+01	299.0	301	306	296	5	5	0.28094

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