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Using GC-FID to Quantify the Removal of 4-*sec*-Butylphenol from NGS Solvent by NaOH

Frederick V. Sloop, Jr.
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Chemical Sciences Division

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LIST OF ABBREVIATED TERMS

Cs-7SB	1-(2,2,3,3-tetrafluoropropoxy), 3-[4-(*sec*-butyl)phenoxy]-2-propanol (solvent modifier)
CSSX	Caustic-Side Solvent Extraction process
DCM	dichloromethane / methylene chloride
FID	flame ionization detector
GC	gas chromatography
GC-FID	gas chromatography–flame ionization detection
HCl	hydrochloric acid
Hz	Hertz
MaxCalix	1,3-*alt*-25,27-bis(3,7-dimethyloctyl-1-oxy)calix[4]arene-benzocrown-6
MCU	Modular CSSX Unit at the SRS
mL	milliliter
MΩ	megaohm
NaOH	sodium hydroxide
NG-CSSX	Next Generation Caustic-Side Solvent Extraction process
NGS	Next Generation Solvent
ORNL	Oak Ridge National Laboratory
ppb	parts per billion
psi	pounds per square inch
QA	Quality Assurance
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SBP	4-*sec*-butylphenol
Sep funnel	separatory funnel
SRS	Savannah River Site
TiDG	*N*, *N*', *N*"-triisodecylguanidine (stripping agent or "suppressor" in the solvent)
µL	microliter
w/w	weight to weight

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ABSTRACT

A caustic wash of the solvent used in the Next-Generation Caustic-Side Solvent Extraction (NG-CSSX) process was found to remove the modifier breakdown product 4-*sec*-butylphenol (SBP) with varying efficiency depending on the aqueous NaOH concentration. Recent efforts at ORNL have aimed at characterizing the flowsheet chemistry and reducing the technical uncertainties of the NG-CSSX process. One technical uncertainty has been the efficacy of caustic washing of the solvent for the removal of lipophilic anions, in particular, the efficient removal of SBP, an important degradation product of the solvent modifier, Cs-7SB. In order to make this determination, it was necessary to develop a sensitive and reliable analytical technique for the detection and quantitation of SBP. This report recounts the development of a GC-FID-based (Gas Chromatography–Flame Ionization Detection) technique for analyzing SBP and the utilization of the technique to subsequently confirm the ability of the caustic wash to efficiently remove SBP from the Next Generation Solvent (NGS) used in NG-CSSX. In particular, the developed technique was used to monitor the amount of SBP removed from a simple solvent and the full NGS by contact with sodium hydroxide wash solutions over a range of concentrations. The results show that caustic washing removes SBP with effectively the same efficiency as it did in the original Caustic-Side Solvent Extraction (CSSX) process.

1. INTRODUCTION

This report describes the development of a simple gas-chromatography (GC) based method for quantifying the concentration of 4-*sec*-butylphenol (SBP) in the Next Generation Solvent (NGS) used in the Next-Generation Caustic-Side Solvent Extraction (NG-CSSX) process and the use of the developed GC method in determining the efficacy of the caustic solvent-wash step in the NG-CSSX flowsheet. In general, solvent cleanup is an essential component in any industrial solvent extraction process to prevent the buildup of deleterious impurities in the solvent.[1] For this purpose, the NG-CSSX process[2–4] and its forerunner, the Caustic-Side Solvent Extraction (CSSX) process,[5–10] employ a solvent wash using dilute sodium hydroxide. Although the function of this wash step is not entirely understood, stripping efficiency degrades without it, ultimately leading to declining ability of the overall process to remove cesium from the salt waste.[5,11,12]

For the present study, SBP was selected as an indicator of the efficiency of caustic solvent washing. It is a primary breakdown product of the solvent modifier Cs-7SB (see below for its structure) and therefore one of the possible solvent impurities that needs to be removed by solvent washing.[5] The anionic form of SBP and other lipophilic anions impair stripping if allowed to build up in the solvent.[4,5,13] To suppress the deleterious effect of such rogue anions on stripping, a lipophilic organic base called the "suppressor" is added to the solvent. In CSSX, the suppressor is tri-*n*-octylamine (TOA),[5–7,11] while in NG-CSSX, the suppressor is a guanidine. Initially, the guanidine employed in NGS was *N*,*N*'-dicyclohexyl-*N*"-isotridecylguanidine (DCiTG),[2–4,14,15] but its modest loss to the aqueous stripping solution led to a switch to the more lipophilic guanidine *N*,*N*',*N*"-triisodecylguanidine (TiDG).[16,17] In replacing the CSSX process by the more powerful NG-CSSX process, the question arises as to whether the caustic wash performs as effectively in NG-CSSX as in CSSX. To address this question and thereby reduce the technical risk of deploying NG-CSSX with TiDG as the suppressor, the partitioning of SBP between the NG-CSSX process solvent and aqueous sodium hydroxide solutions was measured as a function of the sodium hydroxide concentration. Although SBP itself may not actually be an analytically prominent impurity in the flowsheet chemistry,[11,12] it is the key breakdown product of the Cs-7SB modifier, and its partitioning to aqueous NaOH solutions serves as a useful indicator of the capacity of caustic wash solutions to remove lipophilic anions from the solvent.

In the developed analytical method, the SBP analyte is introduced via syringe injection onto a GC column filled with a stationary phase with which various molecules in the introduced sample interact differentially according to their chemical and physical properties as they are swept along by a gaseous mobile phase, in this case hydrogen. Upon exiting the column, the analyte molecules are detected via a FID (flame ionization detector) in which a hydrogen-fueled flame pyrolizes organics to form cations and electrons, which generate a current when they pass between a pair of electrodes. This current appears as a peak on a chromatogram that is assigned an identity based upon known molecular behaviors.

This analytical method was developed in a step-wise fashion by first utilizing a simplified solvent in order to locate the SBP peak, then followed by analysis of the full NGS to reflect real-world conditions and uses of the method and to ascertain what additional chemical manipulations might become necessary for the analysis to be successful. GC conditions were arrived at by first selecting a GC column with physical characteristics and performance criteria that would maximize the opportunity to separate, isolate and quantify any SBP in NGS. Analytical conditions were then developed for SBP by using suitable starting conditions based upon previous experience with similar classes of chemical compounds and mixtures, which were then incrementally modified until a suitable final methodology was found.

Once a suitably sensitive GC-FID-based method was developed, the technique was used to monitor the effectiveness of various sodium hydroxide washes in removing SBP from a simple solvent and from the newly developed and currently deployed NGS. The results were then compared with the corresponding data reported for the CSSX solvent. The comparison consequently reflects upon the long-term technical risk in the deployment of the NG-CSSX process, now in use for one year at full scale in the Modular CSSX Unit (MCU) at the Savannah River Site (SRS).[17]

2. EXPERIMENTAL SECTION

2.1 SOLVENT COMPOSITIONS

2.1.1 Materials

Solvent components were obtained from commercial sources and judged to be of adequate purity for use as received. 1-(2,2,3,3-Tetrafluoropropoxy),3-[4-(*sec*-butyl)phenoxy]-2-propanol (Cs-7SB modifier, Lot No. MOD2012-M-1), 1,3-*alt*-25,27-bis(3,7-dimethyloctyl-1-oxy)calix[4] arene-benzocrown-6 (MaxCalix, Lot No. 79-008-1), and the guanidine suppressor *N*,*N*',*N*''-tris(3,7-dimethyloctyl)guanidine in the form of its HCl salt (TiDG, Lot No. 79-221-1), were all obtained from Marshallton Research. Isopar L, Lot No. US67377E was obtained from ExxonMobil. The 4-*sec*-butylphenol (SBP) was acquired from TCI America.

Water for preparation of all aqueous solutions was first distilled and then deionized using a Milli-Q® gradient A10 filtering system equipped with a Quantum™ Ex Ultrapure Organex Cartridge (18.2 MΩ•cm at 25 °C, total organic content 4 ppb).

Appropriate amounts of the various components were weighed using an ORNL Metrology calibrated Ohaus AR2140 Adventurer balance in concert with a calibrated set of check weights that were used both prior to and immediately after using the balance to weigh solvent components. Comparisons of balance readings were made using both 1.0000 g and 10.0000 g check weights.

2.1.2 Methods

Solvents were prepared by weighing appropriate amounts of extractant, modifier, and suppressor into volumetric flasks and diluting with Isopar L to the mark. Assuming 100% purity of as-received solvent components, the actual concentrations for NGS are shown in Table 2.1.

The formulation for the NGS used in these experiments was 0.050 M MaxCalix, 0.50 M Cs-7SB, and 0.003 M TiDG in Isopar L diluent. This is the formulation in use in the MCU.[17] After it was thoroughly mixed, the solvent was washed by sequential contacts with equal volumes of 0.010 M HCl, H_2O, followed by decreasing concentrations of NaOH (0.3 M, 0.1 M, 0.03 M, and 0.01 M), and then repeatedly with H_2O until the solution was pH neutral. The washing protocol was adopted from methodology used in the development of the CSSX process in which minor impurities in as-received solvent components were removed by washing with respectively the HCl and NaOH solutions.[5] While NGS used in the MCU is not subjected to this washing protocol during solvent preparation, it was necessary to prewash the solvent used in this study in order to remove any minor impurities in Cs-7SB, mainly SBP, prior to making measurements. SBP is a known impurity in as-received Cs-7SB. This protocol placed the solvent in a uniform initial condition, with the guanidine in the neutral state in which it is found in the MCU's solvent hold tank and throughout most of the flowsheet.

For initial testing, a SBP-spiked Simple Solvent (Table 2.2) was prepared which consisted of 0.50 M Cs-7SB and 0.010 M SBP in Isopar L.

Table 2.1. Composition of the NGS employed in testing

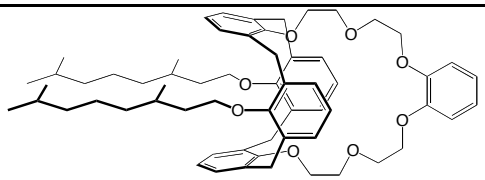
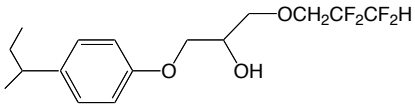
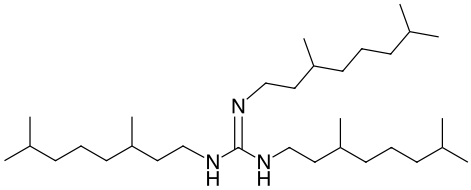
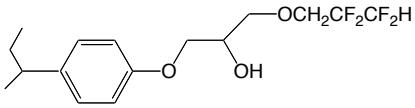
Compound	Structure	Molecular Weight (g/mol)	Actual Concentration (mol/L)
1,3-*alt*-25,27-Bis(3,7-dimethyloctyl-1-oxy)calix[4]arene-benzocrown-6 0.050 M MaxCalix		955.435	0.050
1-(2,2,3,3-Tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol 0.50 M Cs-7SB		338.37	0.50
N,*N*',*N*''-Tris(3,7-dimethyloctyl)guanidine 0.003 M TiDG		516.39 as HCl form	0.003
Isopar L	C_{12} isoparaffinic hydrocarbon		

Table 2.2. Composition of the simple solvent employed in testing

Compound	Structure	Molecular Weight (g/mol)	Actual Concentration (mol/L)
1-(2,2,3,3-Tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol 0.50 M Cs-7SB		338.37	0.50
Isopar L	C_{12} isoparaffinic hydrocarbon		

2.2 SOLVENT WASHING

2.2.1 Materials

A 50% NaOH (w/w) solution, was obtained from JT Baker. Concentrated hydrochloric acid, GR, was obtained from EM Science.

Washing solutions were prepared through appropriate dilutions of commercial 50% NaOH and concentrated HCl using distilled deionized 18.2 MΩ•cm water. The solutions prepared included 0.01 M HCl and 0.30 M, 0.10 M, 0.03 M and 0.01 M NaOH.

2.2.2 Methods

Both the simple solvent and the full NGS were subjected to the same washing protocol for the removal of minor impurities. Using a separatory funnel the solvents were contacted sequentially with equal volumes of 0.01 M HCl, H_2O, and decreasing concentrations of NaOH (0.30 M, 0.10 M, 0.03 M and 0.01 M), and finally with H_2O until the contact was pH neutral.

2.3 GC PROTOCOL

2.3.1 Materials

GC analyses were performed using a Hewlett Packard HP6850 Series GC System with Agilent Chem Station data and control software. The instrument was fitted with an Agilent J&W CP8907 GC column with a VF-1ms stationary phase. The column measured 15 m (L) x 0.25 mm (OD) x 0.39 mm (ID). A Parker Balston H2PEM-100 Hydrogen Generator supplied hydrogen for the FID and carrier gas.

The Agilent J&W CP8907 GC column was selected for this analysis since it exhibits low polarity and is highly inert. Manufacturer's specifications indicate that this column has a 100% dimethylpolysiloxane stationary phase that is highly dispersive and will afford the rapid elution of highly volatile hydrocarbons due to lack of hydrogen-bonding strength. It is characterized by low bleed (which allows for increased sensitivity) and the 0.25 mm ID makes for higher column efficiency, providing approximately 4,750 theoretical plates per meter. The combination of film thickness and column ID gives a column capacity of 50–100 ng of sample, which permits longer sample retention time on the column while the 15-meter column length is suitable for samples containing few solutes.

The 4-*sec*-butylphenol, Lot No. FHF01, used to spike both the simple solvent and the NGS solvent, was obtained from TCI America.

Additional laboratory equipment employed included a VWR Ultrasonic Cleaner/Heating Bath (model 97043-988), VWR Digital Vortex Mixer (model 14005-824), VWR Clinical 50 centrifuge and EM Science ColorpHast pH strips. A variety of Eppendorf Research pipettes, VWR thermometers, an Ohaus AR2140 balance and a check weight set used in this work, were calibrated by ORNL Metrology (accredited to ISO/IEC 17025 by the National Voluntary Laboratory Accreditation Program).

2.3.2 Methods

The starting point for method development used conditions that were previously employed for analyzing the guanidine suppressor[4] of NGS. The initial program was designated 4-sBPA-M (see Table 2.3). The test samples included 0.01 M SBP in a simple solvent comprised of 0.5 M Cs-7SB in Isopar L, 0.01 M SBP in Isopar L, and 0.01 M SBP in dichloromethane (DCM).

QA/QC for this work necessitates the use of certain calibrated equipment. Liquid transfers are performed using calibrated pipettes, and either graduated or volumetric glassware. A weighing protocol is followed in which a calibrated Ohaus balance (ORNL designator X249310) is used in conjunction with a set of calibrated check weights (ORNL designator A001507). Typically two check weights (usually 1 g and 10 g) are weighed both before and after the weighing of chemical reagent as a check on the consistency of the balance.

Table 2.3. Step-wise adjustments to basic program

Method	Rate °C/min	Temp. °C	Hold time min.	Total time (min)
4-sBPA-M		80	10	10
	50	260	0	13.6
	4	300	10	33.6
4-sBPB-M		110	3	3
	100	260	0	4.5
	4	300	10	24.5
4-sBPC-M		80	3	3
	100	260	0	4.8
	4	300	10	24.8
4-sBPD-M		80	5	5
	300	260	0	5.6
	4	300	10	25.6
4-sBPE-M		80	10	10
	50	260	0	13.6
	4	300	10	33.6
4-sBPF-M		110	3	3
	100	260	0	4.5
	4	300	10	24.5
4-sBPG-M		80	3	3
	100	260	0	4.8
	4	300	10	24.8

An Agilent/HP 6850 Gas Chromatograph equipped with Agilent Chem Station data and control software, a FID detector and an Agilent J&W CP8907 GC column was used. An injection volume of 5 µL was introduced via 2:1 split injection into the injection port that was set at a temperature of 180 °C. The carrier gas was H_2 set in constant flow mode at 2.6 mL/min (a nominal head pressure of 9.00 psi, to give an average linear velocity of 79 cm/s). The detector was set at 300 °C with an H_2 flow of 35 mL/min, a compressed air flow of 280 mL/min, and no make-up gas. The data rate was 20 Hz with a minimum peak of 0.1 min.

The signal peak for the SBP in both Isopar L and in the simple solvent, was obscured due to a very long tail attributed to the Isopar L. So as to avoid the Isopar L FID signal, the method development was

undertaken using 0.01 M SBP in DCM. A semi-systematic approach was then taken in which most parameters (initial temperature, hold time, temperature climb rate, and total time) were varied.

In order for the GC software to calculate the amount of SBP in any given sample, a standard curve was constructed using a dilution series (Table 2.4) of SBP ranging in concentration from 0.0 M to 0.01 M.

Table 2.4. Serial dilutions of stock 0.01 M 4-*sec*-butylphenol for standard curve

[SBP] in M	Amount of 0.01 M SBP added (µL)	Amount of DCM added (µL)	ng SBP / µL
0.01	1500	0	1502.2
0.0075	1125	375	1126.0
0.005	750	750	750.0
0.0025	375	1125	375.5
0.001	150	1350	150.2
0.0005	75	1425	75.1
0.0	0	1500	0.0

Unless otherwise specified, solvent solutions were prepared by weighing solvent components into volumetric flasks and diluting with Isopar L. All solvents were prewashed prior to use as described in Section 2.2.2.

A series of experimental scrub solutions were prepared by diluting 50% (w/w) NaOH (JT Baker) with 18.2 MΩ•cm water in volumetric glassware. Transfers of the concentrated NaOH were accomplished via the use of calibrated pipettes.

Water for preparation of all aqueous solutions was first distilled and then deionized using a Milli-Q® gradient A10 filtering system equipped with a Quantum™ Ex Ultrapure Organex Cartridge (18.2 MΩ•cm at 25 °C, total organic content 4 ppb).

2.4 SODIUM HYDROXIDE WASH TESTS

A successful solvent washing protocol[4] developed for the original CSSX solvent was tested with a simple solvent as an assessment of the washing process, then with NGS to be certain that the SBP-removal protocol would also work with the new solvent formulation.

2.4.1 Materials

Materials and equipment utilized were the same as that described in section 2.1.1 of this report.

2.4.2 Methods

The preparation of solvents (both simple solvent and NGS) is described in detail in section 2.1.2 of this report. The solvent samples contained varying concentrations of SBP to simulate the presence of this degradation product of the Cs-7SB modifier.

Several 5-mL samples of prewashed simple solvent (Table 2.2) were spiked at 0.01 M, 0.005 M or 0.001 mM with SBP. The simple solvent so spiked was then washed two times with 0.10 M NaOH as a test of the ability of NaOH to remove the SBP from the solvent. The NaOH wash was added in equal

volume to the solvent, then contacted twice via vortexing at 3000 rpm for 30 s each time. To separate the aqueous from the organic phase, each sample was then centrifuged at 3500 rpm for eight min. The solvent phase was removed and the remaining aqueous phase acidified by adding 100 µL of concentrated HCl resulting in a measured pH of 3.0. This acidified aqueous phase was then contacted with an equal volume of dichloromethane (DCM) via vortexing twice at 3000 rpm for 30 s each time. The aqueous and organic layers were then separated, one from the other, via centrifugation at 3500 rpm for eight min. The DCM layer was isolated and analyzed for SBP by GC method 4-sBPG-M, which was developed specifically for quantifying this impurity.

Various 5-mL aliquots of pre-washed NGS (see Table 2.1) were spiked at 1 mM with SBP to simulate this level of degradation of the modifier. These spiked NGS samples were then subjected to the previously described NaOH wash protocol for removing SBP, but with the exception that fourteen different concentrations of NaOH (1.5 M, 1.0 M, 0.9 M, 0.6 M, 0.45 M, 0.3 M, 0.15 M, 0.10 M, 0.045 M, 0.03 M, 0.015 M, 0.01 M, 0.0015 M and 0.001 M) were tested to see what effect these variations of the wash protocol would have on SBP removal. The contacting was then carried out in the same manner as previously described above for the simple-solvent tests. The subsequent acidification of the NaOH wash layer and the extraction of SBP into DCM was also performed as described above for simple-solvent testing. The isolated DCM layer was subsequently analyzed by GC method 4-sBPG-M.

3. RESULTS AND DISCUSSION

3.1 GC METHOD

Due to the presence of a large and prominent 'tail' from Isopar's FID signal that masks the signal attributable to SBP, it is necessary to extract the SBP out of the solvent prior to its quantification by GC-FID. This is accomplished by contacting the solvent sample with an equal volume of 0.1 M NaOH, then vortexing it twice for 30 s each time. The vortexed sample is then centrifuged at 3500 rpm for 8 min with the subsequent removal of the solvent phase. The remaining aqueous phase is acidified by the addition of concentrated HCl and then extracted with an equal volume of DCM. The extraction is performed by vortexing the combined sample twice for 30 s each time, followed by its centrifugation at 3500 rpm for 8 min. The aqueous layer is discarded and the DCM, now containing the SBP, is subjected to analysis by GC. The GC method developed for this application, was given the designator 4-sBPG-M. The method, established for an Agilent/HP 6850 Gas Chromatograph equipped with Agilent Chem Station data and control software, a FID detector and an Agilent J&W CP8907 GC column, is described in detail in Table 3.1. Subjecting the DCM extracted samples to these analytical conditions resulted in a clean, symmetrical SBP peak at 4.116 min (Fig. 3.1).

Table 3.1. Program (4-sBPG-M) established for 4-*sec*-butylphenol analysis

ALS –
Syringe – 10.0 µL
Inj. Vol – 5.0 µL

Pre inj.		Post inj.	
Sample washes	2		
Solv. A washes	3	3	Solvent A = Water
Solv. B washes	3	3	Solvent B = Methanol
Sample Pump		0	

Inlet –
Heater 180 °C
Pressure 9 psi
Total flow (H_2) 12.6 mL/min
Mode: Split Split ratio 2:1 5.2 mL/min

Signals –
Data Rate/ minimum peak width = 20 Hz / 0.1 min

Column –
Mode: Constant Flow
Set Point:
Pressure: 9 psi
Flow: 2.6 mL/min
Average Velocity: 79 cm/sec
Post run: 3.477 mL/min

Oven –
Initial Oven: 80 °C
Equilibrium time: 0.50 min
Max. temp.: 350 °C
Post run: 50 °C
Post run time: 0.00 min

Detector –
Heater: 300 °C
H2 Flow: 35.0 mL/min
Air Flow: 280 mL/min
✓Flame
✓Electromenter

	Rate °C/min	Temp. °C	Hold Time min	Total Time (min)
4-sBPG-M		80	3	3
	100	260	0	4.8
	4	300	10	24.8

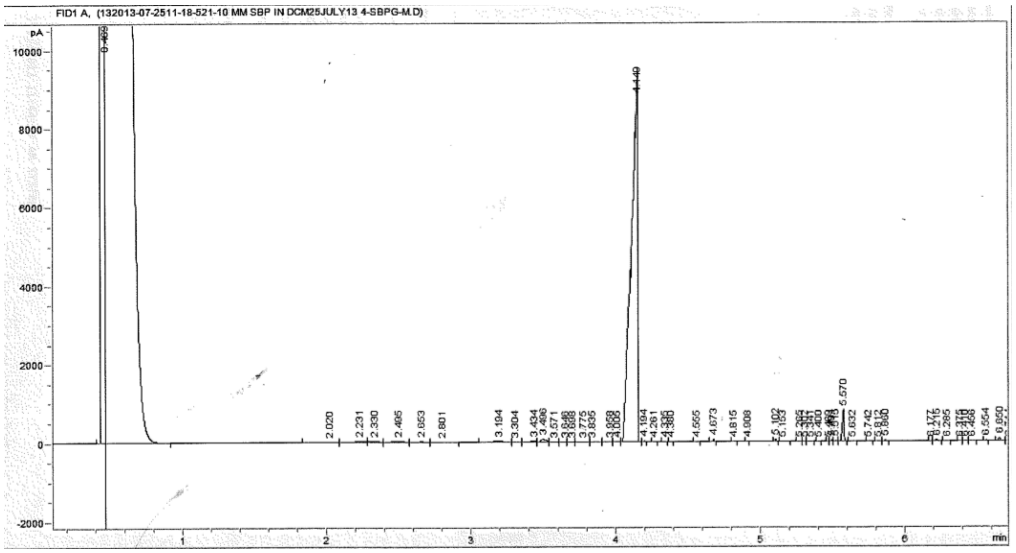


Fig. 3.1 Chromatogram showing symmetrical SBP peak obtained using method 4-sBPG-M.

In order for the GC software to calculate the amount of SBP in any given sample, a standard curve was constructed for method 4-sBPG-M using a dilution series (Table 2.4) of SBP ranging in concentration from 0.0 M to 0.01 M. The calibration curve so constructed (Fig. 3.2) showed an excellent agreement between the data collected and the line fit with a linear correlation coefficient of 0.99972. As such, this standard curve was used for the purpose of quantitation in all SBP analyses.

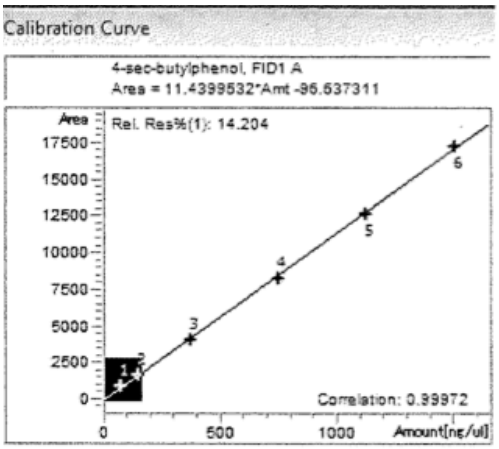


Fig. 3.2 Calibration curve of SBP in DCM obtained using method 4-sBPG-M.

3.2 SODIUM HYDROXIDE SOLVENT WASHING

The solvent breakdown component SBP is an impurity found in the modifier and a radiolytic degradation product that's been found to negatively impact stripping performance.[4,5] As such, SBP must be removed from NGS solvent in a dedicated process step. A successful solvent washing protocol developed for the original CSSX solvent was tested, first with a simplified solvent composition, then with NGS solvent to be certain that this SBP-removal procedure would work with the new NGS solvent.

3.2.1 Simple Solvent

Pre-washed simple solvent (Table 2.2), spiked at 0.01 M, 0.005 M or 0.001 M with SBP, readily gave up the majority of the SBP spike to the 0.01 M NaOH wash in just two wash steps. Three replicates of simple solvent (5 mL each) containing SBP at 0.001 M concentration averaged a transfer of 78% of the SBP to the first 0.1 M NaOH wash (Table 3.2, Fig. 3.3). After a second equal-volume wash with 0.1 M NaOH, approximately 99% of the SBP had been removed from the solvent by this procedure (Table 3.2, Figure 3.4). Similarly, simple-solvent samples containing SBP at 0.005 M and 0.01 M concentrations were subjected to the 0.1 M NaOH washes. Interestingly, two equal volume washes of the simple solvent containing 0.005 M SBP saw an average of 92.5% of the SBP removed from the solvent (Table 3.3), whereas two 0.1 M NaOH washes of the simple solvent containing 0.01 M SBP saw the contaminant removed quantitatively (Table 3.4).

Table 3.2. Removal of 0.001 M 4-*sec*-butylphenol using two × 0.1 M sodium hydroxide washes[a]

		Solvent wash 1		Solvent wash 2		
Replicate	Total SBP (ng/uL)	SBP recovered by wash 1 (ng/μL)	% SBP recovered	SBP recovered by wash 2 (ng/μL)	% SBP recovered	Total % SBP recovered
1	150	118.8	79.3	27.2	18.1	97.4
2	150	119.9	80.0	32.7	21.8	101.8
3	150	114.1	76.1	31.5	21.0	97.9
Average	150	117.6 ± 3.1	78.4 ± 2.1	30.5 ± 2.8	20.3 ± 1.9	98.7 ± 2.4

[a] Removal of 0.001 M SBP spike from simple solvent (0.5 M Cs-7SB in Isopar L) by washing twice with equal volumes (5 mL) of 0.1 M NaOH. O/A = 1:1. Experiment run in triplicate. SBP quantified by GC. Error was determined by calculating a single sigma standard deviation for the three replicates.

Table 3.3. Removal of 0.005 M 4-*sec*-butylphenol using two (2) × 0.1 M sodium hydroxide washes[a]

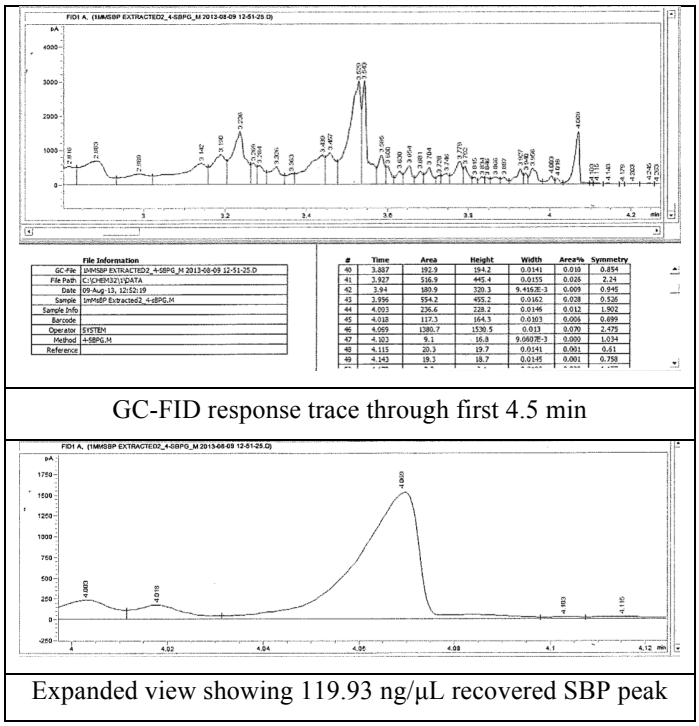
		Solvent wash 1		Solvent wash 2		
Replicate	Total SBP (ng/uL)	SBP recovered by wash 1 (ng/μL)	% SBP recovered	SBP recovered by wash 2 (ng/μL)	% SBP recovered	Total % SBP recovered
1	750	573.7	76.5	107.2	14.3	90.8
2	750	582.1	77.6	111.5	14.9	92.5
3	750	590.9	78.8	116.2	15.5	94.3
Average	750	582.2 ± 8.6	77.6 ± 1.1	111.7 ± 4.5	14.9 ± 0.6	92.5 ± 1.7

[a] Removal of 0.005 M SBP spike from simple solvent (0.5 M Cs-7SB in Isopar L) by washing twice with equal volumes (5 mL) of 0.1 M NaOH. O/A = 1:1. Experiment run in triplicate. SBP quantified by GC. Error was determined by calculating a single sigma standard deviation for the three replicates.

Table 3.4. Removal of 0.01 M 4-*sec*-butylphenol using two (2) × 0.1 M sodium hydroxide washes[a]

		Solvent wash 1		Solvent wash 2		
Replicate	Total SBP (ng/uL)	SBP recovered by wash 1 (ng/μL)	% SBP recovered	SBP recovered by wash 2 (ng/μL)	% SBP recovered	Total % SBP recovered
1	1500	1272	84.7	227	15.1	99.9
2	1500	1287	85.8	248	16.6	102.4
3	1500	1270	84.7	232	15.5	100.1
Average	1500	1276 ± 10	85.1	236 ± 11	15.7 ± 0.7	100.8 ± 1.3

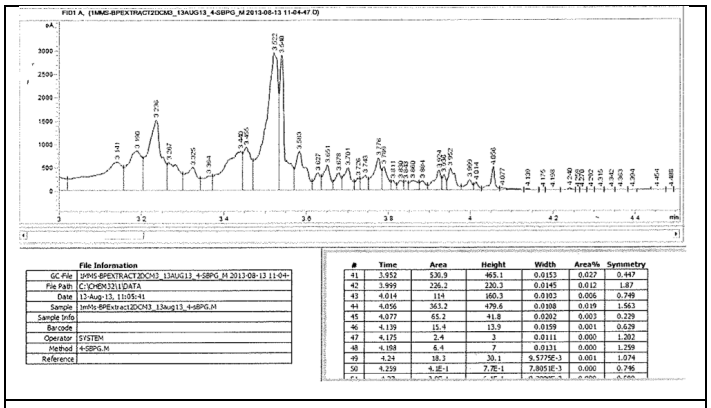
[a] Removal of 0.01 M SBP spike from simple solvent (0.5 M Cs-7SB in Isopar L) by washing twice with equal volumes (5 mL) of 0.1 M NaOH. O/A = 1:1. Experiment run in triplicate. SBP quantified by GC. Error was determined by calculating a single sigma standard deviation calculation.



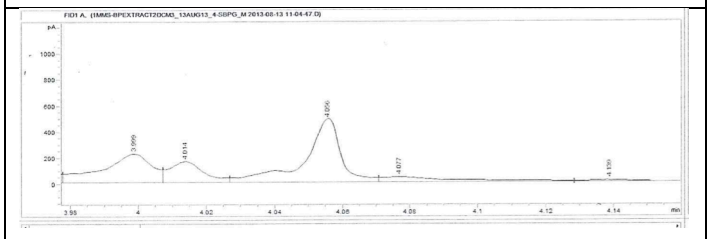
GC-FID response trace through first 4.5 min

Expanded view showing 119.93 ng/µL recovered SBP peak

Figure 3.3. GC-FID trace of SBP removed by first contact of 0.001 M SBP spiked simple solvent with 0.1 M NaOH wash.



GC-FID response trace through first 4.5 min



Expanded view showing 31.549 ng/µL recovered SBP peak

Figure 3.4. GC-FID trace of SBP removed by second contact of 0.001 M SBP spiked simple solvent with 0.1 M NaOH wash.

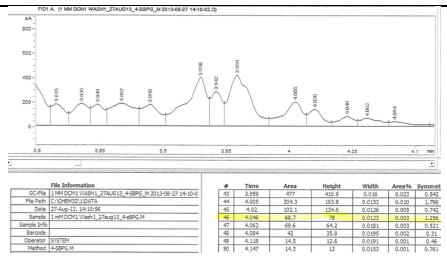
3.2.2 Removal of 4-*sec*-Butylphenol from NGS by Washing with Various Concentrations of Sodium Hydroxide

Various 5-mL aliquots of pre-washed NGS (Table 2.1), spiked at 0.001 M with SBP (150 ng/µL), were seen to give up some amount of the SBP spike to single NaOH washes ranging from 0.001 M to 1.5M as measured by the GC-FID method 4-sBPG-M (Fig. 3.5, Table 3.5). Each contacted sample was analyzed three times, with measured values of SBP showing only very small differences between measurements. Over the range of NaOH concentrations tested, the amount of SBP removed from the NGS ranged between 3.35% with the 0.001 M NaOH wash to 68% SBP transferred to the 0.6 M NaOH wash (Table 3.5, Fig. 3.6). Decreasing amounts of SBP were seen to transfer to the wash with increasing NaOH concentrations beyond 0.6 M.

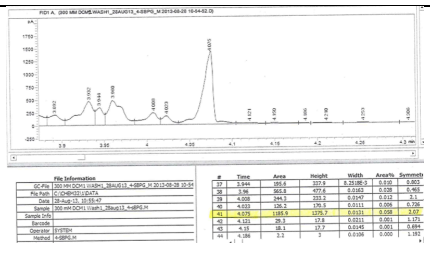
Table 3.5. Removal of 4-*sec*-butylphenol from full NGS by single sodium hydroxide washes of various concentrations

		[a]4-*sec*-Butylphenol (ng/µL)			
NaOH Wash (M)	**[b]Peak Area**	**SBP removed from solvent**	**SBP remaining in solvent**	**% SBP removed**	**Partition Ratio (O/A)**
0.001	57.9 ± 16.9	5.0 ± 1.5	144.9 ± 1.5	3.35 ± 0.98	28.8 ± 11.2
0.0015	60.5 ± 14.7	5.3 ± 1.3	144.7 ± 1.3	3.50 ± 0.85	27.6 ± 8.5
0.010	167 ± 3	14.5 ± 0.2	135.5 ± 0.2	9.65 ± 0.15	9.36 ± 0.16
0.015	201 ± 28	17.4 ± 2.5	132.6 ± 2.5	11.6 ± 1.6	7.61 ± 1.15
0.030	329.8 ± 6.4	28.6 ± 0.6	121.4 ± 0.6	19.1 ± 0.4	4.2 4± 0.10
0.045	429 ± 43	37.3 ± 3.7	112.7 ± 3.7	24.9 ± 2.5	3.02 ± 0.43
0.10	683 ± 52	59.3 ± 4.6	90.7 ± 4.5	39.6 ± 3.0	1.53 ± 0.19
0.15	784 ± 72	68.1 ± 6.2	81.9 ± 6.2	45.4 ± 4.2	1.20 ± 0.19
0.30	1137 ± 50	98.8 ± 4.3	51.1 ± 4.3	65.9 ± 2.9	0.52 ± 0.67
0.45	1063 ± 58	92.3 ± 5.1	57.7 ± 4.1	61.5 ± 3.4	0.63 ± 0.88
0.60	1178 ± 54	102.4 ± 4.7	47.6 ± 4.7	68.3 ± 3.1	0.47 ± 0.07
0.90	1079 ± 47	93.8 ± 4.1	56.2 ± 4.1	62.5 ± 2.7	0.60 ± 0.07
1.00	1025 ± 22	89.0 ± 1.9	61.0 ± 1.9	59.3 ± 1.3	0.69 ± 0.04
1.50	173.8 ± 0.9	15.1 ± 0.1	134.9 ± 0.1	10.1 ± 0.1	8.94 ± 0.05

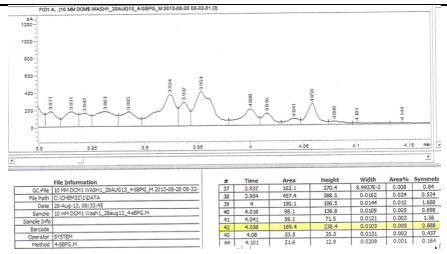
[a]Full NGS (0.050 M MaxCalix, 0.50 M Cs-7SB, and 0.003 M TiDG) was spiked with SBP to 0.001 M (150 ng/ µL) and contacted at 1:1 O/A with either 0.001, 0.0015, 0.01, 0.015, 0.03, 0.045, 0.1, 0.15, 0.3, 0.45, 0.6, 0.9, 1.0, or 1.5 M NaOH. Following the contacting, the mixture was vortexed for 60 s, then centrifuged at 3,000 rpm for 6 min to separate the phases. The aqueous phase was isolated, acidified with HCl and extracted into DCM for analysis by GC-FID.
[b]Each peak area value is an average of three (3) analyzed samples. Error was determined for each series of three replicate samples by calculating a single sigma standard deviation.



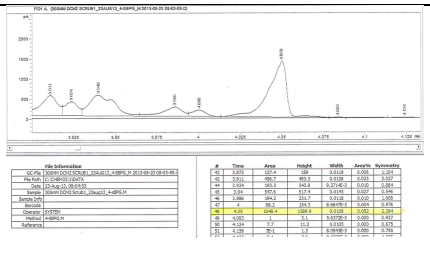
0.001 M NaOH Wash



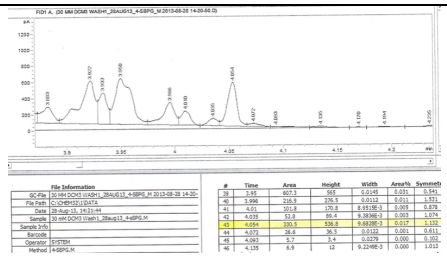
0.3 M NaOH Wash



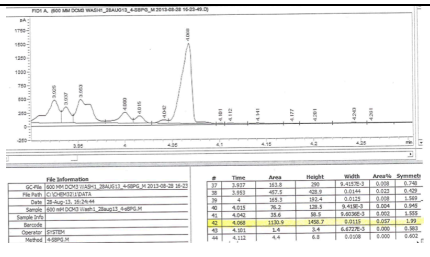
0.01 M NaOH Wash



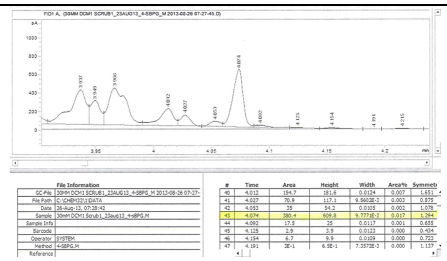
0.45 M NaOH Wash



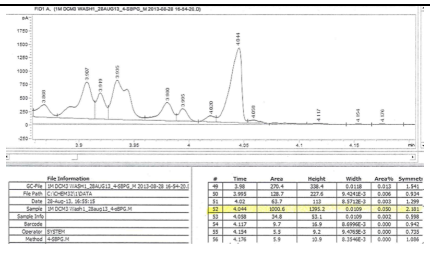
0.03 M NaOH Wash



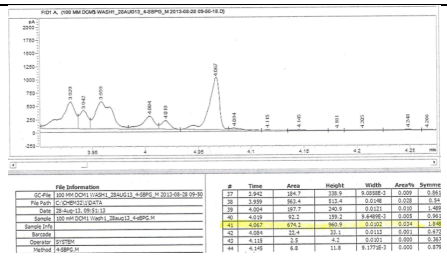
0.6 M NaOH Wash



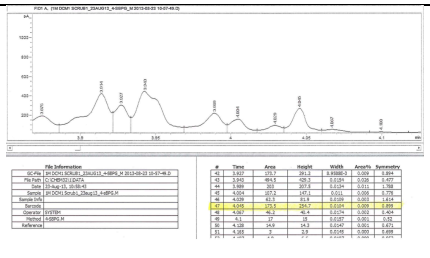
0.045 M NaOH Wash



1.0 M NaOH Wash



0.1 M NaOH Wash



1.5 M NaOH Wash

Figure 3.5. GC-FID traces of SBP removed by contacting 0.001 M SBP spiked full NGS with different concentrations of NaOH.

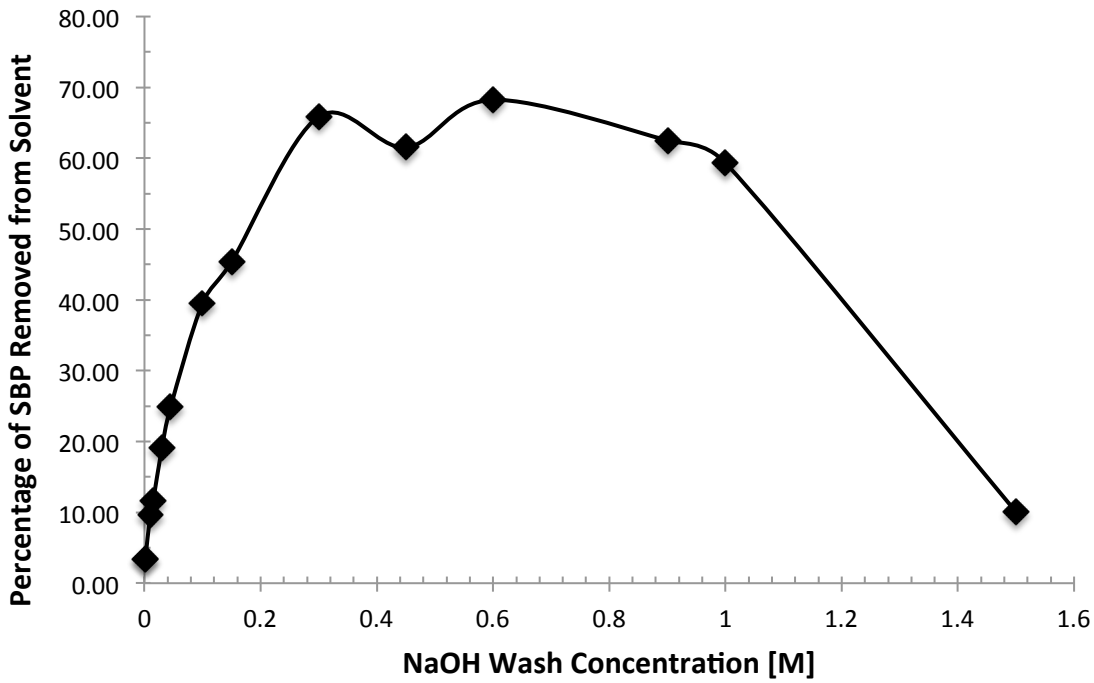


Figure 3.6. Removal of SBP from full NGS by single washes of NaOH of varying concentrations.

3.2.3 Interpretation of 4-*sec*-Butylphenol Partitioning Behavior and Comparison with CSSX Solvent

As shown in Fig. 3.7, SBP partitions to various NaOH solutions less effectively from the full NG-CSSX process solvent than it does from a previous formulation of the CSSX solvent. For the comparison, SBP partitioning data for CSSX were taken from a previous report.[5] The CSSX solvent consisted of 0.010 M calix[4]arene-bis(*tert*-octylbenzo-crown-6) (BOBCalixC6), 0.5 M Cs-7SB, and 0.003 M TOA in Isopar L. (Note that the CSSX solvent later adopted for use in the MCU at SRS and the SRS Salt Waste Processing Facility [6–10] actually uses 0.007 M BOBCalixC6, 0.75 M Cs-7SB, and 0.003 M TOA in Isopar L.) The curves for the full NGS and CSSX solvent have the same basic U-shape, with the full NGS solvent giving the higher partition ratios by a factor of 3–6 in the range 0.01–1 M NaOH. The bottom of the well for each curve occurs in the same range 0.3–1 M NaOH followed by an abrupt upswing at higher NaOH concentrations. Interestingly, the single point for the simple NGS solvent, which lacks the calixarene and suppressor, falls nearly in line with the CSSX partition ratios. The major component of the solvents compared in Fig. 3.7 is the modifier at 0.5 M, which may be considered the primary determinant of the solvation environment in each case. Thus, the higher SBP partition ratios for the full NGS solvent may be ascribed to the effect of the guanidine vs TOA, the effect of the high concentration of MaxCalix at 0.050 M vs BOBCalixC6 at 0.007 M, or some combination of these two effects.

As discussed previously,[5] aqueous NaOH likely washes-out the anionic form of SBP and other lipophilic anionic impurities by deprotonation of the suppressor with release of the anion to the aqueous phase. A simple equilibrium is suggested for the washing reaction:

$$OH^-_{(aq)} + BH^+X^-_{(org)} \rightleftharpoons B_{(org)} + X^-_{(aq)} + H_2O_{(aq)} \tag{3.1}$$

where B is the organic base (suppressor) and X^- is the lipophilic anion. Emerging from the acidic strip section, the suppressor is designed to have tied up all traces of lipophilic anions, allowing the Cs^+ cation to be stripped, as otherwise the lipophilic anions will hold the Cs^+ cations in the organic phase. Equation 3.1 predicts an approximately inverse first-power dependence of the SBP partition ratio vs aqueous NaOH concentration, in agreement with the approximate slope of –1 observed in the downward trend in the range 0.01–0.3 M NaOH. It stands to reason that the more basic guanidine suppressor will resist deprotonation, thus shifting the downward sloping curve to the right. That is, it takes a higher NaOH concentration to get the same washing-out effect with the guanidine suppressor vs that obtained with the weaker TOA as the suppressor.

The upward trend starting at 1 M NaOH is interpreted as the onset of an ion-pair type extraction in which the lipophilic anion is being extracted back into the solvent as the sodium salt, likely bound by the calixarene:

$$Na^+_{(aq)} + X^-_{(aq)} + Calix_{(org)} \rightleftharpoons [CalixNa^+]X^-_{(org)} \tag{3.2}$$

Increasing sodium concentration drives this reaction, so that the effectiveness of NaOH as a washing agent has an upper limit. The higher concentration of MaxCalix (0.05 M) vs BOBCalixC6 (0.010 M) in the proto-CSSX solvent formulation accounts for the higher partition ratios observed for the full NGS in Fig. 3.7.

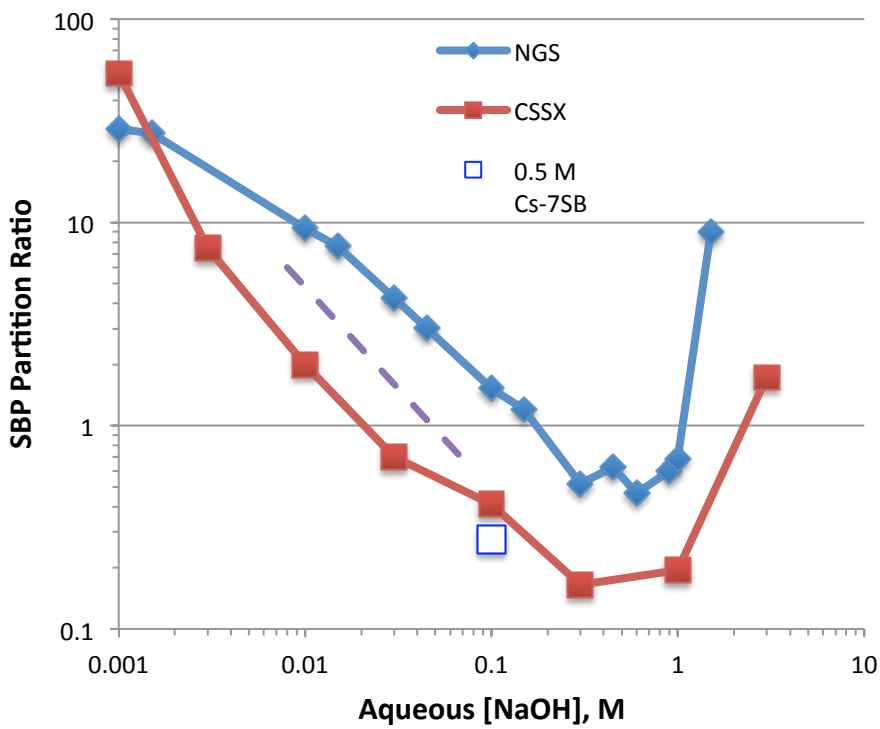


Figure 3.7. Comparison of the 4-*sec*-butylphenol partition ratios for the full NGS (Table 3.5) and CSSX[5] solvent as a function of aqueous NaOH concentration. Also shown is a single point for the simple solvent contacted with 0.1 M NaOH (Table 3.2). The dashed line provides a reference for a slope of –1.

Steady-state buildup of SBP in the solvent is expected to be miniscule. Assuming processing of a million gallons of salt feed per year with an O:A of 1:4 implies 1330–1790 solvent cycles if the solvent inventory is 140–188 gallons.[19, 20] If the annual SBP phenol production in the solvent is equated with the sodium extraction capacity of 0.003 M in year-old degraded solvent and 12% of the SBP is washed out per cycle,[19] then the steady-state concentration of SBP would be expected to rise to a concentration on the order of $(1–2) \times 10^{-5}$ M. Without the washing stages in the flowsheet, SBP would continue to rise until the guanidine suppressor capacity is consumed; this would likely occur on the timeframe of 6–12 months in the MCU.[19] Since the SBP must rise to at least 0.001 M to have any effect on stripping performance,[2] we conclude that caustic washing ensures that there is no risk of negative impacts due to SBP as a degradation product. Considering the SBP washing to represent a model for washing of other lipophilic anionic impurities, it may also be expected that the two 0.03 M NaOH wash stages implemented in the MCU should continue to function adequately for solvent cleanup.

4. CONCLUSIONS

This work has resulted in an accurate GC-FID-based analytical method for quantifying SBP in NGS. Furthermore, the testing protocol was used to quantify SBP removal from both a simplified solvent and full NGS by the NaOH wash protocol previously developed for CSSX solvent. A wide range of NaOH wash concentrations from 0.001 M to 1.5 M was found to exhibit a maximum effectiveness at 0.3–1 M NaOH, removing as much as 68% of a 0.001 M SBP spike on a single contact of the full NGS at 1:1 phase volume ratio at 25 °C. Multiple washes remove further quantities of SBP, approaching quantitative removal. For example, washing the full NGS containing a 0.005 M spike of SBP three times with an equal volume of 0.1 M NaOH solution removes 96% of the SBP.

With a 0.030 M NaOH wash solution used at a 3.75:1 O:A phase volume ratio as used in the two MCU wash stages,[17] SBP partitions weakly to the aqueous phase. Only 5.9% removal of SBP is expected in a single contact, increasing to 12% in two stages. Although the SBP partition ratio for the full NGS is 6-fold higher than that for the proto-CSSX solvent with a 0.030 M NaOH wash, its effectiveness in washing SBP is still comparable to that reported for CSSX with a wash using 0.010 M NaOH at an O:A ratio of 5:1.[5] Since there are no SBP partitioning data for the CSSX solvent composition run at 0.75 M Cs-7SB in the MCU till 2013,[10] a strict comparison of the NGS and CSSX solvents is not possible. However, the higher Cs-7SB concentration of the CSSX solvent would be expected to enhance its SBP partition ratio significantly. Given its more favorable O:A ratio of 3.75:1, NGS washing performance is thus expected to be qualitatively comparable to that of CSSX. Moreover, buildup of SBP is estimated to be on the order of only $(1–2) \times 10^{-5}$ M at steady state in the MCU, a negligible concentration that will have no effect on NGS performance. Given that SBP is considered to be a model anionic solvent contaminant, caustic washing is expected to be an adequate means of cleanup of NGS.

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