

Analysis of Calix[4]Arenne-Based Solvent by Reversed-Phase High-Performance Liquid Chromatography

by

T. L. White

Westinghouse Savannah River Company

Savannah River Site

Aiken, South Carolina 29808

R. A. Peterson

M. P. Maskarinec

Oak Ridge National Lab

J. E. Caton

Oak Ridge National Lab

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Analysis of calix[4]arene-based solvent by reversed-phase high-performance liquid chromatography

Thomas L. White and Reid A. Peterson

Westinghouse Savannah River Technology Center, Aiken, SC 29808, USA

Micheal P. Maskarinec and John E. Caton

Oak Ridge National Laboratory

Abstract

At the Savannah River Site (SRS), one of the processes evaluated for the removal of cesium from alkaline high-level waste is the use of a calix[4]arene-based solvent extraction process. The end result of this process is lower volume, acidic wasted stream containing purified cesium ready for storage by encapsulation in glass (vitrification). A reversed-phase high-performance liquid chromatography (HPLC) analytical method was developed to determine the loss and accumulation of compounds during the use of the calix[4]arene-based solvent in the cesium removal process. This solvent currently consists of a cesium extractant calix[4]arene-bis-(*tert*-octylbenzo-crown-6) (“BOBCalixC6”) at 0.007 M, a modifier 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol (“Cs-7SB”) at 0.75, trioctylamine (TOA) at 0.003 M, and an aliphatic diluent Isopar L. An alternative modifier 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-

tert-octylphenoxy)-2-propanol (“Cs-6”) at 0.5 M and aliphatic diluent Norpar have also been examined using this method. The reversed-phase method has a run time of 30 min. and uses an isopropanol/water mobile phase on a C18 column with an UV detector at 226 nm and 205 nm.

1. Introduction

A processes currently under pursuit by the Department of Energy (DOE) is the removal of radioactive cesium from alkaline high-level waste at the Savannah River Site (SRS) with the goal of safely creating a cesium rich waste stream ready for vitrification and then storage of the radiocative glass. One promising method is the use of a calix[4]arene-based extraction solvent[1] that is resistant to radiolytic and chemical decomposition and readily recycled for continued use. The cesium is concentrated using centrifugal contactors[2] by a three-step process involving an extraction step, a scrub step and a strip step. Cesium is removed from alkaline high-level waste with the calix[4]arene-based solvent during the first step. The scrub step involves contacting the cesium-containing calix[4]arene-based solvent with 0.05 M nitric acid to remove non-cesium salts and the strip step involves contacting the calix[4]arene-based solvent with 0.001 M nitric acid to remove the cesium. A low pH waste stream high in cesium content is the final product.

Reversed-phase chromatography has been utilized to examine substituted calix[n]arene compounds[3-4]. The reversed-phase chromatography methods presented in this paper were developed to monitor [5] the stability and performance of the extraction solvent[6]. The current calix[4]arene-based solvent consists of a cesium extractant calix[4]arene-bis-

(*tert*-octylbenzo-crown-6) (“BOBCalixC6”) at 0.007 M, a modifier 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol (“Cs-7SB”) at 0.75 M, trioctylamine (TOA) at 0.003 M, and an aliphatic diluent Isopar® L. Solutions of Isopar® L or Norpar® diluent with varying concentrations of the components including an alternative modifier 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*tert*-octylphenoxy)-2-propanol (“Cs-6”) (Figure 1) were separated and analyzed using this reversed-phase chromatography method. The trioctylamine concentration was followed by gas chromatography and will be covered in another publication.

2. Experimental

2.1 Materials and reagents and apparatus

The extractant calix[4]arene-bis(*tert*-octylbenzo-crown-6) from IBC Advanced Technologies, Inc. (American Fork, UT). Isopar® L and Norpar® was purchased from Exxon Chemical Company, Houston, Texas. The modifiers Cs-7SB and Cs-6 were obtained from Oak Ridge National Laboratories. Reagent grade compounds 4-*tert*-octylphenol, 4-*sec*-butylphenol and trioctylamine were purchased from Aldrich (Milwaukee, WI). The HPLC grade solvents used are isopropanol (Acros Organics, Geel, Belgium) and deionized water was obtained from a Millipore Milli-Q water system (resistivity 18 M Ω).

The high performance liquid chromatography (HPLC) instrument used was a Hewlett-Packard 1090 HPLC with a diode array detector enclosed in a radiological hood. The

system was controlled using HP ChemStation version 6.0 software. The column used was a Dychrom Chemcosorb 5 ODS-UH 3.2 x 250.

2.2 Standards and preparation

Stock solutions were prepared by weighing the analytes into volumetric flasks and diluting with isopropanol for the reversed-phase method. The stock solutions were then combined to form a stock solution containing all three analytes at high concentrations. Standards were prepared by diluting the stock solution down with isopropanol. The following is an example preparation for standards for reversed-phase HPLC.

Standard solutions were prepared by weighing 20 mg of Cs-7SB, 20 mg of BOBCalixC6 and 100 mg of 4-sec-butylphenol into a separate 10 mL volumetric flask. The flasks containing BOBCalixC6 and 4-sec-butylphenol were diluted with isopropanol/hexane (9:1) solvent. One milliliter of the BOBCalixC6 solution and 0.05 mL of the 4-sec-butylphenol solution were added to the flask containing Cs-7SB and the flask was filled with isopropanol. This stock solution was diluted to make standards. Samples were diluted with isopropanol or chloroform until the analyte concentration was within the range of the linear calibration curve and then analyzed.

3. Discussion and Results

3.1. Reversed-phase HPLC method

Most of the chromatography work was examining the solution-containing Cs-7SB and BOBCalixC6 in Isopar® L. This formulation performed the best in the cesium removal process and so was the focus of much of our effort. The extractant BOBCalixC6 is not

readily soluble in water. Thus, isopropanol was chosen for the mobile phase because it is a relatively non-hazardous solvent, provides good solubility for all of the compounds, and is a good solvent for phenols[7] that arise from the decomposition of the solvent components. In order that the isopropanol concentration would remain high in the mobile phase, a high surface area and high percent carbon (30%) column was chosen for greater retention. The reversed-phase HPLC method is summarized in Table 1. A wavelength of 226 nm was selected for viewing Cs-7SB or Cs-6, and 4-sec-butylphenol or 4-tert-octylphenol while 205 provided the best sensitivity for BOBCalixC6. Figure 2 is a chromatogram of the solvent with 4-sec-butylphenol, an impurity that arises from the decomposition of the modifier Cs-7SB. Linear curves were created over the concentration ranges expected from about a 1:100 dilution or more of the solvent and the results are shown in Table 1.

3.2. Calibration Curves

The analytes were determined to be linear over the concentration ranges present in the solvent after a 1:100 dilution or more (Table 2). The linear relationship between peak area and concentration of Cs-7SB (n = 4; 1690, 1521, 1352, 845) and BOBCalixC6 (n=5; 126, 115, 103, 92, 57) is shown in Table 3. The %R.S.D for the slopes of Cs-7SB is 1% while for BOBCalixC6 it is 2%.

3.3. Intra-day precision

Table 4 summarized the intra-day accuracy and precision of the two solvent components and the major impurity formed after repetitive use. All three compounds were in the

Isopar ® L solvent and diluted to the appropriate concentration for analysis. For Cs-7SB and BOBCalixC6, the %RSD is less than 2%.

4. Conclusion

A method utilizing HPLC with a diode array detector for the detection of the components of a cesium extraction solvent was developed. The modifier and the extractant as well as the major impurities yielded linear calibration curves with good separation. This method was used to evaluate the stability and performance of solvents used for the removal of cesium from high-level waste.

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Table 1: Gradient reverse-phase HPLC method for Isopar L

Method	Conditions
Solvent system	Isopropanol-water
t_0 to t_1 = 10 min	70%/30%
t_2 = 12 min	95%/5%
t_3 = 27 min	95%/5%
t_4 = 29 min	70%/30%
Column	Dychrom Chemcosorb 5 ODS-UH 3.2x250 mm, 5 μ m pore size
Oven temperature	45°C
Flow-rate	0.25 mL
Stop time	33 min
UV	226 nm (modifier), 205 nm (calix)
injection volume	10 μ L
Retention time for 4-sec-butylphenol	7.25 min
Retention time for Cs-7SB	8.4 min
Retention time for calix	23.6 min
Retention time for Cs-6	12.2 min
Retention time for 4- <i>tert</i> -octylphenol	9.5 min
Linear calibration curve	
4-sec-butylphenol	1.0 mg/L to 70 mg/L, correlation = 0.998
Cs-7SBT	1000 mg/L to 2000 mg/L, correlation = 0.999
calix	70 mg/L to 170 mg/L, correlation = 0.999
Cs-6	100 mg/L to 1000 mg/L, correlation = 0.999
4- <i>tert</i> -octylphenol	1.0 mg/L to 10 mg/L, correlation = 0.999

Table 2: Linearity of test compounds

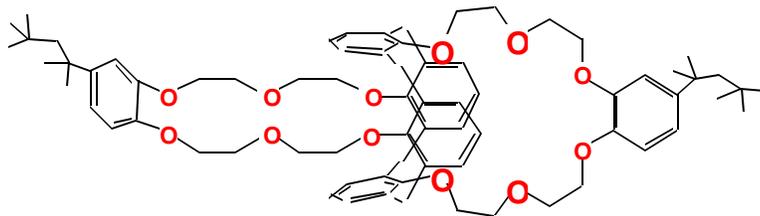
Compound	Conc. range (mg/L)	Slope	y-Intercept	Correlation coefficient
4-sec-butylphenol	6.0-1.0	51	0	0.9999
Cs-7SB	1700-850	32	3359	0.9992
BOBCalixC6	125-60	152	744	0.9992
Cs-6	1000-100	2.5	0.6	0.9994
4-tert-octylphenol	10-1	6	0	0.9996

Table 3: Individual and mean values for the slopes and intercepts.

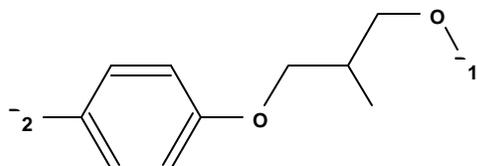
Compound	Curve	Slope	Intercept	r^2
Cs-7SB	1	31.393	3742	1
	2	31.886	3476	0.999
	3	31.335	3488	0.998
	4	32.058	2731	0.999
	mean	31.668	3359.25	
	SD	0.3587	436.4259	
	%RDS	1.1328	12.9918	
BOBCalixC6	1	149.93	884	0.998
	2	149.91	1014	0.999
	3	157.09	251	1
	4	150.75	824	0.998
	mean	151.92	743.25	
	SD	3.4688	337.6126	
	%RDS	2.2833	45.4238	

Table 4: Intra-day accuracy and percision

Run # n=4	Theoretical Conc., mg/L	Found (mean + S.D.) Conc., mg/L	%RSD
4-(sec-butyl)phenol			
1	6.012	6.014 ± 0.141	2.62
2	5.01	4.999 ± 0.141	3.15
3	4.008	4.033 ± 0.339	8.79
4	3.006	2.984 ± 0.217	7.82
5	1.002	1.007 ± 0.084	9.93
Modifier, Cs-7SB			
1	1859	1789.213 ± 71.528	1.80
2	1690	1682.41 ± 92.410	0.76
3	1521	1518.948 ± 93.189	0.79
4	1352	1367.383 ± 96.375	0.66
5	845	839.256 ± 94.914	1.18
BOBCalixC6			
1	126.4	125.471 ± 3.371	1.17
2	114.9	116.103 ± 4.693	0.17
3	103.4	103.302 ± 4.194	0.65
4	91.92	91.896 ± 3.927	1.00
5	57.45	57.292 ± 4.248	1.04



0.01 M Calix[4]arene-bis(*tert*-octylbenzo-crown-6); BoBCalixC6 extractant

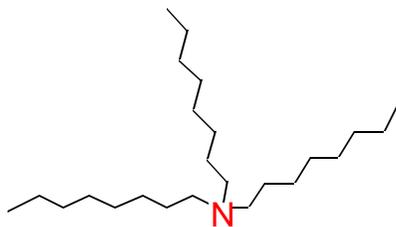


$R_1 = \text{OCH}_2\text{CF}_2\text{CF}_2\text{H}, \text{OCF}_2\text{CF}_2\text{H}$

$R_2 = \textit{sec}$ -butyl, *tert*-octyl

0.5 M 1-(2, 2, 3, 3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol; Cs-7SB

modifier or 0.5 M or 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*tert*-octylphenoxy)-2-propanol



0.001 M trioctylamine; suppressor

Isopar L diluent (a blend of C_{10} - C_{12} branched alkanes with BP = 191-205 °C) or Norpar

12 diluent (a blend of C_{11} - C_{12} linear alkanes with BP = 185-221 °C)

Figure 1. Components of the cesium solvent-extraction solution.

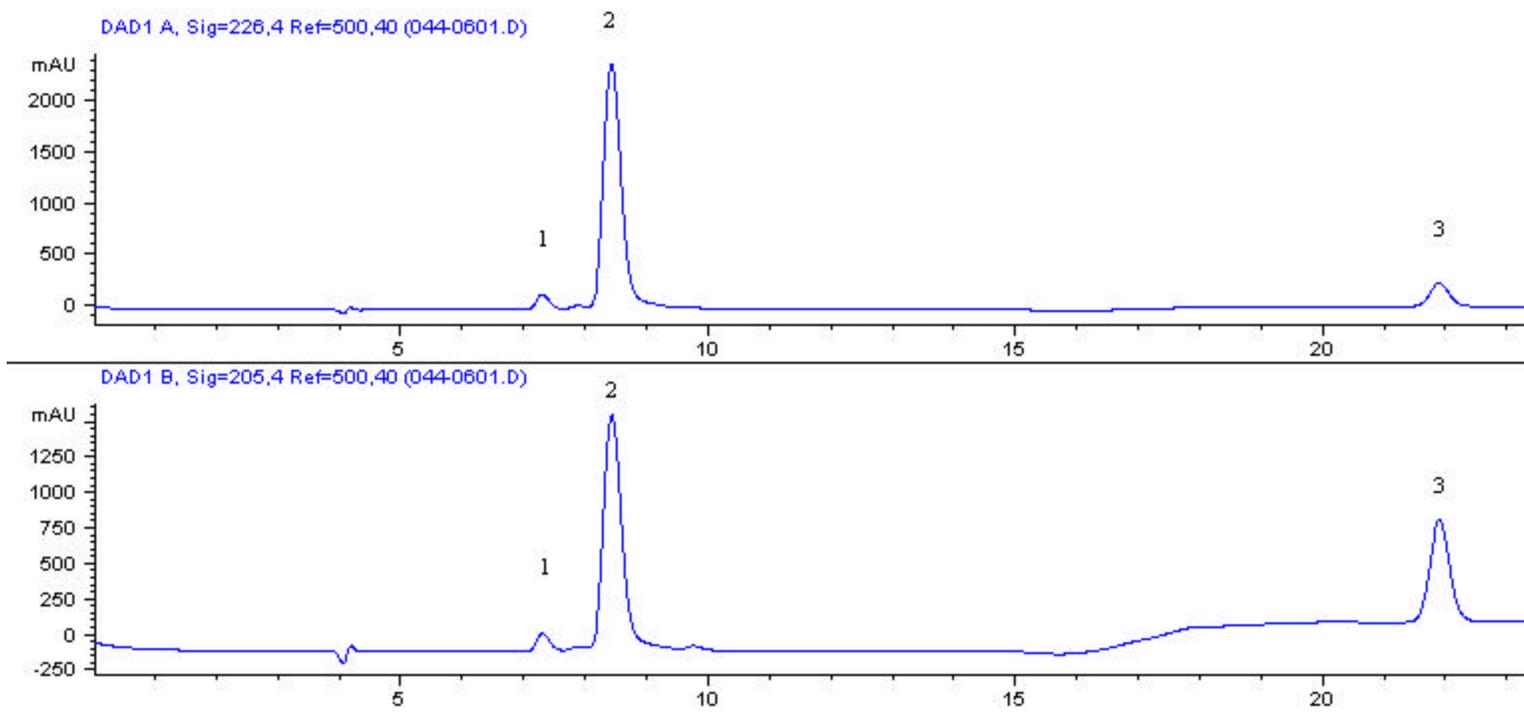


Figure 2. Chromatogram of solvent extraction solution with impurity. 1= 4-sec-butylphenol, 2 = Cs-7SB, 3 = BoBCalixC6.