

Chemical and Analytical Sciences Division

**IMPROVED PERFORMANCE OF THE ALKALINE-SIDE CSEX PROCESS FOR
CESIUM EXTRACTION FROM ALKALINE HIGH-LEVEL WASTE OBTAINED
BY CHARACTERIZATION OF THE EFFECT OF SURFACTANT IMPURITIES**

Lætitia H. Delmau, Gary J. Van Berkel, Peter V. Bonnesen, and Bruce A. Moyer

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6119
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ACRONYMS

ANL	Argonne National Laboratory
BoBCalixC6	Calix[4]arene-bis(<i>tert</i> -octylbenzo-crown-6)
CF	Concentration Factor
Ci	Curie
Cs-3	1-(1,1,2,2-tetrafluoroethoxy)-3-(4- <i>tert</i> -octylphenoxy)-2-propanol
CSEX	Cesium Solvent Extraction
DF	Decontamination Factor
USDOE	U.S. Department of Energy
D_{Cs}	Distribution ratio for cesium
ES-MS	Electrospray Mass Spectrometry
ESP	Efficient Separations Program
Teflon [®] FEP	Fluorinated Ethylene Propylene
FW	Formula Weight
HDDNS	Didodecyl-naphthalene Sulfonic acid
HLW	High Level Waste
ICP	Inductively Coupled Plasma
LMER	Lockheed Martin Research Corporation
M	Mega Ohm
NMR	Nuclear Magnetic Resonance
O/A	Organic to Aqueous volume ratio
ORNL	Oak Ridge National Laboratory
PTFE	Polytetrafluoroethylene
SRS	Savannah River Site
TBP	Tributyl Phosphate
TCLP	Toxic Characteristic Leaching Procedure
TiOA	Triisooctylamine
TOA	Trioctylamine

EXECUTIVE SUMMARY

Improved understanding and performance of the alkaline-side CSEX process has been obtained through the characterization of impurity effects that hinder complete stripping of cesium from the solvent. It is shown in this report that tests of the alkaline-side CSEX process conducted in the summer and fall of 1998 were complicated by the presence of common surfactant anions, undecyl- and dodecylsulfonate, as trace impurities in the two simulants tested. This conclusion was drawn from the results of a series of systematic extraction tests followed by a definitive identification by electrospray mass spectrometry (ES-MS). Based on this understanding, a straightforward preventative measure involving the addition of a lipophilic tertiary amine extractant at a small concentration to the solvent is proposed and demonstrated.

As part of the task "Fission Product Solvent Extraction" supported by the Efficient Separations and Processing Crosscutting Program within the USDOE Office of Environmental Management, the alkaline-side CSEX process has been developed for removal of radio-cesium (^{137}Cs) from alkaline high-level wastes stored in underground tanks at the Hanford Site and Savannah River Site (SRS). As described in a previous report, tests conducted in Fiscal Year 1998 generally demonstrated performance meeting the requirements for cesium removal from the waste to be treated at the SRS. However, discrepancies in stripping behavior were shown to arise from unidentified differences in the batches of waste simulant employed for testing. Various effects such as solvent impurities, kinetics, contacting method, and counting method were eliminated as possible causes of the observed discrepancies. Tests in Fiscal Year 1999 reported herein confirmed the earlier suspicion that the simulants contained lipophilic anionic impurities. Extraction tests demonstrated that the impurities could be concentrated in the solvent, and by ES-MS in the negative-ion mode it was possible to identify the harmful impurities as undecyl- and dodecylsulfonate. Subsequent tests with purchased sodium dodecylsulfonate confirmed that this surfactant could produce decreased stripping performance of the magnitude equivalent to that observed when using the simulant associated with the worse performance. With the identification of the impurity now settled, it is clear that poor stripping arises from ion-pair species in the solvent comprised of the cesium-extractant complex cation and the alkylsulfonate anion. Because the Gibbs energy of transfer of this anion and the complexation of the cesium cation by the extractant are both so favorable, the stripping of the

cesium nitrate from the solvent is correspondingly unfavorable. Thus, once the cesium associated with nitrate ion in the solvent has been stripped, further stripping of the remaining cesium in the solvent becomes inefficient. A simple remedy is the addition of a lipophilic amine such as trioctylamine to the solvent. This well-known amine extractant, once proposed for reprocessing, remains neutral and essentially inert during extraction of the alkaline waste but converts to the trioctylammonium nitrate salt on scrubbing and stripping. This lipophilic salt remains in the organic phase and allows the final traces of cesium in the solvent to be stripped by supplying the alkylsulfonate impurity in the solvent with equivalent cationic charges. Further results regarding this and other improvements to the solvent system will be described elsewhere.

1. PROJECT OBJECTIVE

1.1 OVERALL PROGRAM OBJECTIVES

The work reported herein was conducted as part of the task "Fission Product Solvent Extraction" supported by the Efficient Separations and Processing Crosscutting Program within the USDOE Office of Environmental Management. As the title implies, the task focused on the development of new solvent-extraction technology applicable to the removal of certain fission products, namely technetium-99 (^{99}Tc), cesium-137 (^{137}Cs), and strontium-90 (^{90}Sr), from waste. Efforts within this task have dealt mainly with high-level wastes stored in underground tanks at the Hanford Site, Savannah River Site (SRS) [1-3], and Idaho National Engineering and Environmental Laboratory (INEEL) [4].

Recently, the discovery of a new class of extractants, the calixarene-crowns (or calix-crowns) made it attractive for the first time to selectively remove cesium by solvent extraction from high-level wastes containing high salt concentrations. As originally discovered by European investigators [5-7], the calix-crowns have an unusually strong affinity for Cs^+ ions, with selectivity over Na^+ ions exceeding 10^4 . This discovery triggered an ORNL effort to adapt the new extractants to a solvent-extraction alternative to other technologies being examined at Hanford and the SRS, where the Na/Cs mole ratio characteristic of high-salt tank wastes commonly lies in the range of 10^4 to 10^5 . When the search for alternatives to the In-Tank Precipitation process at the SRS began in the spring of 1998, the development of the ORNL alkaline-side CSEX process was less than a year old and until then had been targeted at the Hanford wastes. Efforts in the spring and summer of 1998 at ORNL were subsequently devoted to further development and testing of this fledgling process to meet the specific needs at the SRS. The results of those tests through Sept. 30, 1998 have been described at length [1]. The present report addresses certain issues (see below) that were still outstanding at the time of the previous report. Further developments and improvements in the alkaline-side CSEX process are not included in the present report but will be reported in future journal publications [8, 9].

1.2 PROCESSING REQUIREMENTS

The particular requirements to be met for removing ^{137}Cs from the liquid high-level waste stream at the SRS were summarized previously [1]. Two key requirements are for a decontamination factor (DF) of 40,000 and a concentration factor (CF) of 12.6. An average waste composition was specified, and a corresponding simulant recipe was prepared. The ionic composition of the simulant formulation used in this report is shown in Table 1.1.

Table 1.1. Alkaline Tank Waste Simulant^a

Species	Concentration (M)
Na^+	6.52
K^+	0.017
Cs^+	2.72×10^{-4}
Al^{3+}	0.440
OH^- (total)	3.32
OH^- (free)	1.54
NO_2^-	0.82
NO_3^-	2.70
F^-	0.0502
Cl^-	0.100
SO_4^{2-}	0.200
CO_3^{2-}	0.230
CrO_4^{2-}	0.015

^aApproximates likely feed for possible implementation of the alkaline-side CSEX process at the SRS. Listed are nominal concentrations; free hydroxide corresponds to the hydroxide concentration after stoichiometric reaction with Al^{3+} ion to give $\text{Al}(\text{OH})_4^-$ ion. The recipe for this simulant (labeled "SRS #4") has been previously reported [10].

1.3 SUMMARY OF THE PREVIOUS RESULTS

A solvent-extraction system designed to selectively extract cesium from simulants of the wastes to be treated at the Savannah River Site was successfully demonstrated in batch tests at ORNL [1]. The system employs a solvent (Figure 1.1) comprised of a calixarene crown, bis(*tert*-octylbenzo-crown-6)calix[4]arene (BoBCalixC6), and a modifier, 1-(1,1,2,2-tetrafluoroethoxy)-3-(4-*tert*-octylphenoxy)-2-propanol (Cs-3), dissolved in a branched aliphatic hydrocarbon diluent (Isopar® L). Several studies were performed on this system to test its properties regarding cesium extraction; minor-component extraction; partitioning of calixarene, modifier, and other minor organic species; and its integrity toward thermolytic and radiolytic conditions. Generally, acceptable results were obtained. The component concentrations were optimized to give both good extraction and stripping. Minor inorganic components were not extracted. The partitioning of the extractant and modifier to the aqueous phase was negligible. The scrub stages were sufficient to remove the extracted species other than cesium from the solvent. However, although the radiation tests performed at SRS showed only minor degradation [11], the results from the chemical stability tests [12] suggested that some improvement in the stability of the modifier in contact with the alkaline simulant would be desirable. The flowsheet calculated from the batch-test results by collaborators at Argonne National Laboratory (ANL) met requirements specified by workers at the SRS [13].

A significant and unexpected discrepancy emerged from comparisons of batch-test results obtained from different batches of the same simulant recipe. The batch tests involved the same extraction, scrub, and strip steps. Whereas the results on extraction and scrubbing were comparable, much less efficient stripping (factor of 4-5) was obtained at ANL. The hindered stripping was also reflected in centrifugal-contactors tests run in July and September 1998 at ANL. A study was then initiated at ORNL to address the origin of this discrepancy. The possible problem of kinetics was initially explored, since the residence time of the solutions in the centrifugal contactors was on the order of one second in the mixing zone. It was soon shown that the extraction kinetics were sufficiently fast for efficient use of centrifugal contactors [14]. We were also concerned with the possible incorporation of a chemical impurity, postulated to be a synthesis by-product or precursor to one of the components of the solvent.

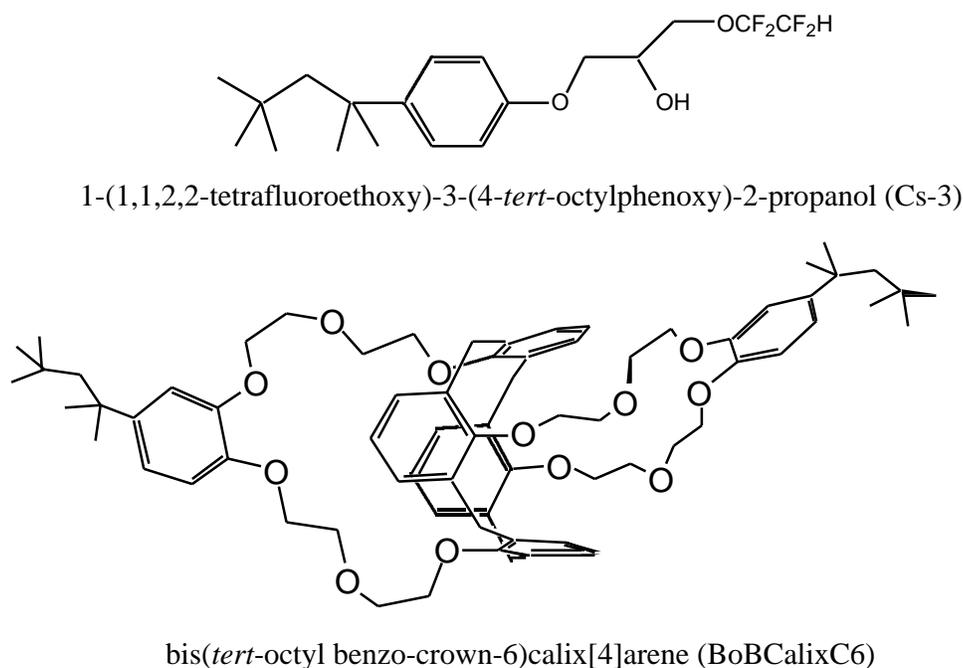


Figure 1.1. Structures of Cs-3 and BoBCalixC6

Controlled addition of traces of 4-*tert*-octyl phenol (the starting material for the modifier synthesis) or tributylphosphate (that was detected in the recycled solvent after the contactor test of July 1998) to the pristine solvent produced no major consequences. Finally, several different procedures of simulant preparation were tested. They differed by the order of salt addition, by the type of container (glass vs. Teflon[®] FEP) used to prepare them, and by addition of a filtration pre-step. These differences also did not produce any change in results, nor did ICP analyses detect significant differences in the simulant compositions [10].

A clue to the origin of the discrepancy was provided when the stripping discrepancy was eliminated by the addition of an amine extractant (trioctylamine at ORNL and triisooctylamine at ANL) at low concentration to the solvent. This led to uniformly low cesium distribution ratios (D_{Cs}) on stripping [10]. Furthermore, addition of a cation-exchange agent (didodecyl naphthalene sulfonic acid, HDDNS) to the system had the opposite effect and increased the D_{Cs} values dramatically. These observations tended to implicate an anionic impurity unique to the tests conducted at ANL.

1.4 QUESTIONS NEEDING TO BE ANSWERED

At the conclusion of the ORNL TM report published in December 1998 [10], it was suggested that the discrepancy in stripping performance came from a chemical difference in the two simulants prepared at ORNL and ANL. Questions concerned a) what was different about the ANL and ORNL simulants, b) whether there was an inorganic or organic impurity in the ANL simulants, c) whether the same material was also present in the ORNL simulants, and d) whether the ORNL simulants actually contained something else to begin with that improved stripping. The purpose of this report is to answer the questions and, if possible, provide a reasonable explanation for how chemical differences in the simulants could impact stripping performance. Although the hypothesis of an anionic impurity in the simulant was mentioned [10], it had not yet been confirmed nor had its origin been determined. However, it was the only obvious explanation for the results obtained at that time. This report presents extensive studies confirming this hypothesis, with consideration of other reasonable explanations.

2. INITIAL TESTS

2.1 INTRODUCTION

The question to be answered in this chapter concerns the origin of the discrepancy in the stripping cesium distribution ratios obtained during extraction, scrubbing, and stripping operations using different batches of simulants prepared according to the same recipe. All potential sources of the discrepancy were carefully checked. Most of the comparative studies were performed at ORNL and involved the use of chemical reagents from both ORNL and ANL, as well as simulant prepared at ANL. Because poor stripping had been obtained at ANL using the solvent prepared at ORNL, it was rational to think that the cause of the discrepancy was introduced by the simulant. Previous results showed that the preparation of the simulant according to the ANL procedure using ORNL materials did not introduce any change. Initially, we used a simulant prepared at ORNL from selected salt samples received from ANL, then compared the cesium distribution ratios with those from the simulant prepared at ANL. We also tested some ANL-prepared simulant at ORNL, which allowed comparison of the physical methods of stirring, centrifuging, and α -counting. Finally, the effect of adding trioctylamine to the solvent was assessed. The results demonstrated that the impurity was likely anionic and lipophilic, and did not originate from the selected salts or water used at ANL.

2.2 EXPERIMENTAL

2.2.1 Materials and Instrumentation

Reagents. All salts and solvents were reagent grade and were used as received. The origin of the salts can be found in the tables describing the simulant tests (Tables 2.1 to 2.5). Distilled, deionized water was obtained from a Barnstead Nanopure filtering system (resistivity 18 M Ω cm) and was used to prepare all aqueous solutions, including the simulants. Nitric acid was Ultrex II grade (J.T. Baker). Dilute nitric acid solutions were prepared by volumetric dilution, and the pH was checked using an Orion Model 230A pH meter with an Orion Ross 8103 pH

Table 2.1. Formulation of ORNL Simulant

C.A.S. Registry #	Salt Manufacturer	Component	Chemical Formula	Formula Weight	Desired Molarity	g needed per Liter	data amount weighed	(for 1 L) Actual Molarity	Species	Concentration M
1310-73-2	EM Science	sodium hydroxide	NaOH	40.00	3.32E+00	132.800	132.8122	3.320E+00	Metals	
7784-27-2	J.T. Baker (analyzed)	aluminum nitrate	Al(NO3)3.9H2O	375.15	4.40E-01	165.066	165.0588	4.400E-01	Al (as Al(OH)4-)	4.400E-01
10588-01-9	Fisher Scientific	sodium dichromate	Na2Cr2O7.2H2O	298.00	7.50E-03	2.235	2.2347	7.499E-03	Cr (as CrO4--)	1.500E-02
497-19-8	J.T. Baker (analyzed)	sodium carbonate	Na2CO3	105.99	2.30E-01	24.378	24.3803	2.300E-01	Cs+ (total)	2.719E-04
7631-99-4	J.T. Baker (analyzed)	sodium nitrate	NaNO3	85.00	1.36E+00	115.600	115.5957	1.360E+00	K+	1.701E-02
7757-79-1	EM Science	potassium nitrate	KNO3	101.11	1.70E-02	1.719	1.7203	1.701E-02	Na+	6.526E+00
7789-18-6	Alpha Aesar 99.99%	cesium nitrate	CsNO3	194.92	2.70E-04	0.053	0.053	2.719E-04	Anions	
7757-82-6	EM Science	sodium sulfate	Na2SO4	142.05	2.00E-01	28.410	28.4111	2.000E-01	Cl-	1.002E-01
7647-14-5	EM Science	sodium chloride	NaCl	58.44	1.00E-01	5.844	5.8554	1.002E-01	F- (nominal)	5.005E-02
7681-49-4	J.T. Baker (analyzed)	sodium fluoride	NaF	41.99	5.00E-02	2.100	2.1016	5.005E-02	NO2-	8.200E-01
7632-00-0	EM Science	sodium nitrite	NaNO2	69.00	8.20E-01	56.580	56.5817	8.200E-01	NO3-	2.697E+00
<p>Notes: Each component was added in the above order as a solid unless otherwise noted, and each component was in solution before adding the next one.</p> <p>Cesium nitrate was added as 0.27 mL of a 1.00 M solution.</p> <p>NaF was predissolved in about 50 mL water.</p>									CO3--	2.300E-01
									SO4--	2.000E-01
									OH- (total)	3.320E+00
									OH- (Free)	1.545E+00
									Theor pH	14.19
									Total Cation	6.543E+00
									Total Anion	6.543E+00
									Radionuclides	Spike Level
									Cs-137	0.7 µCi/mL
									Ratio	Value
Na/Cs	24000									
Na/K	384									
K/Cs	63									

Table 2.2. Formulation of ORNL Simulant Using ANL Salts and ORNL Water (ASOW-A)

C.A.S. Registry #	Salt Manufacturer	Component	Chemical Formula	Formula Weight	Desired Molarity	g needed per Liter	data amount weighed	(for 50 mL) Actual Molarity	Species	Concentration M
1310-73-2	<i>EM Science</i>	sodium hydroxide	NaOH	40.00	3.32E+00	132.800	6.647	3.324E+00	Metals	
7784-27-2	<i>J.T. Baker (analyzed)</i>	aluminum nitrate	Al(NO3)3.9H2O	375.15	4.40E-01	165.066	8.2515	4.399E-01	Al (as Al(OH)4-)	4.399E-01
10588-01-9	sample from ANL	sodium dichromate	Na2Cr2O7.2H2O	298.00	7.50E-03	2.235	0.1116	7.490E-03	Cr (as CrO4--)	1.498E-02
497-19-8	sample from ANL	sodium carbonate	Na2CO3	105.99	2.30E-01	24.378	1.2195	2.301E-01	Cs+ (total)	2.719E-04
7631-99-4	<i>J.T. Baker (analyzed)</i>	sodium nitrate	NaNO3	85.00	1.36E+00	115.600	5.78	1.360E+00	K+	1.711E-02
7757-79-1	sample from ANL	potassium nitrate	KNO3	101.11	1.70E-02	1.719	0.0865	1.711E-02	Na+	6.529E+00
7789-18-6	sample from ANL	cesium nitrate	CsNO3	194.92	2.70E-04	0.053	0.00265	2.719E-04	Anions	
7757-82-6	sample from ANL	sodium sulfate	Na2SO4	142.05	2.00E-01	28.410	1.4207	2.000E-01	Cl-	1.000E-01
7647-14-5	sample from ANL	sodium chloride	NaCl	58.44	1.00E-01	5.844	0.2923	1.000E-01	F- (nominal)	4.996E-02
7681-49-4	sample from ANL	sodium fluoride	NaF	41.99	5.00E-02	2.100	0.1049	4.996E-02	NO2-	8.200E-01
7632-00-0	<i>EM Science</i>	sodium nitrite	NaNO2	69.00	8.20E-01	56.580	2.829	8.200E-01	NO3-	2.697E+00
									CO3--	2.301E-01
									SO4--	2.000E-01
									OH- (total)	3.324E+00
									OH- (Free)	1.549E+00
									Theor pH	14.19
									Total Cation	6.546E+00
									Total Anion	6.546E+00
									Radionuclides	Spike Level
									Cs-137	0.7 µCi/mL
									Ratio	Value
									Na/Cs	24010
									Na/K	382
									K/Cs	63

Notes: Each component was added in the above order as a solid unless otherwise noted, and each component was in solution before adding the next one.

Cesium nitrate was added as 0.5 mL of a stock solution to reach the correct concentration. NaF was predissolved in about 5 mL water.

Table 2.3. Formulation of ORNL Simulant Using ANL salts and ANL Water (ASAW)

C.A.S. Registry #	Salt Manufacturer	Component	Chemical Formula	Formula Weight	Desired Molarity	g needed per Liter	data amount weighed	(for 50 mL) Actual Molarity	Species	Concentration M
1310-73-2	<i>EM Science</i>	sodium hydroxide	NaOH	40.00	3.32E+00	132.800	6.643	3.322E+00	Metals	
7784-27-2	<i>J.T. Baker (analyzed)</i>	aluminum nitrate	Al(NO3)3.9H2O	375.15	4.40E-01	165.066	8.2503	4.398E-01	Al (as Al(OH)4-)	4.398E-01
10588-01-9	sample from ANL	sodium dichromate	Na2Cr2O7.2H2O	298.00	7.50E-03	2.235	0.1119	7.510E-03	Cr (as CrO4--)	1.502E-02
497-19-8	sample from ANL	sodium carbonate	Na2CO3	105.99	2.30E-01	24.378	1.224	2.310E-01	Cs+ (total)	2.719E-04
7631-99-4	<i>J.T. Baker (analyzed)</i>	sodium nitrate	NaNO3	85.00	1.36E+00	115.600	5.778	1.360E+00	K+	1.707E-02
7757-79-1	sample from ANL	potassium nitrate	KNO3	101.11	1.70E-02	1.719	0.0863	1.707E-02	Na+	6.528E+00
7789-18-6	sample from ANL	cesium nitrate	CsNO3	194.92	2.70E-04	0.053	0.00265	2.719E-04	Anions	
7757-82-6	sample from ANL	sodium sulfate	Na2SO4	142.05	2.00E-01	28.410	1.419	1.998E-01	Cl-	9.983E-02
7647-14-5	sample from ANL	sodium chloride	NaCl	58.44	1.00E-01	5.844	0.2917	9.983E-02	F- (nominal)	4.987E-02
7681-49-4	sample from ANL	sodium fluoride	NaF	41.99	5.00E-02	2.100	0.1047	4.987E-02	NO2-	8.205E-01
7632-00-0	<i>EM Science</i>	sodium nitrite	NaNO2	69.00	8.20E-01	56.580	2.8307	8.205E-01	NO3-	2.696E+00
									CO3--	2.310E-01
									SO4--	1.998E-01
									OH- (total)	3.322E+00
									OH- (Free)	1.547E+00
									Theor pH	14.19
									Total Cation	6.545E+00
									Total Anion	6.545E+00
									Radionuclides	Spike Level
									Cs-137	0.7 µCi/mL
									Ratio	Value
									Na/Cs	24010
									Na/K	382
									K/Cs	63

Notes: Each component was added in the above order as a solid unless otherwise noted, and each component was in solution before adding the next one.

Cesium nitrate was added as 0.5 mL of a stock solution to reach the correct concentration.

NaF was predissolved in about 5 mL water.

Deionized water from ANL was used.

Table 2.4. Formulation of Simulant Containing Only One of the ANL Salts Prepared With ORNL Water (ASOW-B)

C.A.S. Registry #	Salt Manufacturer	Component	Chemical Formula	Formula Weight	Desired Molarity	g needed per Liter	data amount weighed	(for 50 mL) Actual Molarity	Species	Concentration M
1310-73-2	<i>EM Science</i>	sodium hydroxide	NaOH	40.00	3.32E+00	132.800	6.65	3.325E+00	Metals	
7784-27-2	<i>J.T. Baker (analyzed)</i>	aluminum nitrate	Al(NO3)3.9H2O	375.15	4.40E-01	165.066	8.2532	4.400E-01	Al (as Al(OH)4-)	4.400E-01
10588-01-9	sample from ANL	sodium dichromate	Na2Cr2O7.2H2O	298.00	7.50E-03	2.235	0	0.000E+00	Cr (as CrO4--)	0.000E+00
497-19-8	sample from ANL	sodium carbonate	Na2CO3	105.99	2.30E-01	24.378	0	0.000E+00	Cs+ (total)	2.719E-04
7631-99-4	<i>J.T. Baker (analyzed)</i>	sodium nitrate	NaNO3	85.00	1.36E+00	115.600	5.779	1.360E+00	K+	0.000E+00
7757-79-1	sample from ANL	potassium nitrate	KNO3	101.11	1.70E-02	1.719	0	0.000E+00	Na+	5.505E+00
7789-18-6	sample from ANL	cesium nitrate	CsNO3	194.92	2.70E-04	0.053	0.00265	2.719E-04	Anions	
7757-82-6	sample from ANL	sodium sulfate	Na2SO4	142.05	2.00E-01	28.410	0	0.000E+00	Cl-	0.000E+00
7647-14-5	sample from ANL	sodium chloride	NaCl	58.44	1.00E-01	5.844	0	0.000E+00	F- (nominal)	0.000E+00
7681-49-4	sample from ANL	sodium fluoride	NaF	41.99	5.00E-02	2.100	0	0.000E+00	NO2-	8.200E-01
7632-00-0	<i>EM Science</i>	sodium nitrite	NaNO2	69.00	8.20E-01	56.580	2.829	8.200E-01	NO3-	2.680E+00
<p>Notes: Each component was added in the above order as a solid unless otherwise noted, and each component was in solution before adding the next one.</p> <p>Cesium nitrate was added as 0.5 mL of a stock solution to reach the correct concentration. NaF was predissolved in about 5 mL water.</p>									CO3--	0.000E+00
									SO4--	0.000E+00
									OH- (total)	3.325E+00
									OH- (Free)	1.565E+00
									Theor pH	14.19
									Total Cation	5.505E+00
									Total Anion	5.505E+00
									Radionuclides	Spike Level
									Cs-137	0.7 µCi/mL
									Ratio	Value
Na/Cs	20240									
Na/K	NA									
K/Cs	NA									

Table 2.5. Formulation of Simulant Containing Only Four of the ANL Salts Prepared With ORNL Water (ASOW-C)

C.A.S. Registry #	Salt Manufacturer	Component	Chemical Formula	Formula Weight	Desired Molarity	g needed per Liter	data amount weighed	(for 50 mL) Actual Molarity	Species	Concentration M
1310-73-2	<i>EM Science</i>	sodium hydroxide	NaOH	40.00	3.32E+00	132.800	6.6369	3.318E+00	Metals	
7784-27-2	<i>J.T. Baker (analyzed)</i>	aluminum nitrate	Al(NO3)3.9H2O	375.15	4.40E-01	165.066	8.2566	4.402E-01	Al (as Al(OH)4-)	4.402E-01
10588-01-9	sample from ANL	sodium dichromate	Na2Cr2O7.2H2O	298.00	7.50E-03	2.235	0	0.000E+00	Cr (as CrO4--)	0.000E+00
497-19-8	sample from ANL	sodium carbonate	Na2CO3	105.99	2.30E-01	24.378	1.227	2.315E-01	Cs+ (total)	2.719E-04
7631-99-4	<i>J.T. Baker (analyzed)</i>	sodium nitrate	NaNO3	85.00	1.36E+00	115.600	5.78	1.360E+00	K+	1.709E-02
7757-79-1	sample from ANL	potassium nitrate	KNO3	101.11	1.70E-02	1.719	0.0864	1.709E-02	Na+	6.363E+00
7789-18-6	sample from ANL	cesium nitrate	CsNO3	194.92	2.70E-04	0.053	0.00265	2.719E-04	Anions	
7757-82-6	sample from ANL	sodium sulfate	Na2SO4	142.05	2.00E-01	28.410	1.42	1.999E-01	Cl-	0.000E+00
7647-14-5	sample from ANL	sodium chloride	NaCl	58.44	1.00E-01	5.844	0	0.000E+00	F- (nominal)	0.000E+00
7681-49-4	sample from ANL	sodium fluoride	NaF	41.99	5.00E-02	2.100	0	0.000E+00	NO2-	8.217E-01
7632-00-0	<i>EM Science</i>	sodium nitrite	NaNO2	69.00	8.20E-01	56.580	2.835	8.217E-01	NO3-	2.698E+00
									CO3--	2.315E-01
									SO4--	1.999E-01
									OH- (total)	3.318E+00
									OH- (Free)	1.558E+00
									Theor pH	14.19
									Total Cation	6.380E+00
									Total Anion	6.380E+00
									Radionuclides	Spike Level
									Cs-137	0.7 µCi/mL
									Ratio	Value
									Na/Cs	23400
									Na/K	372
									K/Cs	63

Notes: Each component was added in the above order as a solid unless otherwise noted, and each component was in solution before adding the next one.

Cesium nitrate was added as 0.5 mL of a stock solution to reach the correct concentration. NaF was predissolved in about 5 mL water.

electrode. The meter was calibrated (two-point) prior to use. Isopar L isoparaffinic diluent (lot# 0306 10967) was obtained from Exxon Chemical Company, Houston, Texas. The BoBCalixC6 (lot# IBC 980731KC-428) was obtained from IBC Advanced Technologies (American Fork, UT).

Cesium-137 Radiotracers. The ^{137}Cs radiotracer used for spiking the waste simulants was obtained as $^{137}\text{CsCl}$ in 1M HCl from Amersham (Arlington Heights, IL) and was used as received. For experiments where it was necessary to have an acid-free source of $^{137}\text{CsNO}_3$, (as for example experiments aimed at examining the stripping mechanism) a portion of the $^{137}\text{CsCl}$ in 1M HCl was converted to $^{137}\text{CsNO}_3$ in water following a procedure described elsewhere [15].

Gamma Counting of Cesium. The cesium activity in the samples was determined by standard gamma()-counting techniques using a Packard Cobra Quantum Model 5003 gamma counter equipped with a 3" NaI(Tl) crystal through-hole type detector. A counting window of 580 to 750 keV was employed for the 662 keV emission from $^{137\text{m}}\text{Ba}$. Count times varied with the activity of the sample but were generally long enough to ensure that a total of 1000 total counts had been collected. A decay time (following separation of the aqueous and organic phases) of at least 1 hr was employed to ensure that secular equilibrium had been achieved between the extracted ^{137}Cs and its daughter $^{137\text{m}}\text{Ba}$.

2.2.2 Contacting Procedures

The experiments conducted in this report involving cesium radiotracers can be divided into two categories: the "forward" experiments and the sequential contacting experiments. For both categories of experiments, extraction was carried out by rotating the tubes end-over-end at 50-60 RPM for 30 minutes at 25 ± 0.2 °C using a Glass-Col® laboratory rotator and centrifuging (Sanyo MSE Mistral 2000R) for 3 minutes at 4000 rpm at 25 °C. Aliquots of each phase were analyzed for ^{137}Cs activity.

Cesium extraction “forward” experiments

These experiments involved the extraction of cesium from an aqueous phase containing only nitric acid and cesium nitrate by pristine solvent. They were designed to probe the system behavior upon stripping without performing the prerequisite extraction and scrubbing steps. However, it was only a first approximation, since the starting points were different (cesium in the aqueous phase vs. cesium in the organic phase) and since the solvent, unlike for the sequential batch tests, did not contain any other metals or acid carried-over from the scrub stages. Unless noted, experiments were performed by contacting 1.5-mL portions of organic and aqueous phases together in polypropylene tubes (sealed with screw caps equipped with polyethylene inner liners). The aqueous phases were spiked with ^{137}Cs tracer before contact.

Sequential contacting experiments

These batch tests comprised a succession of steps designed to mimic the different stages in an extraction, scrub, and strip cycle. Consecutive contacts consisted of:

- extractions of cesium from a simulant of the SRS high-level waste,
- scrubs of the organic phase with 50 mM nitric acid to remove the other cations extracted during the cesium extraction stages (such as sodium, potassium, and aluminum),
- strips of the organic phase with a mixture of 0.5 mM nitric acid and 0.1 mM cesium nitrate in order to remove all the activity and concentrate the radio-cesium in one clean effluent stream.

After each step, an aliquot was subsampled from both phases for ^{137}Cs activity analyses, and a given volume of solvent was transferred into a new vial for the next step. The volume ratio of the two phases was varied, as will be described below for each experiment.

2.3 RESULTS AND DISCUSSION

2.3.1 Cesium Extraction from Simulants Prepared from ANL Salts

Samples of all the minor simulant component salts and of deionized water were sent to ORNL by the team at ANL. These salts and the water were used to prepare simulants to check whether the impurity originated in one of these salts or from the water. ANL samples of the

major salts employed in the preparation of the simulant [e.g., NaOH, NaNO₂, NaNO₃, and Al(NO₃)₃] were not used, as bottles from different lots were consumed in ANL simulant preparation over several months (therefore decreasing the probability of having the same impurity) without loss of reproducibility. Table 2.6 presents all the results obtained with this simulant and allows comparison to the ORNL simulant.

Table 2.6. Comparison of Batch Results Obtained Using Different Simulants^a

Operation	D_{Cs}					
	ORNL	ANL	ASOW-A	ASOW-B	ASOW-C	ASAW
1 st Extraction	11.21	17.03	11.43	15.55	11.74	11.84
2 nd Extraction	11.20	16.73	10.86	15.09	11.06	11.11
Scrub	0.701	0.809	0.703	0.699	0.707	0.756
1 st Strip	0.038	0.135	0.042	0.034	0.041	0.041
2 nd Strip	0.073	0.264	0.087	0.060	0.026	0.077
3 rd Strip	0.077	0.226	0.078	0.064	0.099	0.072

^a See description of simulants in Tables 2.1 to 2.5. Organic phase: BoBCalixC6 0.01 M + modifier Cs-3 0.2 M in Isopar® L. Aqueous phases: fresh simulant for each extraction, 50 mM nitric acid for the scrubs, 0.5 mM nitric acid + 0.1 mM cesium nitrate for the strips. Contacts were run at 25 °C and O/A = 1. All data were obtained from measurements at ORNL.

It may be seen from the data in Table 2.6 that stripping is approximately 4-fold less efficient with the simulant received from ANL. However, stripping was relatively unaffected when the selected ANL salts or deionized water were used. Thus, the putative impurity leading to the previously observed discrepancy did not originate from the water or the selected ANL simulant salts.

2.3.2 Influence of Physical Methods

The influence of physical methods involved in contacting and counting was checked

indirectly and ruled out as the source of stripping discrepancies [1]. Several experiments performed at ANL were repeated at ORNL using samples of solvent and simulant received from ANL. Thus, the only differences lay in the physical methods adopted to perform the cesium extraction experiments. The ANL procedure involved immersing the samples in a 25 °C water bath, vortexing the samples for a few minutes, immersing the samples again in a 25 °C water bath, centrifuging, and then separating and counting the two phases -counting in HPGE well-type detector. The counting technique by -liquid scintillation was also used on a few samples to confirm the accuracy of the -counting method. At ORNL, the procedure involved rotating the tubes end-over-end for at least half an hour at 25 °C, centrifuging, and then separating and counting the two phases by -counting (details are given in the Experimental Section). Two observations were made:

- ANL and ORNL results agreed; therefore, the methods used to run the experiments were adequate and equivalent in results.
- Poor stripping results were obtained at ORNL with ANL simulant (Table 2.6).

2.3.3 Influence of Multiple Extractions

Two experiments were conducted to test the possibility of impurity build-up in the organic phase upon extraction. One experiment was performed using the ANL simulant, the other using the ORNL simulant. Fresh solvent was contacted at total of five times with the simulant (four times with cold simulant, the fifth time with simulant containing ^{137}Cs tracer), scrubbed once, and then stripped three times. The results are presented in Table 2.7.

The effect on the stripping efficiency was dramatic. An increase of stripping cesium distribution values may be seen for both ANL and ORNL simulants, strongly suggesting some impurity build-up in both cases. However, the decrease in stripping efficiency (increase of D_{Cs}) was less dramatic for the ORNL simulant. The results suggest that, in each case, an impurity must be highly extractable and remains so through scrubbing and stripping steps.

Table 2.7. Influence of Multiple Contacting^a

Operation	D_{Cs}			
	ORNL	ORNL (4 pre-equilibrations) ^b	ANL	ANL (4 pre-equilibrations) ^b
1 st Extraction	11.21	<i>b</i>	17.03	<i>b</i>
2 nd Extraction	11.20	9.42	16.73	14.44
Scrub	0.701	0.695	0.809	0.796
1 st Strip	0.038	0.045	0.135	0.214
2 nd Strip	0.073	0.119	0.264	0.775
3 rd Strip	0.077	0.118	0.226	0.739

^a Organic phase: BoBCalixC6 0.01 M + modifier Cs-3 0.2 M in Isopar® L. Aqueous phases: ANL or ORNL simulants for the extractions, 50 mM nitric acid for the scrub, 0.5 mM nitric acid + 0.1 mM cesium nitrate for the strips. Contacts were run at 25 °C and O/A = 1. ^bThe pre-equilibrations were carried out using the same aqueous simulant, but without ¹³⁷Cs tracer. The fifth contact also contained no tracer, and the value of D_{Cs} was not determined, as indicated in the first row of the data shown.

2.3.4 Influence of Simulant Pre-Wash

Having established that the presence of impurities in the simulants was likely, a series of experiments was conducted to determine whether portions of impurities could be removed by washing the simulant with different types of diluents or solvents (Table 2.8). Washes with only Isopar® L or hexane did not change the stripping results, which suggests that although the putative impurity is lipophilic, its extraction requires polar solvent components. Accordingly, when Cs-3 modifier is added to the diluent (at a concentration equal to the one used in the solvent containing the calixarene), there is a fair improvement in the stripping values. This indicates that some of the impurity was removed from the simulant during the washes, consistent with it being either a neutral compound or a lipophilic salt.

Table 2.8. Influence of Simulant Washes with Different Solvents and Diluents^a

Operation	ANL simulant	Washed with Isopar® L five times	Washed with Isopar® L+ modifier Cs-3 five times	Washed with hexane five times	Washed with hexane+ modifier Cs-3 five times
1 st Extraction	17.03	17.04	17.64	^b	16.69
2 nd Extraction	16.73	16.60	16.61	17.33	16.54
Scrub	0.809	0.840	0.771	0.968	0.765
1 st Strip	0.135	0.136	0.040	0.162	0.047
2 nd Strip	0.264	0.254	0.064	0.239	0.084
3 rd Strip	0.226	0.202	0.057	0.211	0.075

^a Organic phase: BoBCalixC6 0.01 M + modifier Cs-3 0.2 M in Isopar® L. Aqueous phases: ANL simulant (type of wash, see in the table) for the extractions, 50 mM nitric acid for the scrub, 0.5 mM nitric acid + 0.1 mM cesium nitrate for the strips. Contacts were run at 25 °C and O/A = 1. ^bThe pre-equilibration was carried out using the same aqueous simulant, but without ¹³⁷Cs tracer.

2.3.5 Influence of Trioctylamine Addition

Results from a previous series of experiments run at ORNL involving the addition of trioctylamine (TOA) to the solvent provided support to the conclusions mentioned in the preceding subsection [1]. Trioctylamine converts to the large lipophilic trioctylammonium cation when in contact with the acid scrub and strip stages. If the hypothesis that a lipophilic anion is being extracted into the organic solvent is correct, then a large lipophilic cation added to the solvent in excess concentration would be expected to nullify the anion's effect. That is, all of the cesium present in the solvent as the cesium-calixarene complex can be stripped as cesium nitrate, since the alkylammonium nitrate salt supplies the needed nitrate co-anion, and the negative equivalents of lipophilic anion in the solvent are compensated by the positive equivalents of the ammonium cation. Data collected at both ANL and ORNL demonstrated a dramatic improvement in stripping upon addition of trioctylamine to the solvent [1]. At ANL, 0.1 mM triisooctylamine (TiOA) gave good values of D_{Cs} in the range of 0.036-0.04 on stripping.

Using a simulant prepared at ANL, it was shown at ORNL that the addition of 0.1 mM TOA to the solvent after the third strip decreased D_{Cs} from 0.26 to 0.024.

2.4 CONCLUSIONS

The following observations were made earlier [1]:

- Cesium distribution ratios on stripping the solvent after contact with the ANL simulant were significantly higher than after contact with the ORNL simulant. This observation held true regardless of
 - a. where the experiments were performed
 - b. where fresh solvent was prepared
 - c. where the minor salts or water originated.
- Solvent that had contacted ANL simulant displayed decreased strippability, even after undergoing scrubbing and stripping steps. However, moderate improvement in stripping of this used solvent could be effected by multiple washings with dilute NaOH solutions [10].

The following observations could be made from the present experiments:

- Repeated contacts of the solvent with either the ORNL or the ANL simulant decreases the stripping performance, though the effect is more pronounced with the ANL simulant.
- Precontacting the ANL simulant with a solvent containing modifier and diluent improves the stripping performance.

From these observations, one may conclude that harmful chemical impurities in both simulants are the likely cause of the irreproducibility in stripping performance. The preparation of fresh solvent, the procedures used for phase-contacting, and the instrumental methods of analysis can be ruled out. The putative impurities must be lipophilic, and they are likely anionic. In the ANL simulant, the impurities are either the same but in higher concentrations, or are different but more deleterious to stripping, as compared with the ORNL simulant.

3. ELECTROSPRAY EXPERIMENTS

3.1 INTRODUCTION

With the establishment that the irreproducibility in stripping performance was likely caused by an anionic impurity that was co-extracted with cesium, it was desirable to subject the extraction solvent to direct analysis for the impurity. A sensitive technique for this purpose is electrospray mass spectrometry (ES-MS). The softness of the technique allows dissociation of the ion-paired species present in the solution without breaking the structures of the ions. In addition, charged complexes of ions with neutral molecules can be detected. Depending on the chosen mode, either cations or anions can be observed. In view of the evidence implicating anionic impurities, the solvent was taken through extraction, scrub, and strip steps and analyzed at each step by ES-MS in the negative ion mode.

3.2 EXPERIMENTAL

3.2.1 Materials and Contacting Procedure

The experiments were performed using the solvent and the two simulants from ANL and ORNL (Table 2.1). A solution of a commercially-available dish detergent on hand at ORNL (Joy[®] liquid gel) in water was also analyzed.

For the first experiment, the pristine solvent was contacted 10 times with the ANL simulant (O/A ratio = 0.2). After each extraction, the aqueous phase was removed and replaced by fresh simulant. After the 10th extraction, an aliquot of the solvent was reserved (2 mL), and the remainder contacted once with an equal volume of scrub solution (nitric acid 50 mM). Again, an aliquot of the solvent was saved, and the remainder contacted once with an equal volume of strip solution (nitric acid 0.5 mM and cesium nitrate 0.1 mM). For the second experiment, the pristine solvent was contacted twice with a double volume of simulant (either ANL or ORNL simulant). Successive extraction, scrub and strip steps were carried out by rotating the solutions end-over-end at 50-60 rpm (Glass-Col[®] laboratory rotator) in Teflon[®] FEP

tubes for half an hour at 25 ± 0.2 °C and centrifuging (Sanyo MSE Mistral 2000R) for 3 minutes at 4000 rpm at 25 °C.

3.2.2 Electrospray Analysis

ES-MS was performed on a PE SCIEX API 165 single quadrupole mass spectrometer (Concord, Ontario, Canada) outfitted with a TurboIonSpray source. A 30-cm long, Teflon® encapsulated fused silica transfer tube (75 µm-id. fused silica encapsulated in 1/16 in. o.d. Teflon, CETAC Technologies, Inc.) connected a 3.5-cm-long stainless steel ES emitter (400 µm-o.d., 100-µm-i.d.) to the stainless steel 254 µm-i.d. bore-through bulkhead grounding port built into the source. The emitter held at ca. 4.5 kV was placed 1.5-2.5 cm from the curtain gas plate aperture and angled to spray across the aperture. Nitrogen was used for sample nebulization. No "turbo gas" was used in these experiments. Sample was introduced to the instrument using a syringe pump to deliver solution loaded into 1.0 mL plastic syringes (Becton Dickinson Co., Franklin Labs, NJ) at a flow rate of 5.0 µL/min. Resulting spectra were the sum of five individual scans from m/z 30-1000 using a 0.1 m/z step size and a 5.0 ms dwell time. All the electrospray rinses and clean up were done with a mixture of dichloromethane (EM, HPLC grade) and acetonitrile (anhydrous, EM) 50% - 50% in volume. Ten-fold dilutions of all the samples were also made with this mixture.

3.3 RESULTS AND DISCUSSION

3.3.1 Overview of the Solvent at Different Stages

The ES-MS spectra reflected the general expectations regarding major species present in the solvent during the extraction-scrub-strip sequence and pointed at the likely anionic impurity. A blank was first run in order to determine the different peaks introduced by the acetonitrile-dichloromethane mixture. The spectrum of the pristine solvent in cation mode is shown in Figure 3.1. Overall signal intensity was weak, but it is interesting to note that the most intense peak results from the potassium-BoBCalixC6 complex, the potassium likely being introduced during the synthesis of the calixarene. The cation-mode spectrum of the solvent after ten

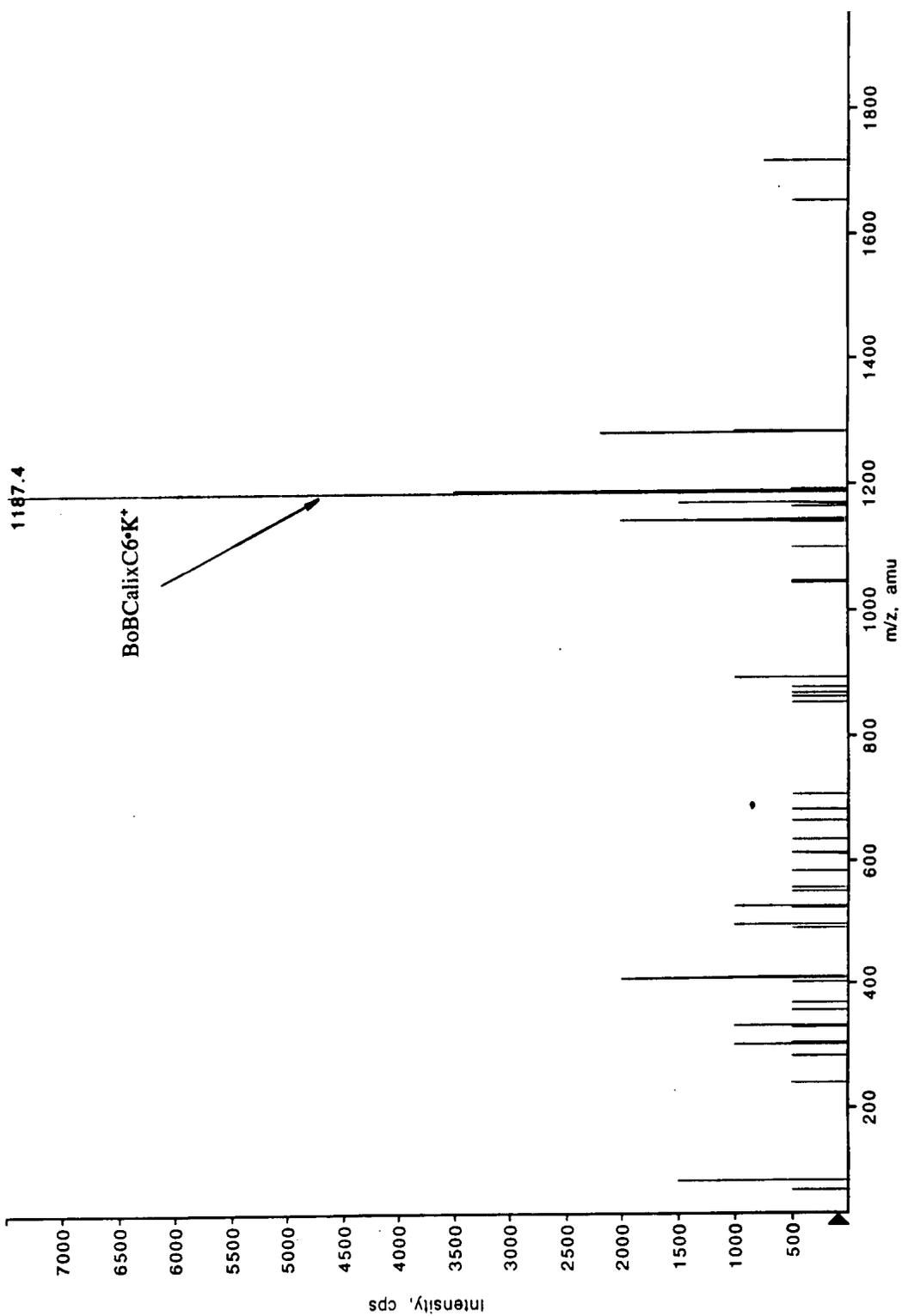


Figure 3.1. Cation-Mode Electrospray Spectrum of the Pristine Solvent.
Solvent: BoBCalixC6 0.01 M and modifier Cs-3 0.2 M in Isopar® L.

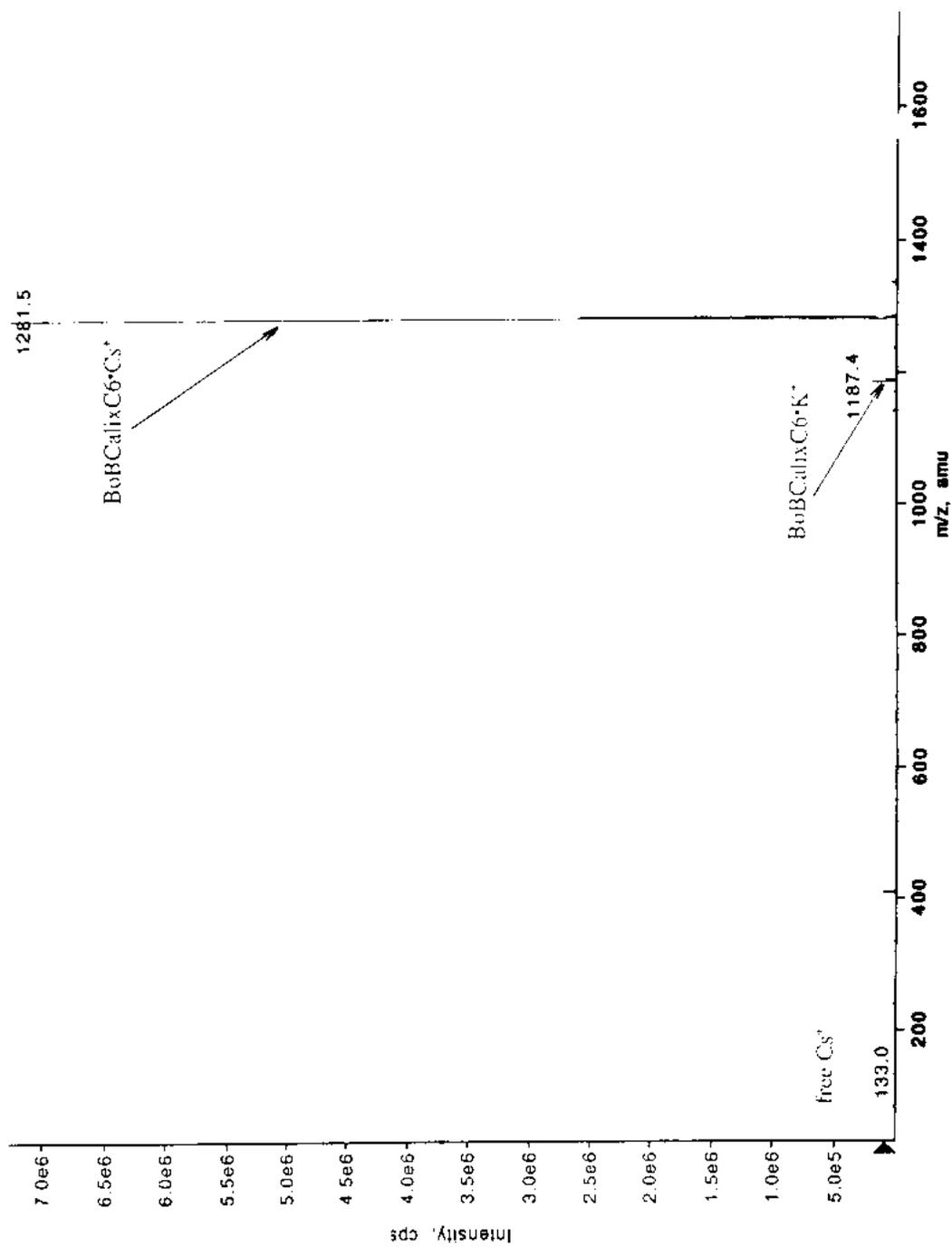


Figure 3.2. Cation-Mode Electrospray Spectrum of the Solvent Contacted 10 times with the ANL Simulant. Solvent: BoBCalixC6 0.01 M and modifier Cs-3 0.2 M in Isopar® L contacted 10 times with ANL simulant at O/A = 0.2 and T = 25 °C.

contacts with ANL simulant shows that cesium is the major cation extracted after contact with the simulant (Figure 3.2). From previous extraction results, it is known that sodium and potassium are weakly extracted, and in spite of the large excess of these two cations in the simulant, the peaks corresponding to their complexes with the calixarene are barely detectable.

In view of the complexity of the simulant, a variety of different anions may be expected to be present in the organic phase. The most complicated spectrum in the anion mode is the one of the solvent after extraction (Figure 3.3). Indeed, a variety of anions together with their adducts with the Cs-3 alcohol modifier could be assigned to peaks. The presence of anion-modifier adducts is consistent with the modifier acting as an anion-solvating agent. Because of the high efficiency of the scrubbing and stripping stages, the corresponding spectra (Figures 3.4 and 3.5) show a disappearance of many peaks, such as those associated with $\text{Al}(\text{OH})_4^-$, that were intense in the extraction spectrum in the anion mode. It is of interest to observe that, as expected, nitrate is the predominant anion remaining after one scrub and one strip. It was already hypothesized that the impurity would remain in the solvent after the stripping stages and would tend to build-up. That indeed seems to be the case for the doublet of peaks present at molecular weights of 235 and 249. The spectrum of the scrubbed solvent (Figure 3.4) shows a large increase of the relative ratios of these peaks to those corresponding to other anions (the complete identification will be explained below). The same phenomenon is observed with the spectrum of the stripped solvent (Figure 3.5).

3.3.2 Peak Identifications

The assignment of the ES-MS peaks is presented by reference to Figure 3.3 (extraction stage), since this spectrum is the most complex. All the peaks found in the other spectra can be interpreted by comparison with it. The peaks originating from the blank solution (acetonitrile-dichloromethane) are clearly marked on the spectrum.

The spectrum in Figure 3.3 can be divided into three groups. The first group can be found at molecular weights below 300 amu, containing all the non-complexed anions. It is uncertain whether they actually exist in the organic phase as discrete anions or as complexes that were

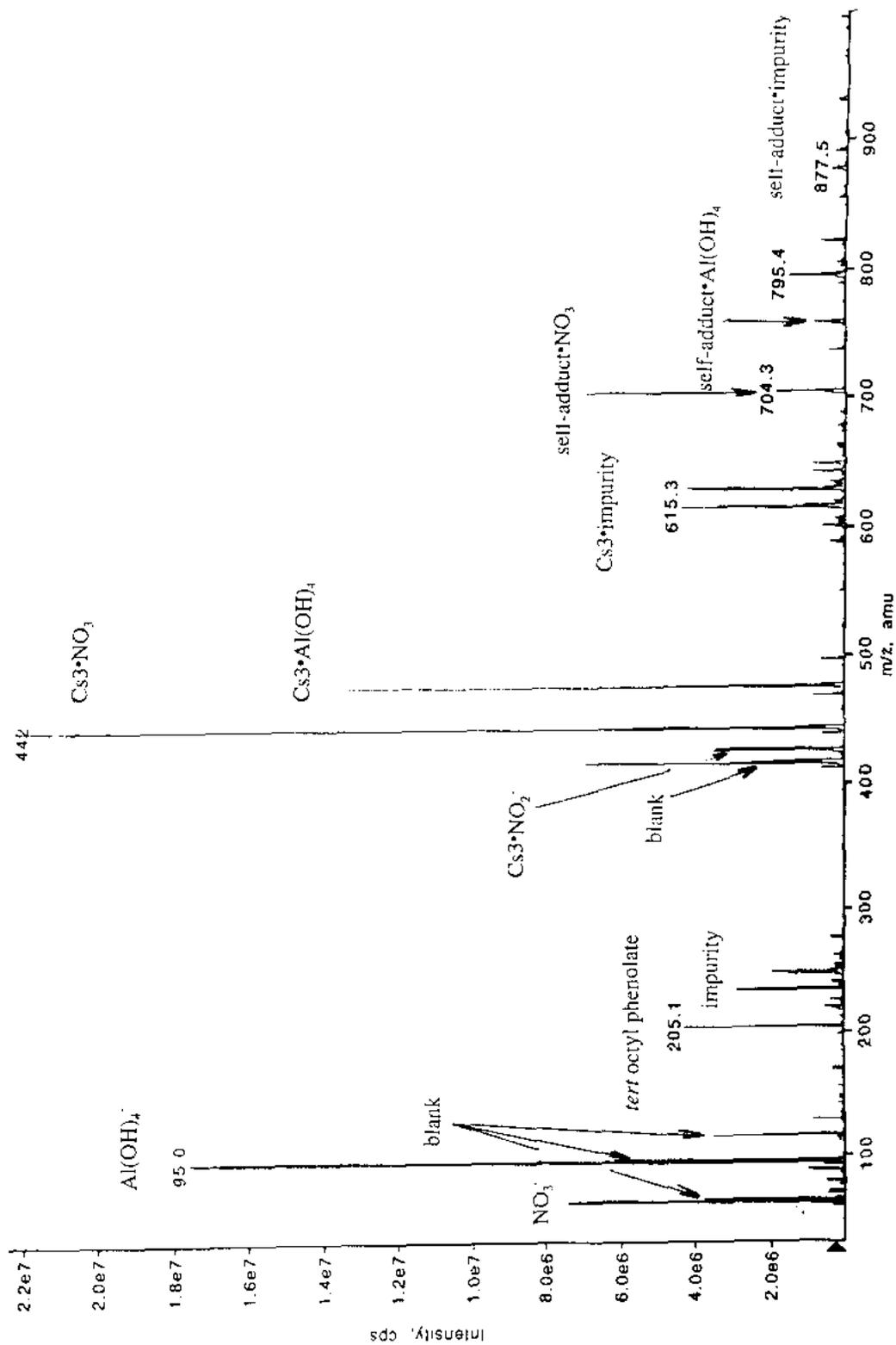


Figure 3.3. Anion-Mode Electrospray Spectrum of the Solvent Contacted 10 times with the ANL Simulant. Solvent: BoBCalixC6 0.01 M and modifier Cs-3 0.2 M in Isopar® L contacted 10 times with ANL simulant at O/A = 0.2 and T = 25 °C.

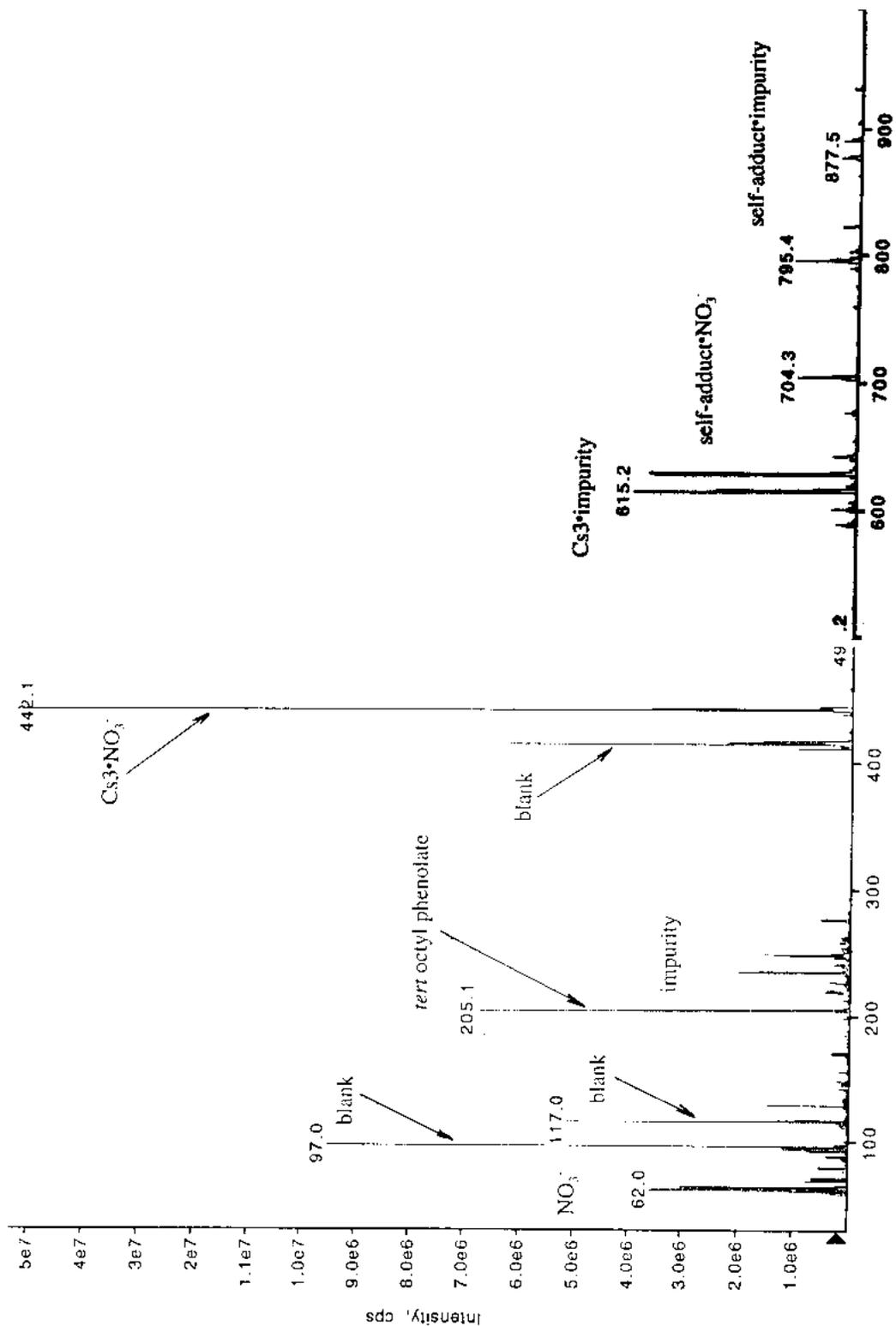


Figure 3.4. Anion-Mode Electrospray Spectrum of the Scrubbed Solvent.
 Solvent: BoBCalixC6 0.01 M and modifier Cs-3 0.2 M in Isopar® L contacted with ANL simulant then scrubbed with 50 mM nitric acid at O/A = 1 and T = 25 °C.

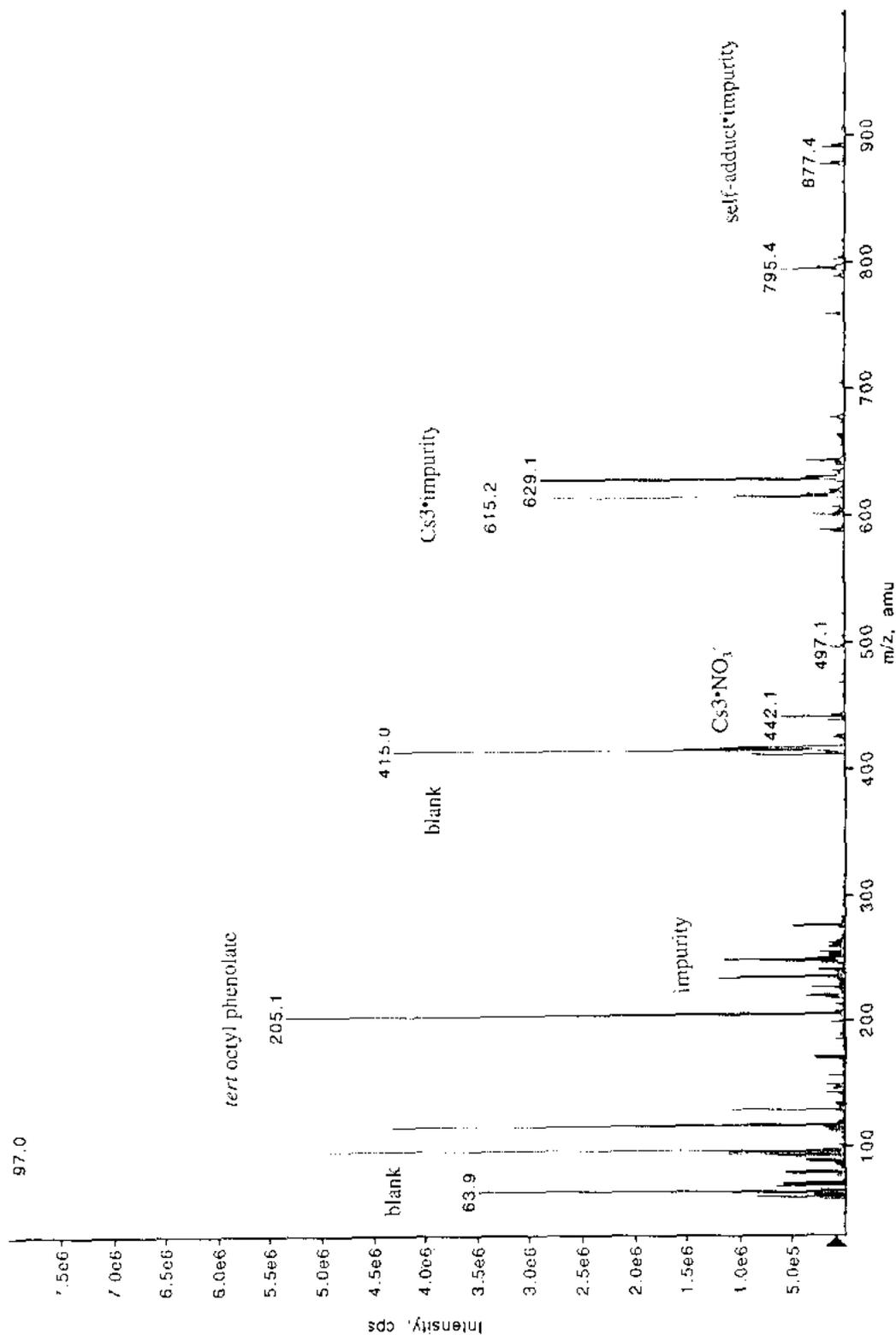


Figure 3.5. Anion-Mode Electrospray Spectrum of the Stripped Solvent.
 Solvent: BoBCalixC6 0.01 M and modifier Cs-3 0.2 M in Isopar® L contacted with ANL simulant, then scrubbed once with 50 mM nitric acid, and then stripped once with 0.5 mM nitric acid / 0.1 mM cesium nitrate at O/A = 1 and T = 25 °C.

solvent during the scrub (Figure 3.4) and strip (Figure 3.5) contacts, there is a decrease in the population of their adducts with the Cs-3 modifier (442 and 475 amu for the nitrate and tetrahydroxyaluminate adducts, respectively) with a concomitant relative increase in the populations of the Cs-3 adduct with the 235 and 249 amu species at 615 and 629 amu. It can be seen that, as the solvent is scrubbed and then stripped, the population of the adducts of the 235 and 249 amu species with both the Cs-3 modifier and the self-adduct increase relative to the peaks corresponding to the free 235 and 249 amu species. This could be because, with the inorganic anions largely washed out of the solvent, the modifier and self-adduct are now more available to form associations with the lipophilic anions comprising the 235 and 249 amu peaks. This observation is also consistent with the result described in Chapter 2 illustrating that washing the simulant with a solution of the Cs-3 modifier in Isopar[®] L appears to remove the lipophilic anionic impurity. These results suggest that two anionic impurities (235 and 249 amu) are extracted and cannot be effectively washed from the organic phase by the scrubbing and stripping operations. Their tenacity is promoted by their association with the Cs-3 modifier in the solvent.

3.3.3 Comparison Between Simulants

The previous experiment was repeated with the two simulants prepared at ANL and at ORNL, this time involving only two contacts were performed prior to the electrospray analysis. Whereas the intensities of the peaks in these spectra are much weaker, they are sufficiently high to allow comparison to previously discussed spectra. The two spectra (relevant areas) are presented in Figures 3.7 and 3.8. The impurity detected in the ANL simulant is also clearly present in the ORNL simulant, but in quantities approximately 10 times less.

3.3.4 Identification of the Impurity

The lipophilic nature of the impurities and the apparent presence of the same anionic impurities in both simulants suggest the possibility of detergent residues. A distinct possibility is that the peaks at 235 and 249 amu correspond to undecyl- and dodecylsulfonate. The 14-amu

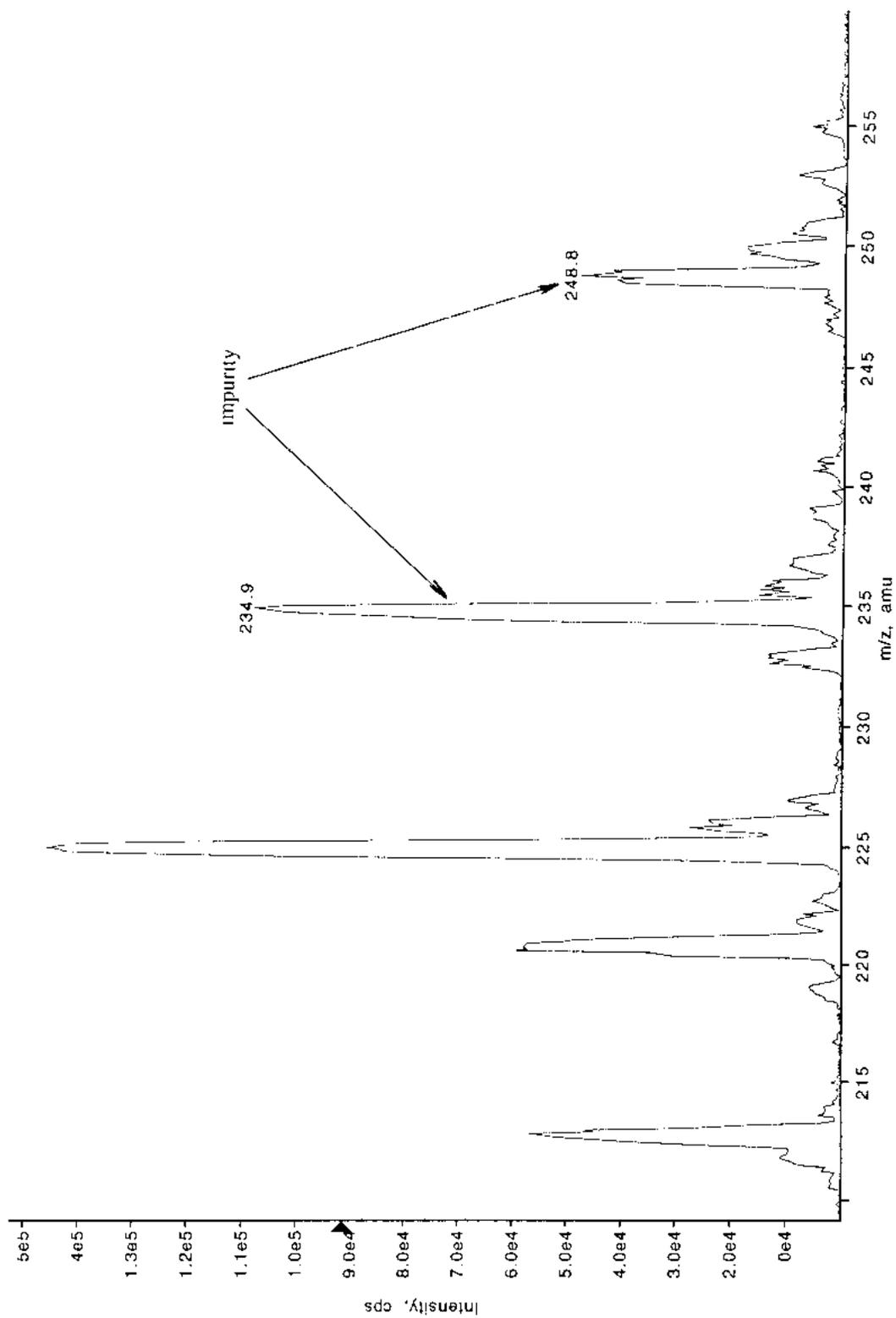


Figure 3.7. Anion-Mode Electrospray Spectrum of the Solvent Contacted Twice with the ANL Simulant. Solvent: BoBCalixC6 0.01 M and modifier Cs-3 0.2 M in Isopar® L contacted twice with ANL simulant at O/A = 0.2 and T = 25 °C.

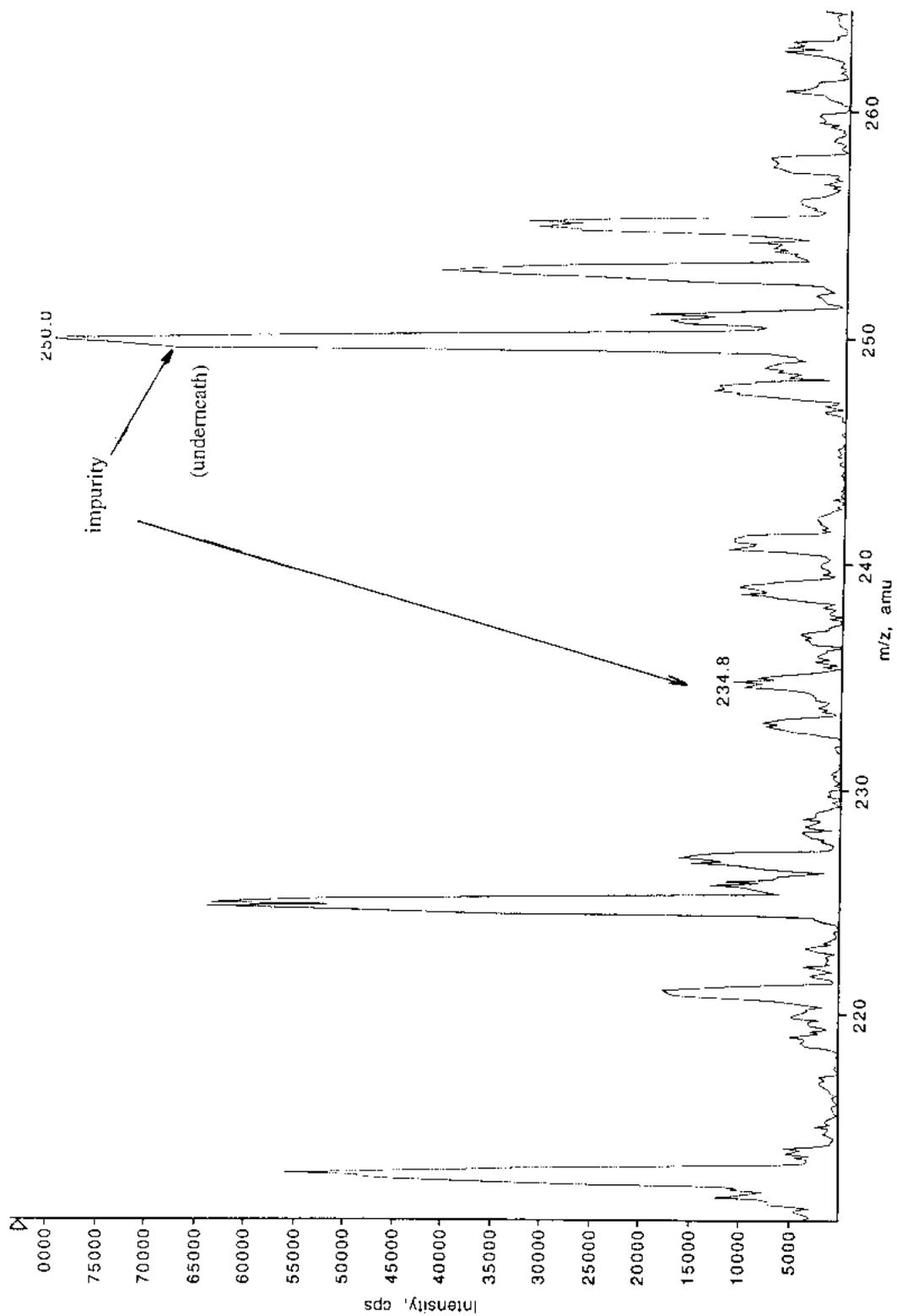


Figure 3.8. Anion-Mode Electrospray Spectrum of the Solvent Contacted Twice with the ORNL Simulant. Solvent: BoBCalixC6 0.01 M and modifier Cs-3 0.2 M in Isopar® L contacted twice with ORNL simulant at O/A = 0.2 and T = 25 °C.

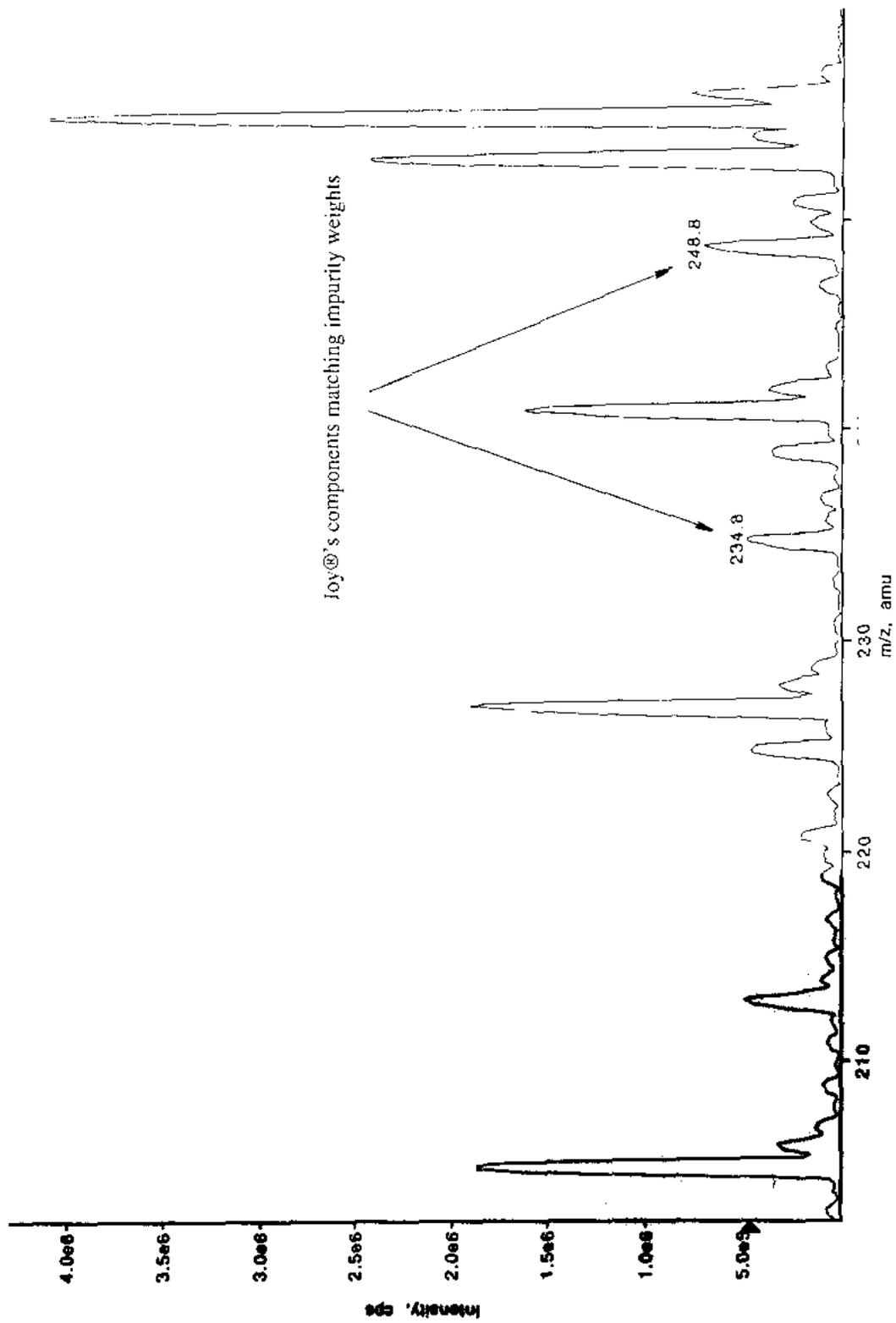


Figure 3.9. Anion-Mode Electrospray Spectrum of a 100,000 dilution of Joy® Liquid Gel. Dilution in deionized water.

difference seems particularly telling in that it corresponds to a single difference of a methylene unit $-\text{CH}_2-$ that would be typical in commercial detergents. The two sulfonate anions would be expected to be lipophilic and well-solvated by the alcohol modifier used in the solvent. Gibbs energies of transfer G_{tr}° of simple ions may provide a crude estimate of the magnitude of the lipophilicity of dodecylsulfonate. For acetate and nitrate, G_{tr}° values from water to methanol are given as 13 and 16 kJ/mol, respectively [16]. If we make the assumptions that the methanol approximates the solvation of Cs-3 modifier, that acetate approximates methane sulfonate, and that each aliphatic carbon adds -2.8 kJ/mol to G_{tr}° [17], one may see that transfer of the dodecylsulfonate to the solvent is likely very favorable in absolute terms and relative to nitrate. Thus, it is understandable how these surfactant anions introduced to the solvent could hinder stripping. Once all of the nitrate in the solvent has been effectively stripped in stage-wise operation, leaving only the surfactant anions as counter ions for the cesium-calixarene complex, stripping would be expected to practically cease. In the next chapter, it will be shown that this expectation can be validated using sodium dodecylsulfonate as a model surfactant.

As for the initial source of the surfactant impurities, no definitive answer exists. Soaps and detergents commonly contain salts of lipophilic anions. Such detergent residues could be present as trace impurities in the bulk chemicals used to prepare the various simulants, and since the simulants differed in the source of the bulk chemicals (e.g., NaOH), it is plausible that the detergent residue level in the simulants would differ as well. Since detergents are also used to clean glassware and other laboratory containers, residues incompletely removed by rinsing with distilled water are likely sources of contamination of laboratory solutions. It is also possible that charged species such as detergent residues will adhere better to glass surfaces than to non-polar surfaces such as Teflon[®] FEP, and thus the type of lab-ware used to prepare the simulants may contribute to variations in the amount of detergent residues present. Following a recommendation from our collaborators at ANL, a sample of Joy[®] detergent, the brand of detergent used to clean glassware at ANL, was analyzed by ES-MS. Figure 3.9 shows the ES-MS spectrum of a 10^5 dilution in water of a sample of this particular brand of detergent that was available at ORNL. The detergent was analyzed to determine whether the peaks at 235 and 249 amu (assigned to undecyl- and dodecylsulfonate) found in the simulant and solvent, or perhaps variants (e.g., chain-length homologs), would be present in a common detergent. As can be seen in Figure 3.9, peaks at 235 and 249 amu (as well as many other peaks) are present in the

spectrum, indicating a possibility that a detergent, possibly Joy[®], might be the source of these sulfonate anions.

3.4 CONCLUSIONS

The conclusions that may be made from the ES-MS experiments are as follows:

- The lipophilic impurity in the simulants is likely a mixture of undecyl- and dodecylsulfonate.
- The cesium complex in the solvent is a simple 1:1 cesium-calixarene complex mono-cation.
- The anions are present in three forms: free, complexed with one molecule of Cs-3 alcohol, and complexed with a self-adduct of Cs-3 (a degradation product).
- Although various anions are extracted, scrubbing removes all but nitrate and the lipophilic impurity anions.
- On stripping, the lipophilic impurity anions predominate.

In the next chapter, the results of solvent-extraction experiments used to test the effect of dodecylsulfonate as a model impurity anion are discussed.

4. QUANTIFICATION AND REMEDIATION

4.1 INTRODUCTION

As shown above, alkyl sulfonates, lipophilic anions omnipresent in detergents, were determined by electrospray mass spectrometry to be present in solvents that displayed relatively poor behavior on stripping. To confirm that the presence of alkyl sulfonates in the solvent does in fact negatively impact stripping performance, pristine solvent was contacted with simulant or stripping solution containing authentic sodium dodecylsulfonate at various concentrations. The cesium distribution coefficients obtained using simulants spiked with sodium dodecylsulfonate were also compared to those obtained with the simulants believed to contain alkyl sulfonate impurities. Another point of interest is to approximate the quantity of sulfonate impurity present in the affected simulants. Finally, the analysis of the problem will allow a possible remediation through the incorporation of trioctylamine in the solvent. As was previously discussed, the effects produced by the impurity had been shown to be suppressed by the use of a trialkylamine [1].

4.2 EXPERIMENTAL

4.2.1 Materials and Preparation of Solutions

Three types of experiments were performed, requiring three different solutions. A stock solution of sodium dodecylsulfonate (Aldrich, 99+%) at 10^{-2} M in 0.5 mM nitric acid containing cesium nitrate at 0.1 mM was prepared and used for subsequent dilutions (with 0.5 mM nitric acid/0.1 mM cesium nitrate). These solutions were used to check the effects of the presence of the sulfonate anion in the strip solution on the cesium distribution ratios and to establish the possibility of remediation by the trioctylamine (TOA). The corresponding organic phases containing 10^{-4} M and 10^{-3} M TOA were prepared as new small batches of solvent. The experiment designed to generate a standard curve to be used to quantify the level of impurity present in the ANL simulant was performed with three solutions of ORNL simulant spiked with known volumes of sodium dodecylsulfonate (from a stock solution of sulfonate 10^{-2} M in water).

The volume added was small enough not to have an influence on other component concentrations.

4.2.2 Contacting Procedures

The experiments showing the influence of the sulfonate presence on cesium distribution ratios and the remediation with TOA were performed as “ D_{Cs} forward” experiments. The procedure was described in Section 2.2.2. The approximation of the impurity concentration was achieved through a batch experiment (see 2.1.2)

4.3 RESULTS AND DISCUSSION

4.3.1 Effect of Dodecylsulfonate Anion on Cesium Extraction

The experiments investigating the effects of the presence of dodecylsulfonate ion involved obtaining cesium distribution ratios under stripping conditions (“forward” D_{Cs} experiments). Controlled amounts of sulfonate in the sodium salt form were added to the aqueous phase containing nitric acid 0.5 mM and cesium nitrate 0.1 mM (stripping solution). Cesium distribution ratios obtained under these conditions are presented in Figure 4.1. The effects of extremely low amounts of sulfonate (under 10^{-5} M) are already detectable. A quantity of sulfonate greater than 10^{-4} M results in a quantitative extraction of cesium by the calixarene. Any sulfonate concentration greater than 10^{-5} M in a system would thus prohibit efficient stripping. This result confirms that traces of impurities were sufficient to produce high stripping values when using the ANL simulant. In addition, the cesium distribution ratio of 0.04 usually obtained for the second strip in the extraction-scrub-strip sequence using ORNL simulant corresponds to the D_{Cs} value obtained for a concentration of dodecylsulfonate 10 times lower than the one required for a distribution ratio of 0.2. This is consistent with the observations by ES-MS.

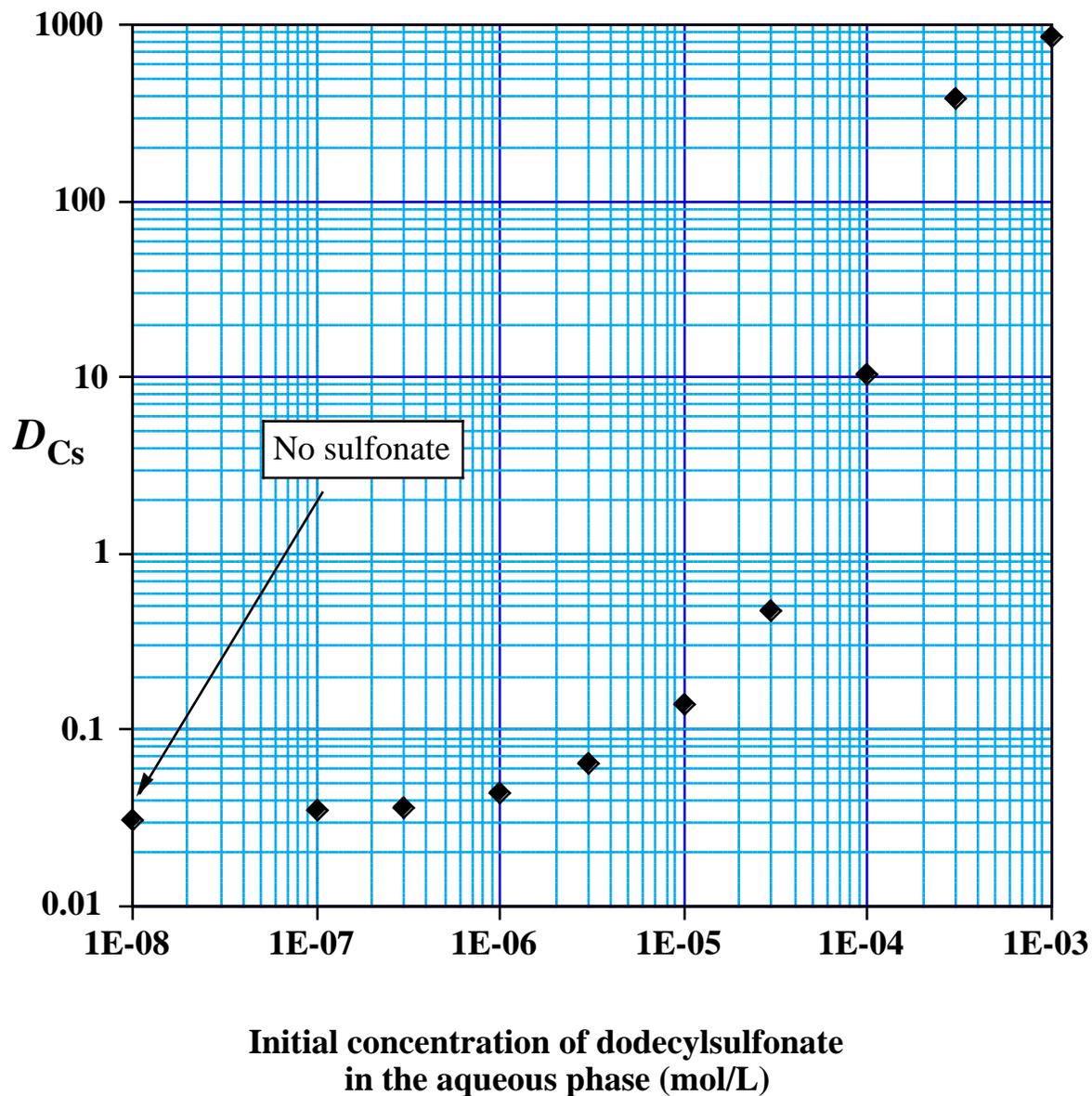


Figure 4.1. Effect of Dodecylsulfonate Anion on Cesium Distribution Ratios Under Stripping Conditions. Organic phase: [BoBCalixC6] = 0.01 M and [Cs-3] = 0.2 M in Isopar®L. Aqueous phase: [CsNO₃] = 0.1 mM and [HNO₃] = 0.5 mM. Contacts were made at O/A ratio = 1 (0.75 mL of each phase) and T = 25 °C with varying concentrations of dodecylsulfonate added to the aqueous phase.

4.3.2 Approximation of the Quantity of Sulfonate Present in ANL Simulant

The previous experiment showed that the effects of minute amounts of sulfonate present in the system are dramatic. A concentration of dodecylsulfonate equal to 1.3×10^{-5} M is sufficient to obtain D_{Cs} values in a “forward” experiment comparable to the ones obtained on stripping with ANL simulant (Table 2.6). When progressing through the procedure in Table 4.1, the solvent is contacted twice with the simulant. If it is assumed that the sulfonate is entirely extracted by the solvent during the extraction stages and does not partition during the scrubbing steps, one can estimate that the quantity of impurity present initially in the simulant is approximately 6.5×10^{-6} M. To examine the effect of dodecyl sulfonate on D_{Cs} values in sequential contacting, three solutions of ORNL simulant spiked with different concentrations of sodium dodecylsulfonate (10^{-6} M, 6.5×10^{-6} M, and 10^{-5} M) were prepared. Two extraction steps for each simulant solution were followed by two scrubs and three strips. The results are reported in Table 4.1.

Table 4.1. Cesium Distribution Ratios in Batch Tests Involving ORNL Simulant Containing Controlled Amounts of Sulfonate^a

Operation	D_{Cs}			
	ORNL simulant	ORNL simulant + 10^{-6} M sulfonate	ORNL simulant + 6.5×10^{-6} M sulfonate	ORNL simulant + 10^{-5} M sulfonate
1 st Extraction	11.78	11.66	11.94	11.78
2 nd Extraction	10.97	10.88	11.01	10.92
Scrub	0.705	0.701	0.711	0.730
1 st Strip	0.035	0.036	0.050	0.060
2 nd Strip	0.061	0.065	0.102	0.129
3 rd Strip	0.066	0.069	0.104	0.135

^aOrganic phase: BoBCalixC6 0.01 M + modifier Cs-3 0.2 M in Isopar® L. Aqueous phases: ORNL simulant (with different concentration of sulfonate) for the extractions, 50 mM nitric acid for the scrub, 0.5 mM nitric acid + 0.1 mM cesium nitrate for the strips. Contacts were run at 25 °C and O/A = 1.

It may be readily seen that trace concentrations of dodecyl sulfonate in the simulant indeed have a marked effect on stripping performance. However, the concentrations of dodecyl sulfonate in the simulant necessary to raise D_{Cs} on stripping to the level of the ANL simulant (Table 2.6) would be significantly larger than the 6.5×10^{-6} M estimated from “forward” stripping (Fig. 4.1). This may indicate that the sulfonate may not be entirely extracted from the simulant and may also partition somewhat during the scrubbing and stripping stages. Therefore, the remaining quantity of lipophilic anion in the stripping stages would be less than anticipated. Overall, the experiment confirms that only minute amounts of soap residues would need to be present in the ANL simulant to render stripping less effective. The effect of dodecyl sulfonate is regarded to be of the correct magnitude to account for the difficulty with stripping with the ANL simulant.

4.3.3 Remediation with Trioctylamine

In view of the probable identity of the anionic impurities that hinder stripping, one can understand the action of trioctylamine in blocking that effect (see Section 2.3.5). As before, cesium distribution ratios were measured under stripping conditions (forward D_{Cs} experiments) using a spike of sodium dodecylsulfonate in various concentrations in the aqueous phase. The solvent contained either no TOA or TOA at 10^{-4} or 10^{-3} M. The dramatic blocking effect is shown in Figure 4.2. It may be seen that a TOA concentration at ten times the aqueous sulfonate concentration suffices to suppress the impurity effect nearly completely. The fact that the TOA does not appear to be acting stoichiometrically may simply reflect the incomplete conversion of the amine to the ammonium form, which would likely require higher acidities.

4.4 CONCLUSIONS AND FURTHER DEVELOPMENTS

Solvent-extraction experiments showed that dodecylsulfonate could approximately account for the impurity effect observed using simulants. Minute amounts of this impurity can cause a significant decrease in cesium stripping performance, as proven by the controlled addition of sulfonate in the simulant. The effect of an impurity in the system can be blocked by

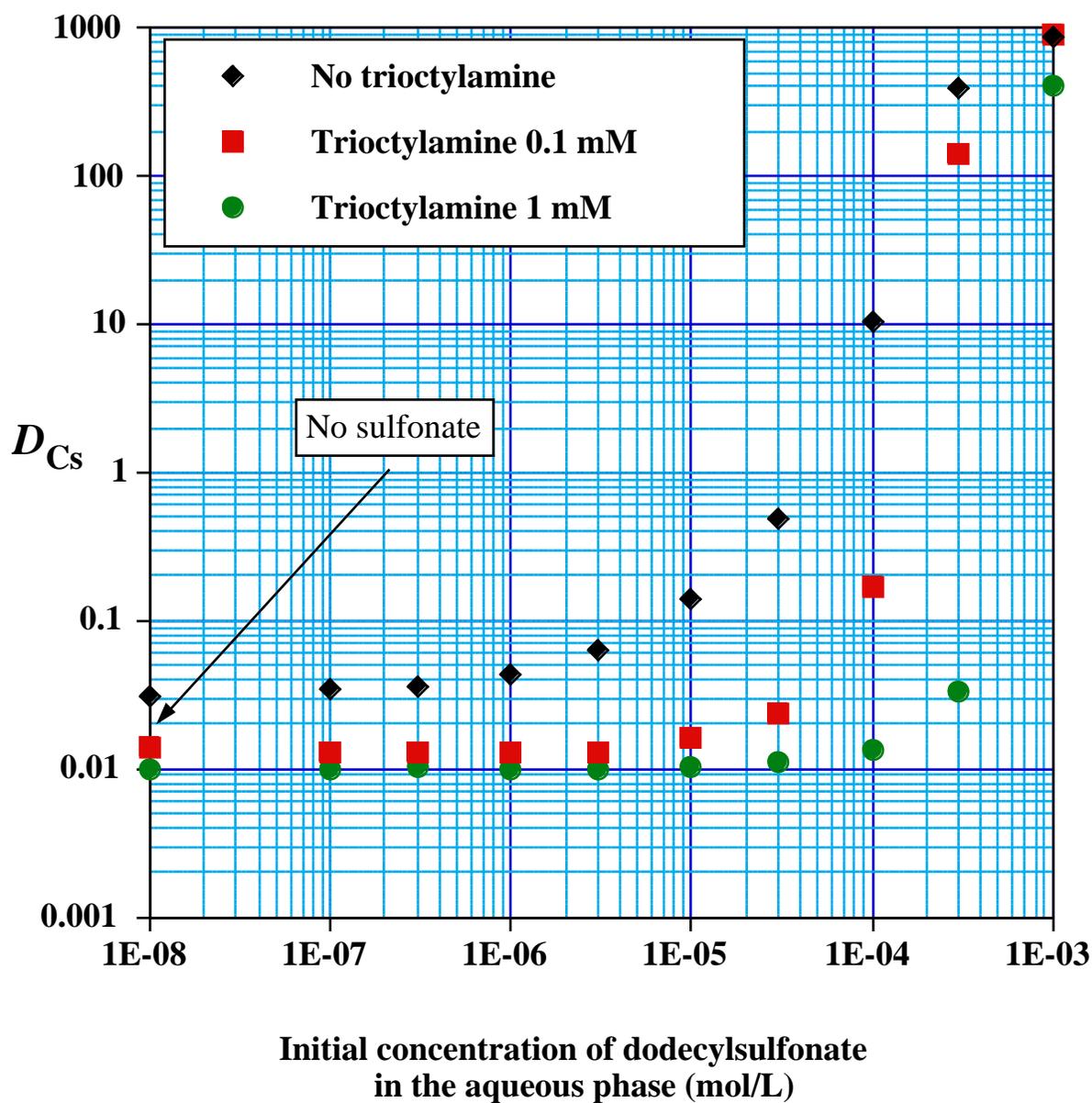


Figure 42. Effect of TOA on Cesium Extraction in the Presence of Dodecylsulfonate Anion in the Stripping Phase. Organic phase: [BoBCalixC6] = 0.01 M, [Cs-3] = 0.2 M, and trioctylamine in Isopar®L. Aqueous phase: [CsNO₃] = 0.1 mM and [HNO₃] = 0.5 mM. Contacts were made at O/A ratio = 1 (0.75 mL of each phase) and T = 25 °C with varying concentrations of dodecylsulfonate added to the aqueous phase.

the addition of trioctylamine to the solvent. In the stripping steps occurring under acidic conditions, the amine is partly protonated and replaces cesium as the impurity counter-ion, allowing cesium stripping efficiency to remain excellent. These studies have thereby led to improvements in the solvent composition, resulting in a more robust solvent able to achieve performance meeting SRS requirements. A preliminary report has been submitted for publication [2]. Complete details about these and other improvements will be given in future publications.

5. REFERENCES

- [1] Bonnesen, P.V.; Delmau, L.H.; Haverlock, T.J.; and Moyer, B.A. *Alkaline-Side Extraction of Cesium from Savannah River Tank Waste Using a Calixarene-Crown Ether Extractant*; Report ORNL/TM-13704, Oak Ridge National Laboratory: Oak Ridge, TN, December, 1998
- [2] Moyer, B.A.; Bonnesen, P.V.; Delmau, L.H.; Haverlock, T.J.; Sachleben, R.A.; Leonard, R.A.; Conner, C.; Lumetta, G.J. "Solvent Extraction of Tc and Cs from Alkaline Nitrate Wastes," Proc. Internat. Solvent Extraction Conference (ISEC '99), Barcelona, Spain, July 11-16, 1999 (In Press).
- [3] Application to U.S. Patent Office: Moyer, B.A.; Bonnesen, P.V.; Sachleben, R.A.; Presley, D.J. "Solvent and Process for Extracting Cesium from Alkaline Waste Solutions," Ser. No. 09/146,800, Sept. 3, 1998.
- [4] Bonnesen, P.V.; Haverlock, T.J.; Engle, N.L.; Sachleben, R.A.; Moyer B.A. "Development of Process Chemistry for the Removal of Cesium from Acidic Nuclear Waste by Calix[4]arene-Crown-6 Ethers," in *Calixarene Molecules for Separations*, G. J. Lumetta and R. D. Rogers, Eds., ACS Symposium Series, American Chemical Society, Washington, D. C. (In Press).
- [5] Dozol, J.-F.; Böhmer, V.; McKervey, A.; Lopez Calahorra, F.; Reinhoudt, D.; Schwing, M.-J.; Ungaro, R.; Wipff, G. *New Macrocyclic Extractants for Radioactive Waste Treatment: Ionizable Crown Ethers and Functionalized Calixarenes*, Report EUR-17615, European Community, Luxembourg, 1997
- [6] Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud, F.; Fanni, S.; Schwing, M.-J.; Egberink, R.J.M.; de Jong, F.; Reinhoudt, D.N. *J. Am. Chem. Soc.*, **1995**, *117*, 2767

- [7] Hill, C.; Dozol, J.-F.; Lamare, V.; Rouquette, H.; Eymard, S.; Tournois, B.; Vicens, J.; Asfari, Z.; Bressot, C.; Ungaro, R.; Casnati, A. *J. Inclusion Phenom. Mol. Recognit. Chem.*, **1994**, *19*, 399
- [8] Bonnesen, P.V.; Delmau, L.H.; Moyer, B.A.; Leonard, R.A. (Manuscript to be submitted to *Solvent Extr. Ion Exch.*)
- [9] Delmau, L.H.; Bonnesen, P.V.; Moyer, B.A. *Sep. Sci. Technol.*, to be submitted
- [10] Reference 1, Chapter 7.
- [11] Crawford, C.L.; Fondeur, F.F.; Peterson, R.A.; White, T.L. *Radiation Stability of Calixarene Based Solvent System*; Report WSRC-TR-98-00371; Westinghouse Savannah River Co.: Aiken, SC, October 2, 1998.
- [12] Reference 1, Chapter 6.
- [13] Leonard, R. A., Conner, C., M. W. Liberatore, Sedlet, J., Aase, S. B., and Vandegrift, G. F. *Evaluation of an Alkaline-Side Solvent Extraction Process for Cesium Removal from SRS Tank Waste using Laboratory-Scale Centrifugal Contactors*, Report ANL-99/14, Argonne National Laboratory, Argonne, IL, August 1999 (in press).
- [14] Reference 1, Chapter 3.
- [15] Haverlock, T.J.; Bonnesen, P.V.; Sachleben, R.A.; Moyer, B.A. *J. Inclusion Phenom. Mol. Recognit. Chem.* (In press).
- [16] Marcus, Y. Ion Properties; Marcel Dekker: New York, 1997.
- [17] Hansch, C.; Leo, J. Substituent Constants for Correlation Analysis in Chemistry and Biology; Wiley-Interscience: New York, 1979.