SAND2013-9948P

Sandia National Laboratories

Operated for the U.S. Department of
Energy by

Sandia Corporation

Charles R. Bryan
P.O. Box 5800 MS 0779
Albuquerque, NM 87185

Phone: (505) 284-2762
Fax: (505) 284-2348
Internet: crbryan@sandia.gov

Date: November 13, 2013

Subject: Analysis of Saltsmart^{TM} Samples from Holtec Test Run

To: Laszlo Zsidai, Holtec International

Laszlo,

We have completed chemical analysis of the Saltsmart^{TM} samples collected by Holtec during their recent dry run. In order to better understand the results of the analyses, we prepared additional samples here at Sandia and also evaluated those. These include SaltSmart^{TM} blanks and samples collected from surfaces with known salt loadings. I have appended a writeup of our results.

To summarize, the Holtec samples, collected from metal surfaces pre-coated with a known salt assemblage, contained a larger suite of salts that those initially deposited on the surfaces. Apparently, additional dust/salts were unintentionally allowed to accumulate on the test surfaces during preparation for the dry run. This made assessing the efficiency of removal and the potential for preferential sampling of some salt components over others difficult to evaluate, as the exact composition of the salts present on the sampled surface was no longer known. However, additional tests with samples prepared here at Sandia indicate that the Saltsmart^{TM} sensors are effective at sampling salts on metal surfaces. The tests also confirmed that the contamination observed in the Holtec samples was not from the fluid used to extract the salts, or leached from parts of the sensors themselves. Given that the Saltsmart^{TM} sensors apparently sample surface salts in an unbiased fashion, we were able to estimate (with some uncertainty), the intentionally-deposited fraction and the contaminant fraction of the salts on the surfaces that Holtec sampled. This information may allow Holtec to assess the efficiency of salt removal under the sampling conditions during the dry run.

Charles R. Bryan, Ph.D (Geochemistry)
Storage and Transportation Technologies Department
Sandia National Laboratories

Analysis of SaltSmart^{TM} test samples from Holtec

Charles Bryan and David Enos

1. Samples received from Holtec

Samples were received via overnight mail from Lazlo Zsidai. The seven samples were stored in sealed plastic bags when received; a quick survey showed that the wicks (the thin white strip that actually contacts the surface of interest) were spotted and discolored. The samples were stored in a refrigerator until analysis, several days later. When the samples were removed from the refrigerator and the plastic storage bags opened, a description of the wick was recorded; these are provided in Table 1. The wicks were significantly discolored. There are several potential causes for the discolorations described in the table. These include (1) the salt coated metal panels may have not been cleaned prior to salt deposition, (2) the salt coated panels could have been contaminated after deposition while they were installed on the surface of the container, (3) the SaltSmart^{TM} devices could have been set on a contaminated surface prior to or following being used to acquire a sample from the container surface, or (4) Biological materials (e.g., mold or fungi) may have grown on the wicks during storage and shipping. The latter alternative seems unlikely, however, as the stains largely washed off the wicks during leaching to extract the salts.

Table 1. Description of SaltSmart^{TM} wicks upon opening the plastic shipping bags.

Sample #	Description of wick
1	Slightly discolored (light yellow) with small gray specks and slightly larger brown specks
2	Medium brown staining over ~1/3 of the surface, small yellow patches in the remaining area, small gray particles.
3	Light yellow staining over ½ the surface, small yellow-brown spot, gray specks.
4	Large black spot with yellow-brown halo (the rubber support behind the wick was aso discolored), some gray particulates.
5	Light yellow staining, a few gray particulates.
6	Light-to-moderate yellow staining.
7	Light yellow staining over 1/3 to ½ of the surface, brown particulates.

For analysis, the SaltSmart^{TM} sensors were removed from the plastic shipping bags and split open along the seam with a small chisel (breaking them down into their component parts, as shown in Figure 1).

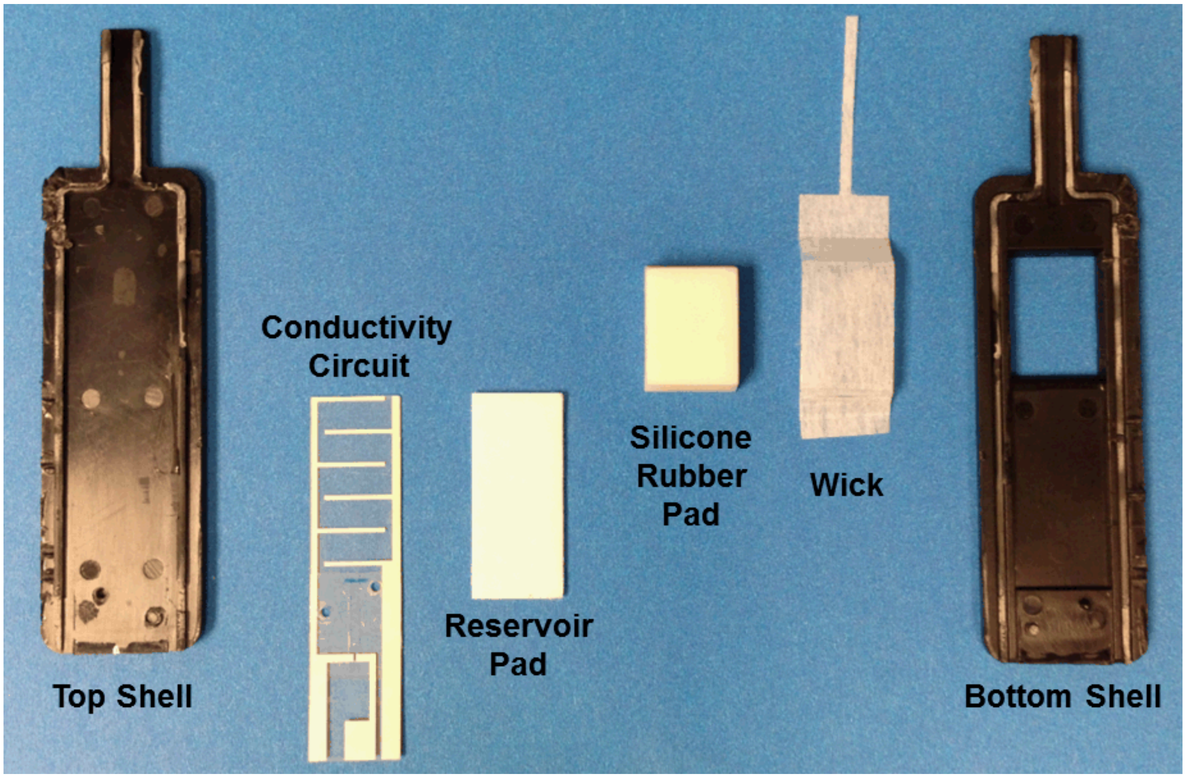


Figure 1. Dissassembled SaltSmart^{TM} Device

The wick and the reservoir pad inside the SaltSmart^{TM} device were removed and transferred to a pre-weighed 50 ml polypropylene screw-cap sample tube. The wick was commonly dry, but the reservoir pad was wet. Moisture was observed on other plastic internal pieces of the sensors, and on the inside surfaces of the two halves of the shell. The internal pieces, and the inside surfaces of the shells, were rinsed with deionized water (>18MΩ) and the water transferred to the polypropylene sample tubes containing the wicks and pads. A total water volume of 10-15 ml per sample was the target. The samples were placed on a shaker table overnight to equilibrate the salts in the wick and pad with the solution, and then, the solutions were sampled for analysis.

Five ml of the solution was extracted from the sample tubes and retained for anion analysis by ion chromatography (IC). Anionic analytes were F^-, Cl^-, Br^-, NO_2^-, NO_3^-, SO_4^{-2}, and PO_4^{-3}. IC analyses were done with a Dionex ICS-1100 RFIC Ion chromatograph with a Dionex Ionpac AS-23 RFIC column and AG-23 guard column, and a Dionex AERS 500 suppressor. Blanks were run between all standards and samples to minimize carryover. Because the range of concentrations in the samples was unknown, six standards and a blank were used; however, a subset of the standards (never less than three and a blank) was used when calculating sample concentrations; standards that were higher than necessary to bracket the unknowns were not used. This was done because the calibration curves were based on the least squares method, which over-weights higher-concentration standards and results in larger errors for values in the lower part of the range. The standards were made by dilution of stock Dionex IC anion standards.

For cation analysis, the remaining fluid (5-9 ml in volume) was extracted from the sample tubes and spiked to contain 2% Optima-grade HNO_3 and 1 mg/L Sc as an internal standard, and brought to a volume of 10 ml for analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES). ICP-OES analyses were done using a sequential Perkin-Elmer Optima 8000 ICP-OES, in both axial and radial viewing modes. Analytes examined were Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}. A minimum of two wavelengths were evaluated for each element; collected spectra were evaluated for interfering peaks, and for each element, the wavelength was chosen that best reproduced known standard concentrations when the standards were analyzed as unknowns. Concentrations were estimated using integrated peak areas. Five to six standards, made by diluting Spex Certiprep^{TM} Assurance and Claritas-Grade ICP stock standard solutions, were used because the range of the sample concentrations was unknown. As with the anions, sample concentrations were estimated using a subset of the standards (never less than three and a blank), excluding those which were higher than necessary to constrain the sample concentration to avoid overweighting of the higher standards.

After correcting for dilution and the total volume of the leachate, the amounts of each ionic species present in µg per sample, are given in Table 2. Values in µmoles are given in Table 3, and values in micro-equivalents (µeq) are provided in Table 4, along with the charge balances. There are several notable points. First, measurable amounts of virtually every ion evaluated were present. According to Steve Marschman (INL), the deposited salts were $NaCl+Na_2SO_4+MgCl_2$, mixed in the same proportion as they occur in ASTM synthetic seawater (ASTM D1141-98) . However, a much more complex mixture of salts was extracted from the SaltSmart^{TM} sensors. Steve indicates that the metal plates were cleaned prior to salt deposition, so it would seem likely that the plates were contaminated at the site, during preparation for use. Steve and Dave have indicated the production facility where the samples were prepared for attachment to the mockup was fairly dusty. Contamination of the surface may have occurred there, or perhaps the SaltSmart^{TM} sensors were contaminated when lowered into the Hi-Storm overpack, or when retrieved, during the dry run. Considering the discoloration of the SaltSmart^{TM} wicks, the latter possibility seems reasonable.

Some of the charge balances are poor, and in all cases the poor charge balances suggest a deficiency of anions. Based upon typical water chemistry, the missing anion could be carbonate/bicarbonate. As can be seen in the data, samples with better charge balances had very little calcium. As such, it seems likely that calcium carbonate was present a contaminant.

It should also be noted that the fluids extracted from the SaltSmart^{TM} sensors exhibited different wetting characteristics on polypropylene pipette tips than was observed for deionized water. A call to the SaltSmart^{TM} company confirmed that the wicks are impregnated with a surfactant to help flow. Although the surfactant is proprietary, the company representative indicated that the surfactant is organic, and does not contain any common ions. It is not known if this surfactant may have contributed to the measured analytes, or affected the results indirectly through changes in the wettability or flow properties of the sample. However, the IC elution curves for several of the samples had minor peaks that occurred at periodic intervals (mostly before the Cl peak); these appear to be spurious, and may have been due to fluctuations in flow rate or column retention due to the presence of the surfactant. Blanks are being run to verify that the surfactant is not contributing to the measured ion load.

Table 2. Ion Concentrations Recovered from the Holtec SaltSmart^{TM} Samples (µg/sample).

	Sample #						
Ion	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**
Na^+	169	85.9	67.0	31.8	34.3	32.8	48.2
K^+	6.9	*1.2*	24.0	3.0	5.0	3.1	*0.59*
Ca^{2+}	24.5	5.0	26.3	21.4	26.0	22.8	3.4
Mg^{2+}	14.6	5.8	10.1	6.8	8.7	7.1	3.5
F^-	0.93	0.49	1.1	0.48	0.98	0.36	0.12
Cl^-	236	132	82.8	35.9	35.4	37.3	80.4
Br^-	2.1	n.d.	n.d.	0.56	0.51	1.5	n.d.
NO_3^-	1.6	1.4	1.5	n.d.	n.d.	1.0	0.95
SO_4^{2-}	87.8	23.3	69.8	55.2	74.9	60.0	16.4
PO_4^{3-}	n.d.	2.0	n.d.	1.8	n.d.	1.6	1.9
Sum, µg	543	257	283	157	186	168	155
µg/cm^2 *	181	86	94	52	62	56	52

* Assuming SaltSmart^{TM} sample area of 3 cm^2

Note: Gray, italicized values for K are somewhat higher than the blanks, but are only poorly quantified.

Table 3. Ion Concentrations recovered from the Holtec SaltSmart^{TM} samples (µmol).

	Sample #						
Ion	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**
Na^+	7.35	3.74	2.91	1.38	1.49	1.43	2.10
K^+	0.175	*0.030*	0.613	0.077	0.127	0.079	*0.015*
Ca^{2+}	0.611	0.124	0.656	0.534	0.649	0.570	0.084
Mg^{2+}	0.602	0.238	0.414	0.279	0.360	0.292	0.145
F^-	0.049	0.026	0.057	0.026	0.051	0.019	0.006
Cl^-	6.65	3.73	2.33	1.01	0.999	1.05	2.27
Br^-	0.026	n.d.	n.d.	0.007	0.006	0.019	n.d.
NO_3^-	0.026	0.023	0.025	n.d.	n.d.	0.017	0.015
SO_4^{2-}	0.914	0.243	0.727	0.575	0.780	0.624	0.170
PO_4^{3-}	n.d.	0.021	n.d.	0.019	n.d.	0.017	0.020

Note: Gray, italicized values for K are somewhat higher than the blanks, but are only poorly quantified.

Table 4. Ion Concentrations recovered from the Holtec SaltSmart™ samples (μeq).

	Sample #						
Ion	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**
Na^+	7.35	3.74	2.91	1.38	1.49	1.43	2.10
K^+	0.175	*0.030*	0.613	0.077	0.127	0.079	*0.015*
Ca^{2+}	1.22	0.25	1.31	1.07	1.30	1.14	0.17
Mg^{2+}	1.20	0.476	0.827	0.558	0.720	0.585	0.290
F^-	0.049	0.026	0.057	0.026	0.051	0.019	0.006
Cl^-	6.65	3.73	2.33	1.01	1.00	1.05	2.27
Br^-	0.026	n.d.	n.d.	0.007	0.006	0.019	n.d.
NO_3^-	0.026	0.023	0.025	n.d.	n.d.	0.017	0.015
SO_4^{2-}	1.83	0.485	1.45	1.15	1.56	1.25	0.341
PO_4^{3-}	n.d.	0.060	n.d.	0.056	n.d.	0.052	0.059
Sum cations	9.95	4.49	5.67	3.09	3.64	3.23	2.57
Sum anions	8.58	4.33	3.87	2.25	2.62	2.41	2.69
Chrg bal. % *	7.4	1.8	18.8	15.6	16.3	14.6	-2.3

* Charge balance = (Cations – Anions)/(Cations + Anions) * 100

Note: Gray, italicized values for K are somewhat higher than the blanks, but are only poorly quantified.

2. Additional samples prepared at Sandia

To assess whether the apparent contaminants may have been present in the ampoule fluid, or on components of the SaltSmart™, blank samples were run at Sandia. Also, given the evidence of contamination to the samples, it may be difficult to assess the efficiency of extraction from the samples provided by Holtec. Hence, it was decided to run an independent test, depositing the same salts ($NaCl+Na_2SO_4+MgCl_2$, mixed in a slightly different proportion than they occur in ASTM synthetic seawater) on three polished 316L SS coupons at known concentrations, and measuring the amounts extracted by the SaltSmart™. Prior to salt deposition, the samples were degreased in acetone, then ultrasonically cleaned in a mild alkaline detergent solution and finally rinsed in deionized water. The salts were dissolved in water and deposited by hand using an airbrush. The mass deposited was determined by weighing the coupons before and after salt deposition. The surfaces were analyzed in a horizontal position, with the SaltSmart™ sensor taped to the surface for a given time interval.

The following samples were analyzed:

(1) Three blanks were analyzed, two using a 10 minute contact time, and one using an 8 minute time.

(2) Three different loadings were used, 185 μg/cm², 322 μg/cm², and 615 μg/cm². Two samples were run at 322 μg/cm², with contact times of 6 and 8 minutes, respectively. This was done

because a relatively large amount of water was observed left on the surface at 8 minutes, and the desire was to determine if less water would be left behind at the shorter contact time and if salt extraction would be as efficient.

(3) The unused fluid from the ampoules was analyzed, to verify that it contained no inorganic salts.

(4) To test whether a significant amount of salt remains in the wick after extraction, or whether it is all in the pad, a SaltSmart^{TM} device was attached to a treated surface, and then removed after 8 minutes. The downstream end wick was immediately cut free from the pad using a razor. Upon analysis, the wick was analyzed separately from the pad (an all other internals, which were rinsed with DI water and the rinsate collected). If the wick is effectively rinsed during the sampling, then it might be appropriate to cut the wick off the sample immediately after collecting the sample; this would eliminate contamination that might be deposited on the wick as the sample is being retrieved.

During sampling, it was apparent that using a 10 minute extraction period left significant water on the sample surface (see Figure below). Reducing the sample time to 8 minutes significantly reduced the quantity of water on the surface, but when this procedure was repeated on a salt contaminated surface, significant water remained on the surface. Optical interrogation of the sampling area suggested that the salt was removed, and that the water was likely around the edge of the sampling pad when in contact with the surface. To assess the total quantity of water required by the SaltSmart^{TM}, one sample was weighed prior to and following extraction. The total quantity was approximately 0.75 ml. A blank extraction was attempted by reducing the total volume of water delivered to the SaltSmart^{TM} to 0.8ml, which still resulted in a significant droplet remaining on the surface. Further reducing to 0.6 ml (less than the capacity of the sensor) significantly reduced the quantity of water remaining on the surface. S. Marschman suggested that some residual water may be unavoidable, as it was held in place due to the surface tension between the wick and stainless steel surface. It should be noted that the method used during the Calvert Cliffs inspection followed this approach, where a well defined quantity of water was used (less than the capacity of the sensor) then the sensor was “filled” the rest of the way from a DI water reservoir after being removed from the storage container surface.

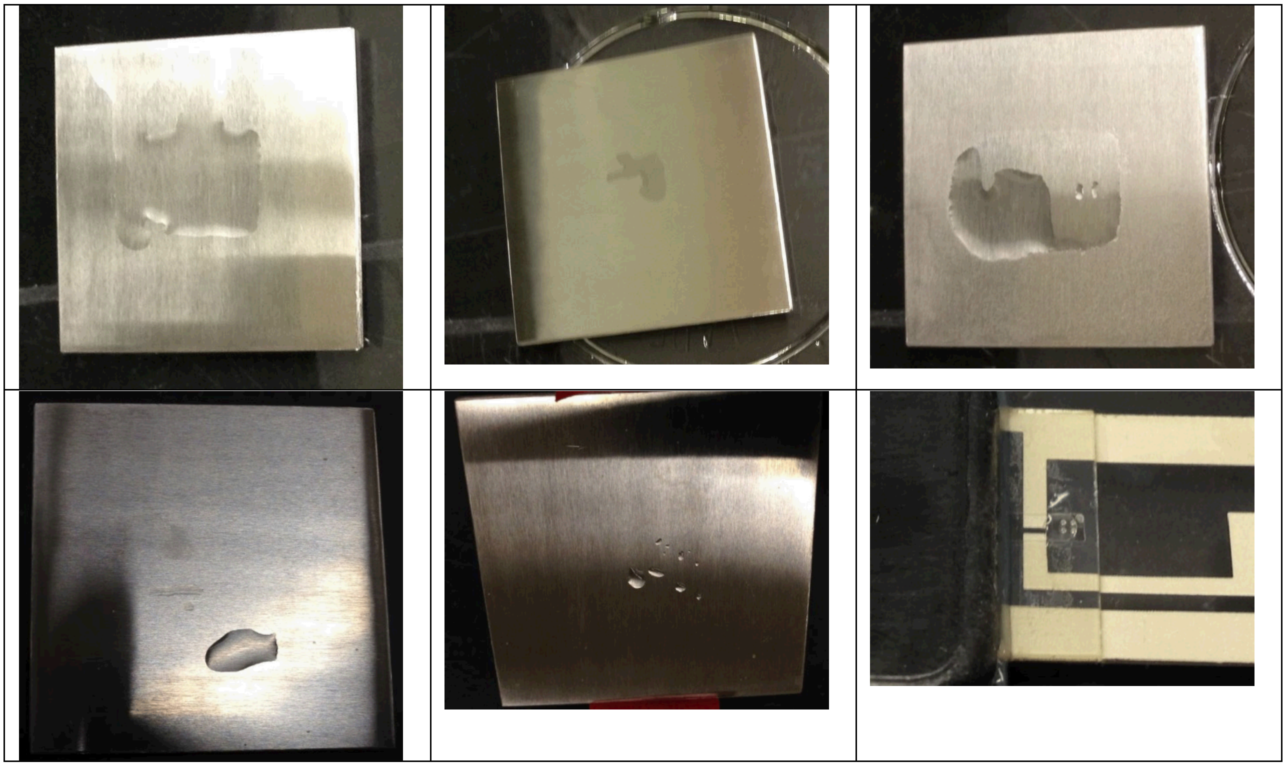


Figure 2. Surfaces after extraction via the SaltSmart^{TM} – top row, 10 minute blank, 8 minute blank, 8 minute salt contaminates surface. Bottom row, 0.8ml total water, 0.6ml total water, and water flowthrough observed on the circuit end of the SaltSmart^{TM} device during sample acquisition.

Analyses of the extracted salts are shown in Table 5 (µg present), Table 6 (µmoles present), and Table 7 (µequivalents present and charge balances).

(1) First, the tree blanks (BL1-10, BL2-10, and Bl3-8) are presented in the order analyzed, and there is progressively less salt in each one. These were analyzed first, after the standards in each case, and it is possible that the surfactant in the ampoule fluid flushed low amounts of adsorbed salts out of the sample lines on the IPC-OES and the IC. In the future, ampoule blanks will be run before collected Saltsmart^{TM} samples, to make sure that this type of carryover does not result in contamination of the actual samples. For all of the blanks, the salt concentrations were very low, barely higher than background, and difficult to quantify accurately (hence, the high charge balance errors).

(2) The total mass of salts recovered, for the four samples which were loaded with a known amount of salts (185-8, 322-8, 322-6, and 615-8), is less than the initial loads. For the lightly-loaded sample, it was only about 53% of the load; for the three more heavily-loaded samples, it was 80-90%. Given that the salts were applied in an aqueous solution, it is likely that some of them dried to form hydrated species such as those that precipitate upon evaporation of sea water. These include Kieserite ($MgSO_4$: H_2O), Pentahydrite ($MgSO_4$:5H_2O), Bloedite ($Na_2Mg(SO_4)_2$:4H_2O), and Bischofite ($MgCl_2$:6H_2O). Hence, the deposited weight probably includes some

crystallographically bound water, and it is reasonable that the recovered salts sum to somewhat less than deposited weight. The recoveries of 80-90% suggest that the Saltsmart^{TM} sensors are very effective in extracting the deposited salts. It is not clear why the sample with the lightest salt load had a lower extraction; however the salt deposition was done by hand using an airbrush, and obtaining an even salt layer for lightly-coated samples is difficult using this technique; it ma be that the sampled area was lightly coated, relative to the rest of the coupon.

The intent was to deposit $NaCl+Na_2SO_4+MgCl_2$ in the same proportion than they occur in ASTM synthetic seawater, but the incorrect amount of $Mg\ Cl_2$ was used in making the solution that was airbrushed onto the samples. Element ratios in the deposited salts vary slightly from seawater values, but can still be used to evaluate whether any preferential removal occurred during extraction. The molar ratios are given in Table 6, and it is clear that the extracted salts match the deposited salts very well. The Salt smarts® were effective in extracting the deposited salts, and no preferential removal of salts was observed.

The charge balance errors for the samples with known coating masses were good (Table 7). The most lightly coated sample had a charge balance error of 4.4%, but the three more heavily coated samples had errors of less than 1%.

The extractions at six and eight (322-6 and 322-8) minutes where very similar, but extraction was about 2% higher in the 8 minute case. I t does not appear that pooling of water on the metal surface, which was more significant for the 8 minute case, negatively impacted extraction. On the other hand, if dripping on a vertical surface is a concern, then doing a 6 minute extraction is nearly as affective as 8 minutes.

(3) The ampoule blank showed only very low salt concentrations, including Ca, F, and Cl. However, the fluid in the ampoule was not diluted at all for IC analysis, and only diluted by a factor of 2 for ICP analysis—hence, the surfactant concentration would have been very high relative to the samples analyzed (for which the salts and remaining surfactant were extracted into 10-15 ml of deionized water). Hence, the surfactant may have flushed small amounts of salts from the instrument tubing. In any case, it is clear that the contribution from the ampoule fluid is negligible.

(4) The wick test was successful in showing that most of the salts are rinsed out of the wick and transported to the pad; only 4.5% of the total salts extracted remained in the wick. Hence, if contamination of the wick is a worry, removing the wick after sample retrieval is probably acceptable. The exact loading on the coupon was not recorded for the wick test.

Table 5. Ion Concentrations Recovered from the Sandia-Prepared SaltSmart™ Samples (µg/sample).

Ion	**Amount, µg**									
	BL1-10	**BL2-10**	**BL3-8**	**185-8 min**	**322-8 min**	**322-6 min**	**615-8 min**	**BL-Amp.**	**Wick-test wick**	**Wick-test pad**
Na^+	nd.	nd.	nd.	93.1	288	283	529	nd.	3.27	142
K^+	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
Ca^{2+}	1.21	0.521	0.445	1.24	1.62	1.69	1.75	0.074	0.246	1.67
Mg^{2+}	nd.	nd.	nd.	7.96	22.8	22.5	39.8	nd.	0.313	13.2
F^-	n.a.	n.a.	n.a.	0.075	n.a.	n.a.	n.a.	0.608	n.a.	n.a.
Cl^-	0.935	0.516	0.349	167	469	459	832	0.571	12.1	196
NO_3^-	2.79	n.a.	n.a.	0.597	0.851	n.a.	0.437	n.a.	0.431	n.a.
SO_4^{2-}	0.607	n.a.	n.a.	24.7	73.2	71.1	127	n.a.	1.84	30.2
Sum, µg	5.54	1.04	0.794	295	855	838	1529	1.253	18.2	383
µg/cm² *	1.85	0.345	0.265	98.3	285	279	510	0.418	6.05	128
Mass/ Dep. mass				53.1%	88.5%	86.7%	82.9%	—	—	—

* Assuming SaltSmart™ sample area of 3 cm²

Table 6. Ion concentrations recovered from the Sandia-prepared Saltsmart® samples (µmol), and molar element ratios, compared to those in the initially –deposited salts.

	Amount, µmol									
Ion	**BL1-10**	**BL2-10**	**BL3-8**	**185-8 min**	**322-8 min**	**322-6 min**	**615-8 min**	**BL-Amp.**	**Wick-wick**	**Wick-pad**
Na$^+$	nd.	nd.	nd.	4.0	12.5	12.3	23.0	nd.	0.142	6.17
K$^+$	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
Ca^{2+}	0.030	0.013	0.011	0.031	0.040	0.042	0.044	0.002	0.006	0.042
Mg^{2+}	nd.	nd.	nd.	0.328	0.937	0.924	1.64	nd.	0.013	0.542
F$^-$	n.d.	n.d.	n.d.	0.004	n.d.	n.d.	n.d.	0.032	n.d.	n.d.
Cl$^-$	0.026	0.015	0.010	4.7	13.2	13.0	23.5	0.016	0.340	5.52
NO$_3^-$	0.045	n.d.	n.d.	0.010	0.014	n.d.	0.007	n.d.	0.007	n.d.
SO$_4^{2-}$	0.006	n.d.	n.d.	0.257	0.762	0.740	1.32	n.d.	0.019	0.315
Element ratios			**Dep salts**							
		SO$_4$/Cl	0.058	0.054	0.058	0.057	0.056	—	0.056	0.057
		Na/Cl	0.97	0.859	0.946	0.951	0.980	—	0.418	1.12
		Na/Mg	13.15	12.4	13.4	13.3	14.0	—	11.04	11.4
		Mg/Cl	0.074	0.069	0.071	0.071	0.070	—	0.038	0.098
		Mg/SO$_4$	1.26	1.28	1.23	1.25	1.24	—	0.672	1.72

Table 7. Ion concentrations recovered from the Sandia-prepared Saltsmart® samples (µeq/sample).

	Amount, µeq/sample									
Ion	**BL1-10**	**BL2-10**	**BL3-8**	**185-8 min**	**322-8 min**	**322-6 min**	**615-8 min**	**BL-Amp.**	**Wick-wick**	**Wick-pad**
Na$^+$	nd.	nd.	nd.	4.05	12.5	12.3	23.0	nd.	0.14	6.17
K$^+$	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
Ca^{2+}	0.060	0.026	0.022	0.062	0.081	0.085	0.087	0.004	0.012	0.083
Mg^{2+}	nd.	nd.	nd.	0.655	1.87	1.85	3.28	nd.	0.026	1.08
F$^-$	n.d.	n.d.	n.d.	0.004	n.d.	n.d.	n.d.	0.032	n.d.	n.d.
Cl$^-$	0.026	0.015	0.010	4.72	13.2	13.0	23.5	0.016	0.340	5.52
NO$_3^-$	0.045	n.d.	n.d.	0.010	0.014	n.d.	0.007	n.d.	0.007	n.d.
SO$_4^{2-}$	0.013	n.d.	n.d.	0.513	1.52	1.48	2.65	n.d.	0.038	0.629
Sum, cat.	0.060	0.026	0.022	4.766	14.5	14.3	26.4	0.004	0.180	7.34
Sum, an.	0.084	0.015	0.010	5.242	14.8	14.4	26.1	0.048	0.386	6.15
Chrg Bal	—	—	—	-4.8	-1.0	-0.6	0.5	—	-36	8.8

3. Further interpretation of samples from Holtec

As shown in the last section, salts are effectively extracted by the Saltsmart™. Therefore, it can be assumed that the measured salt compositions for the Holtec samples are representative of what as on the samples, and must be a mixture of the deposited salts (of known composition) and contaminant salts. If the contaminant salts are assumed to be of constant composition, albeit present in differing amounts and representing different fractions of the total, then the measured values can be assumed to be a binary mixture of the two end-members, the deposited fraction and the contaminant fraction. Knowing the composition of the deposited fraction, it is possible to solve for the composition of the contaminant fraction and for the amount present. For any given sample, a unique solution cannot be derived, but by solving for all of the samples simultaneously, a single, best-fit composition for the contaminant fraction can be derived, and the amount present in each sample estimated. This was done using the Microsoft Excel Solver routine. The calculated composition of the contaminant fraction is given in Table 8, and the amounts of the two end-member salt assemblages present in each sample are given in Table 9. Using these values, the calculated salt compositions for each sample matched the measured values relatively well, suggesting that the contaminant salt fraction is indeed approximately constant in composition. Graphical representations of the measured salt compositions; and those calculated using the best-fit composition of the contaminant fraction and the known composition of the deposited fraction (mixed in the proportions shown in Table 9), are shown in Figure 3.

If this approach is valid, then the deposited salt loadings listed in Table 9 can be compared to the amounts of salt deposited by INL, to assess salt extraction efficiency under the actual Holtec test conditions with the mockup (e.g. vertical panel, remote sampling, etc.)

Table 8. Calculated composition of contaminant fraction in the Holtec samples, normalized to a sodium ion concentration of 1.0 µmole.

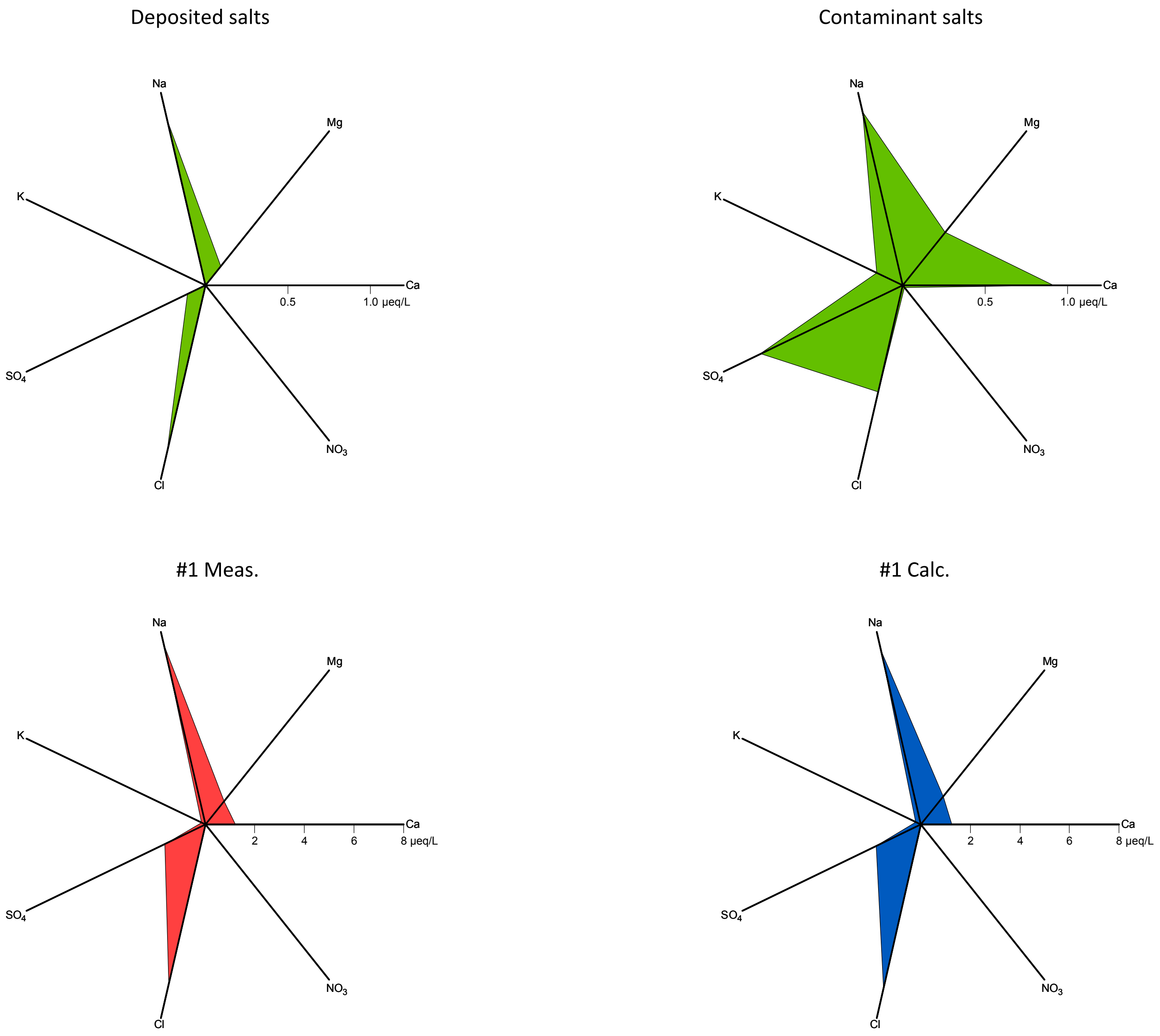
Ion	Contaminant salt, µmol
Na^+	1.0
K^+	0.162
Ca^{2+}	0.422
Mg^{2+}	0.191
F^-	0.029
Cl^-	0.611
Br^-	0.008
NO_3^-	0.011
SO_4^{2-}	0.441
PO_4^{3-}	0.005

Table 9. Amounts of the two end-member salt assemblages present in each sample (µg/sample).

Salts present, µg	**Sample #**						
	#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**
Total salts, µg	543	257	283	157	186	168	155
Deposited fraction, µg	384	237	85	16	0	15	141
Contam. Fraction, µg	159	21	197	141	186	152	14
Deposited fraction, µg/cm^2	128	79	28	5	0	5	47
Contaminant fraction, µg/cm^2	53.1	6.9	65.8	47.0	62.0	50.8	4.8

Note: Surface loadings calculated assuming a contact area of 3 cm^2.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. This document is available as SAND2014P-XXXX.



Deposited salts

Contaminant salts

#1 Meas.

#1 Calc.

Figure 3. Graphical representations of the measured sand calculated salt compositions for the Holtec samples. Top row. Deposited salt composition (L) and estimated contaminant salt composition (R). Second row. Measured (L) and calculated (R) compositions for Sample #1.

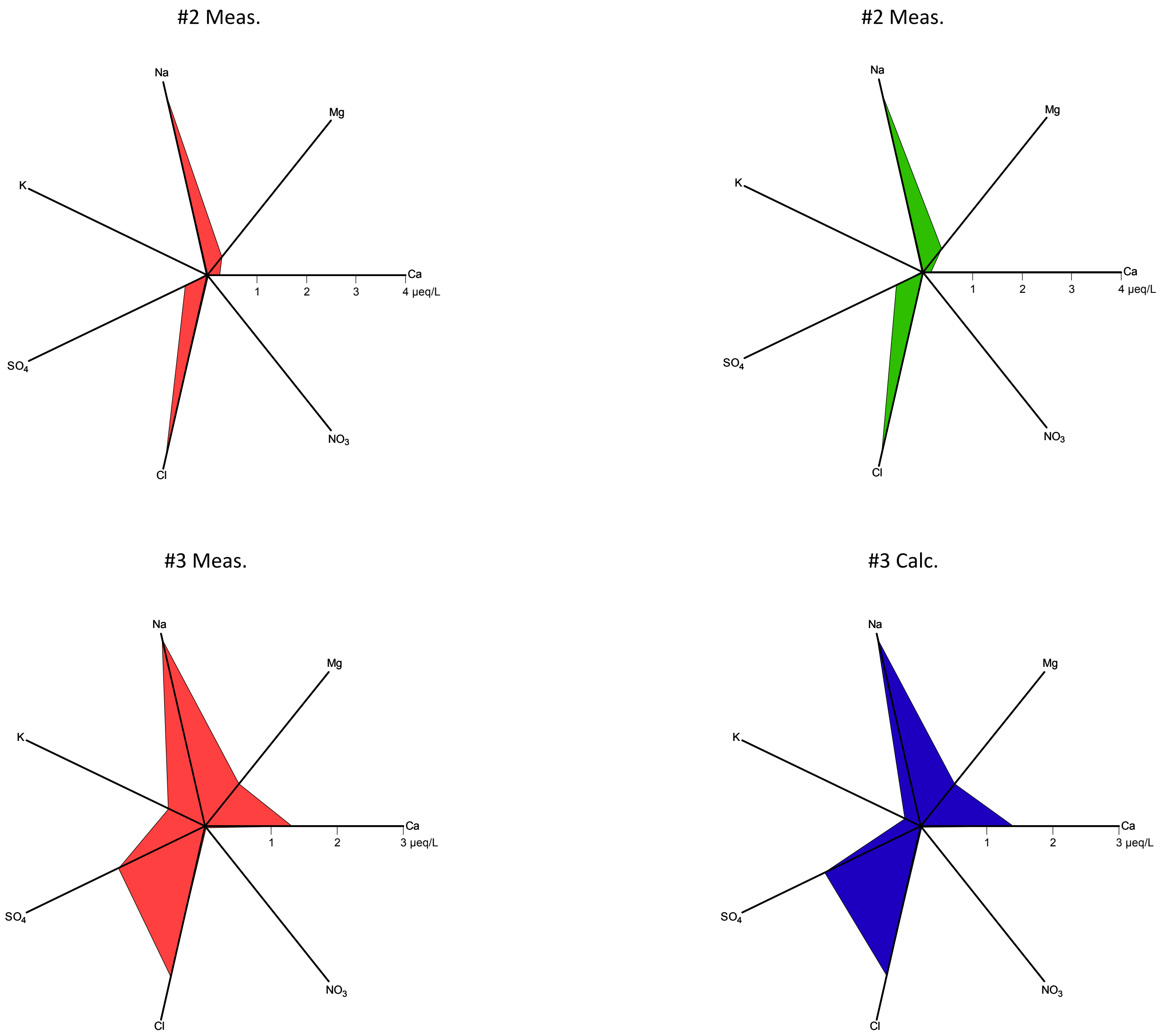


Figure 3, cont. Graphical representations of the measured sand calculated salt compositions for the Holtec samples. Top row. Measured (L) and calculated (R) compositions for Sample #2. Second row. Measured (L) and calculated (R) compositions for Sample #3.

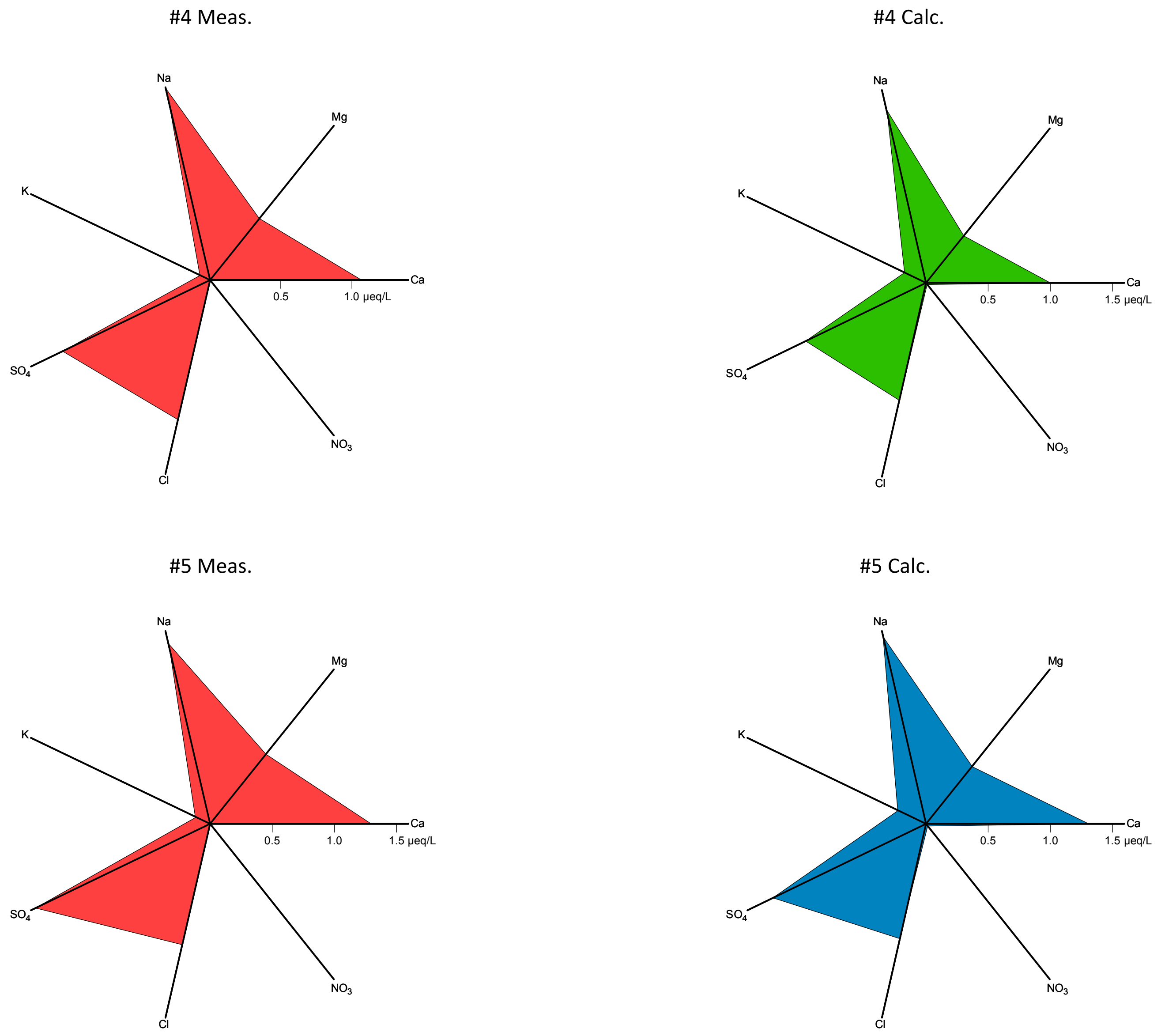


Figure 3, cont. Graphical representations of the measured sand calculated salt compositions for the Holtec samples. Top row. Measured (L) and calculated (R) compositions for Sample #4. Second row. Measured (L) and calculated (R) compositions for Sample #5.

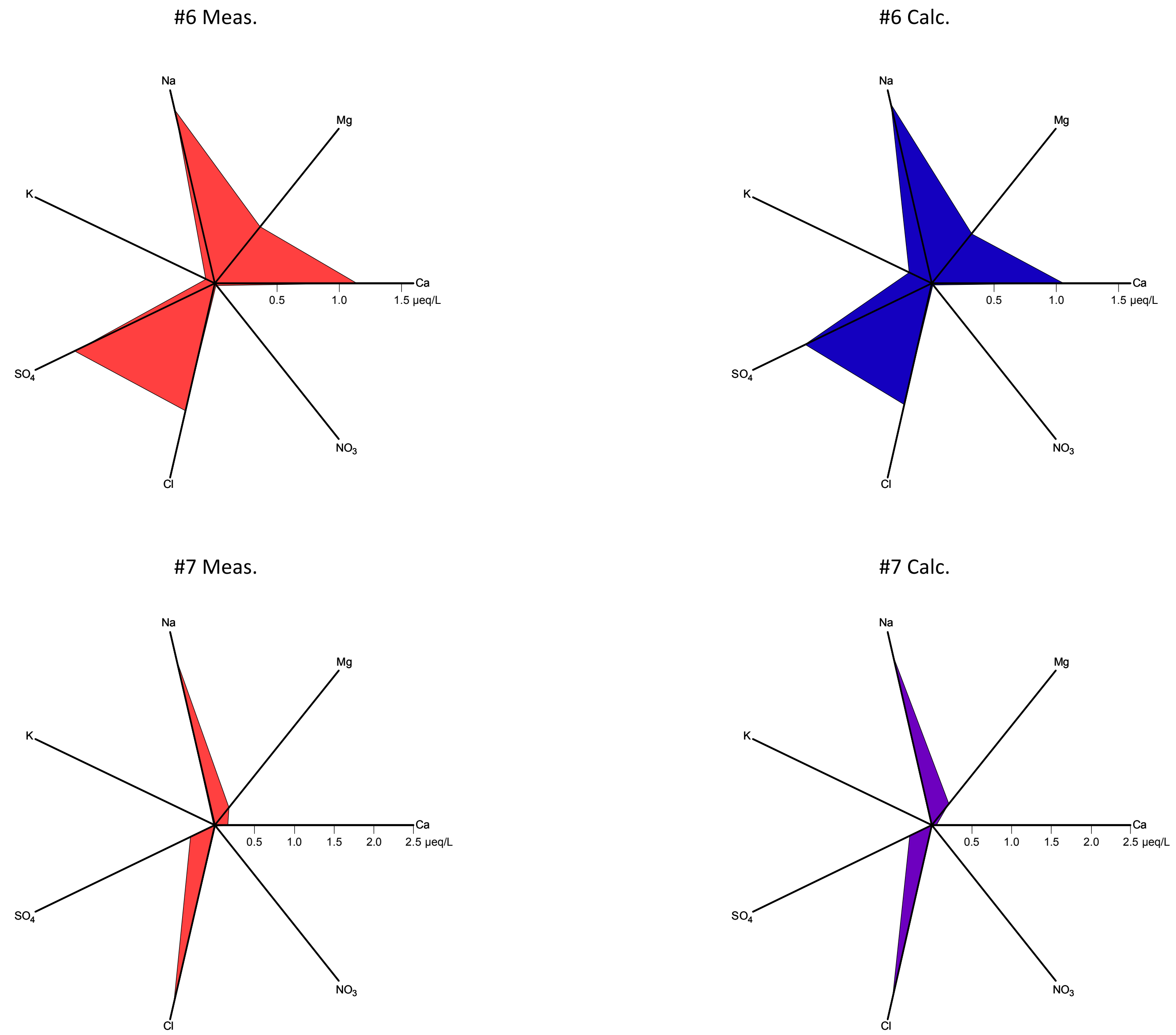


Figure 3, cont. Graphical representations of the measured sand calculated salt compositions for the Holtec samples. Top row. Measured (L) and calculated (R) compositions for Sample #6. Second row. Measured (L) and calculated (R) compositions for Sample #7.