Instrument Qualification of Custom Fabricated Water Activity Meter for Hot Cell Use

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Acronyms and Abbreviations

ATL	Advanced Technologies and Laboratories International, Inc.
a_w	Water Activity
a_w	Water Activity
NaOH	Sodium Hydroxide
PMP	Polymethylpentene
R^2	Coefficient of Determination
RH	Relative Humidity
RPD	Reported Percent Difference

Units

σ	1 standard deviation
%	percent
bar	unit of pressure
°C	degrees Celsius
g	gram
kg	kilogram
mL	milliliter
Mohm	10^6 Ohms
molal	moles/kg H_2O
mole	6.02×10^{23} objects

1. INTRODUCTION

A custom fabricated water activity meter was developed to determine the water activity of electrolyte solutions. More importantly, the meter was developed for use in a hot cell to determine the water activity of supernatant liquids. Water activity is a measure of the intensity with which water associates with non-aqueous molecules in the system. For this reason, the water activity is an important variable in predicting the partitioning of hydrated solid phases during normal Hanford processes such as mixing tank waste types, caustic additions, evaporator campaigns, tank transfers and retrievals, and staging of waste for transfer to the Waste Treatment and Immobilization Plant.

This report describes a custom fabricated water activity meter and the results of the qualification of this meter as described in the laboratory test plan LAB-PLN-11-00012, *Testing and Validation of an Enhanced Acquisition and Control System*. It was calibrated against several NaOH solutions of varying concentrations to quantify the accuracy and precision of the instrument at 20 °C and 60 °C. Also, a schematic and parts list of the equipment used to make the water activity meter will be presented in this report.

2. METHOD

2.1 THEORY OF MEASUREMENT

Water activity can be derived from basic thermodynamic and physical principles. The chemical potential of a substance can be described by Equation 1. Some requirements must be met for this thermodynamic principle. First, pure water is the standard state where the water activity (a_w) is equal to 1 ($a_w = 1$). Second, the system must be at equilibrium at a defined temperature.

Equation 1. Chemical Potential as a Function of Fugacity.

$$\boldsymbol{\mu = \mu_o + RTln(f/f_0)}$$

Where:

μ = chemical potential of substance (water)
μ_o= chemical potential of substance at standard state
R = gas constant
T = temperature of the system at equilibrium
f = fugacity of substance
f_o= fugacity of substance at standard state.

The activity of a substance is defined as $a = f/f_o$. In the case of water, the water activity will be denoted as shown in Equation 2, where *w* is the notation for water.

Equation 2. Water Activity as a Function of Fugacity.

$$a_w = \frac{f}{f_o}$$

Where:

a_w= activity of water.

Fugacity is a metric of the non-ideal deviation of the chemical potential for a real gas from that of an ideal gas. For condensed phases of liquid at near standard pressures (1 bar), the real vapor pressure has nearly the same chemical potential as the vapor pressure of an ideal liquid. Therefore, the fugacity terms in Equation 2 can be estimated and replaced by partial pressure term, as seen in Equation 3.

Equation 3. Estimated Water Activity as a Function of Pressure.

$$a_\mathrm{w} = \frac{P_{H_2O}}{P^*_{H_2O}}$$

Where:

P_{H_2O} = Water Vapor Partial Pressure
$P^*_{H_2O}$ = Water Vapor Saturated Partial Pressure.

The water activity can also be described in terms of equilibrium relative humidity as displayed in Equation 4. The equilibrium relative humidity can be described as the relative humidity of the head space when the solution and head space gasses are in thermodynamic equilibrium.

Equation 4. Equilibrium Relative Humidity.

$$ERH = 100\%\left(\frac{P_{H_2O}}{P^*_{H_2O}}\right) = 100\%(a_w)$$

Where:

ERH = Equilibrium Relative Humidity.

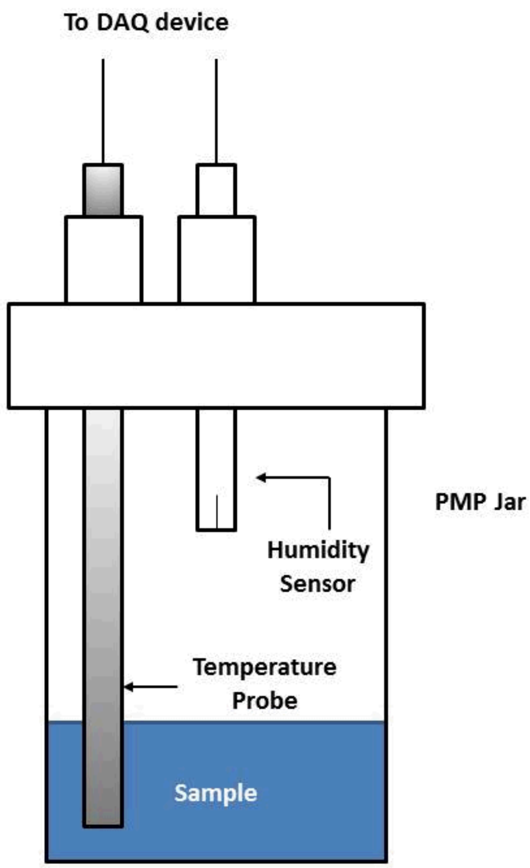
2.2 INSTRUMENTATION

The humidity meter is a 125 mL polymethylpentene (PMP) jar (Nalgene, 2117-0125) with a humidity sensor and temperature probe mounted to the lid of the jar by airtight fittings. Figure 1 is a simple diagram of the water activity meter. During operation, the humidity sensor was in contact with the vapors and gasses in the head space and was used to measure the water concentration and temperature of the head space contents. The temperature probe was in contact with the solution in the jar and was used to measure the temperature of the solution in the vessel. The contents in the jar are sealed from the ambient atmosphere, and because the system is sealed, the water vapor in the head space was in equilibrium with the solution in the vessel at a temperature.

The water activity sensors included a Vaisala humidity sensor (Vaisala, HMP110) and a temperature probe (LabJack, EI1034 Temperature Probe). The humidity sensor is a capacitance-style sensor with a stated accuracy of ±1.7% from 0-90% relative humidity (RH) and ±2.5% from 90-100% RH. The humidity sensor was equipped with a temperature sensor with a stated accuracy of ±0.2 °C from 0 to +40 °C and ±0.4 °C from -40 to 0 °C and +40 to 80 °C. The LabJack temperature probe incorporates a LM34CAZ silicon-type sensor from National Semiconductor mounted inside a stainless steel tube. The stated accuracy of the temperature probe is ±1.1 °C from 0 to 110 °C and ±1.7 °C from -40 to 0 °C. Both the humidity sensor and temperature probe were inserted through the lid of the PMP jar. The humidity sensor was sealed from the outside atmosphere using the supplied mounting flange from Vaisala. The temperature probe was sealed from the outside environment using a ¼-inch panel mount, bore through, compression fitting manufactured by Cole Parmer (Part # EW-06390-10).

The humidity probe and temperature probe were connected to a LabJack U3-HV data acquisition device, which was operated through DAQFactory process control software made by Azeotech. The data acquisition device provided operating voltages to the measurement probes and also provided voltage detection of the probes. The software was used to provide a user interface and convert the output voltages from the measurement probes to usable data.

Figure 1. Simple Diagram of Water Activity Meter.



The water activity of the solution can be determined either directly from the humidity sensor alone or from both the humidity sensor and the temperature probe. Both applications will be explained in the following section along with the advantages and disadvantages of each measurement technique.

2.3 WATER ACTIVITY MEASUREMENT USING HUMIDITY SENSOR ONLY (METHOD 1)

The water activity can be determined with knowledge of the water vapor content and temperature of the headspace, assuming the gases and vapors in the head space are in thermodynamic equilibrium with the electrolyte solution. These two variables can be determined using the humidity probe only. This method has several advantages. These include the use of a single sensor that does not come into contact with the sample, and that no error is introduced during the conversion of the sensor output data to water activity data. Equation 5 is the only required conversion.

Equation 5. Water Activity as a Function of Equilibrium Relative Humidity.

$$a_w = \frac{ERH}{100\%}$$

Where:

a_w = water activity
ERH = Equilibrium Relative Humidity.

2.4 WATER ACTIVITY MEASUREMENT USING HUMIDITY SENSOR AND TEMPERATURE SENSOR (METHOD 2)

The water activity can also be determined using the measured humidity and temperature of the vapor and gases in the head space and the measured temperature of the solution. The humidity and temperature of the head space are determined using the humidity probe; applying these data to Equation 6, the partial pressure of water in the head space can then be determined. The saturated water vapor pressure ($P^*_{H_2O}$) is estimated from the measured solution temperature as determined from the humidity probe using Antoine's Equation (Equation 7). Knowing the value of these variables, the water activity can be determined though Equation 8.

Equation 6. Water Vapor of Head Space as a Function of Relative Humidity.

$$P_{H_2O}(Vapor) = P^*_{H_2O}(Vapor)\left(\frac{RH}{100\%}\right)$$

Where:

RH = Relative Humidity
$P^*_{H_2O}(Vapor)$ = Saturated Water Vapor in the Head Space.

Equation 7. Antoine's Equation.

$$Log_{10}P^*_{H_2O} = A - \frac{B}{T + C}$$

Where:

T = Vapor Space or Solution Temperature as Appropriate in Kelvin
A = 8.10765 (For Water from 0 – 60 °C)
B = 1750.286 (For Water from 0 – 60 °C)
C = 235.000 (For Water from 0 – 60 °C).

Equation 8. Estimated Water Activity as a Function of Vapor Pressure.

$$a_w = \frac{P_{H_2O}\ (Vapor)}{P^*_{H_2O}\ (Solution)}$$

Where:

$P^*_{H_2O}\ (Solution)$ = Saturated Vapor Pressure as determined through Antoine's Equation.

The just-described method is much more robust than determining the water activity using the humidity probe only. For measurements made with the humidity probe alone, only the water vapor in the head space is measured, and care must be taken to ensure the solution is at the same temperature as the head space for an accurate measurement. This was not always the case in these experiments due to environmental and equipment factors. With the system that incorporates the solution temperature, the solution and head space do not have to be at the same temperature, and the saturated vapor pressure of the solution can be instantaneously determined along with the partial pressure of the water vapor in the head space.

2.5 TEMPERATURE CONTROL AT 20 °C

For the experiments conducted at 20 °C , the solutions were cooled using a Peltier cooled dry bath (Torrey Pines Scientific, EchoTherm™[1] IC35) in conjunction with a custom-manufactured aluminum block surrounded with a greenhouse. The aluminum block was milled to fit the water activity meter pictured above in Figure 1, and all but the lid and top sides of the sensors rested inside the aluminum block. The greenhouse surrounded the water activity meter components not directly inside the aluminum block. The greenhouse was constructed of ½-inch thick polyamide insulation walls to thermally isolate the water activity meter and aluminum block from the ambient atmosphere. The dry bath was in contact with the bottom of the aluminum block. To cool the solution in the water activity meter, the dry bath was set to 19 °C (1 °C Resolution), and the resulting solution temperature stabilized to around 19.6 °C. Table 1 shows the average solution temperature and vapor space temperature of the experiments conducted using this system.

Table 1. Average Temperature and 3σ Standard Deviation for 20 °C Experiments. (2 sheets)

Experiment	Average Head Space Temperature (°C)	Head Space Temperature Standard Deviation (3σ)	Average Solution Temperature (°C)	Solution Temperature Standard Deviation (3σ)
2.5 Molal	21.1	0.182	20.0	0.042
5.0 Molal	19.5	0.130	19.4	0.040
5 Molal Duplicate	20.3	0.142	19.8	0.045

[1] EchoTherm is a trademark of Torrey Pines Scientific, Inc., Carlsbad, California.

Table 1. Average Temperature and 3σ Standard Deviation for 20 °C Experiments. (2 sheets)

Experiment	Average Head Space Temperature (°C)	Head Space Temperature Standard Deviation (3σ)	Average Solution Temperature (°C)	Solution Temperature Standard Deviation (3σ)
7.5 Molal	20.0	0.139	19.6	0.042
10 Molal	19.9	0.140	19.6	0.050
12.5 Molal	20.2	0.138	19.8	0.051
15 Molal	20.0	0.140	19.6	0.048
15 Molal Duplicate	20.2	0.144	19.7	0.047
17.5 Molal	20.0	0.150	19.7	0.057
20 Molal	20.5	0.128	19.9	0.037
22.5 Molal	19.5	0.142	19.5	0.052
25 Molal	20.1	0.139	19.8	0.050
25 Molal Duplicate	19.8	0.123	19.6	0.045

2.6 TEMPERATURE CONTROL AT 60 °C

For experiments conducted at 60 °C, the water activity meter was heated using an analog laboratory oven (Quincy Labs, Inc., Model 10-180) manually set to 60 °C. The oven contained two shelves, and the top shelf was lowered to a position that put the water activity meter in the center of the oven. The oven was not temperature controlled and drifted throughout the set of experiments due to varying laboratory temperatures. For this reason, slight adjustments were made to the oven set point when it was observed that the average oven temperature drifted away from a desired temperature of 60 °C. However, the oven temperature did not typically vary more than 1 °C while collecting a data set for an individual experiment. . tabulates the average temperature for each individual experiment.

Table 2. Average Temperature and 3σ Standard Deviation for 60 °C Experiments. (2 sheets)

Experiment	Average Head Space Temperature (°C)	Head Space Temperature Standard Deviation (3σ)	Average Solution Temperature (°C)	Solution Temperature Standard Deviation (3σ)
2.5 Molal	58.2	0.149	58.8	0.068
5.0 Molal	59.8	0.169	60.6	0.059
5 Molal Duplicate	58.7	0.220	60.4	0.093
7.5 Molal	59.5	0.212	60.2	0.071
10 Molal	60.7	0.129	62.0	0.060
12.5 Molal	-	-	-	-
15 Molal	60.5	0.135	61.7	0.063

Table 2. Average Temperature and 3σ Standard Deviation for 60 °C Experiments. (2 sheets)

Experiment	Average Head Space Temperature (°C)	Head Space Temperature Standard Deviation (3σ)	Average Solution Temperature (°C)	Solution Temperature Standard Deviation (3σ)
15 Molal Duplicate	60.9	0.177	63.0	0.062
17.5 Molal	60.7	0.167	62.6	0.079
20 Molal	59.9	0.151	61.3	0.064
22.5 Molal	60.7	0.549	61.2	0.046
25 Molal	60.8	0.490	62.6	0.282
25 Molal Duplicate	59.7	0.157	61.2	0.062

2.7 CALIBRATION SOURCE-NAOH SOLUTIONS

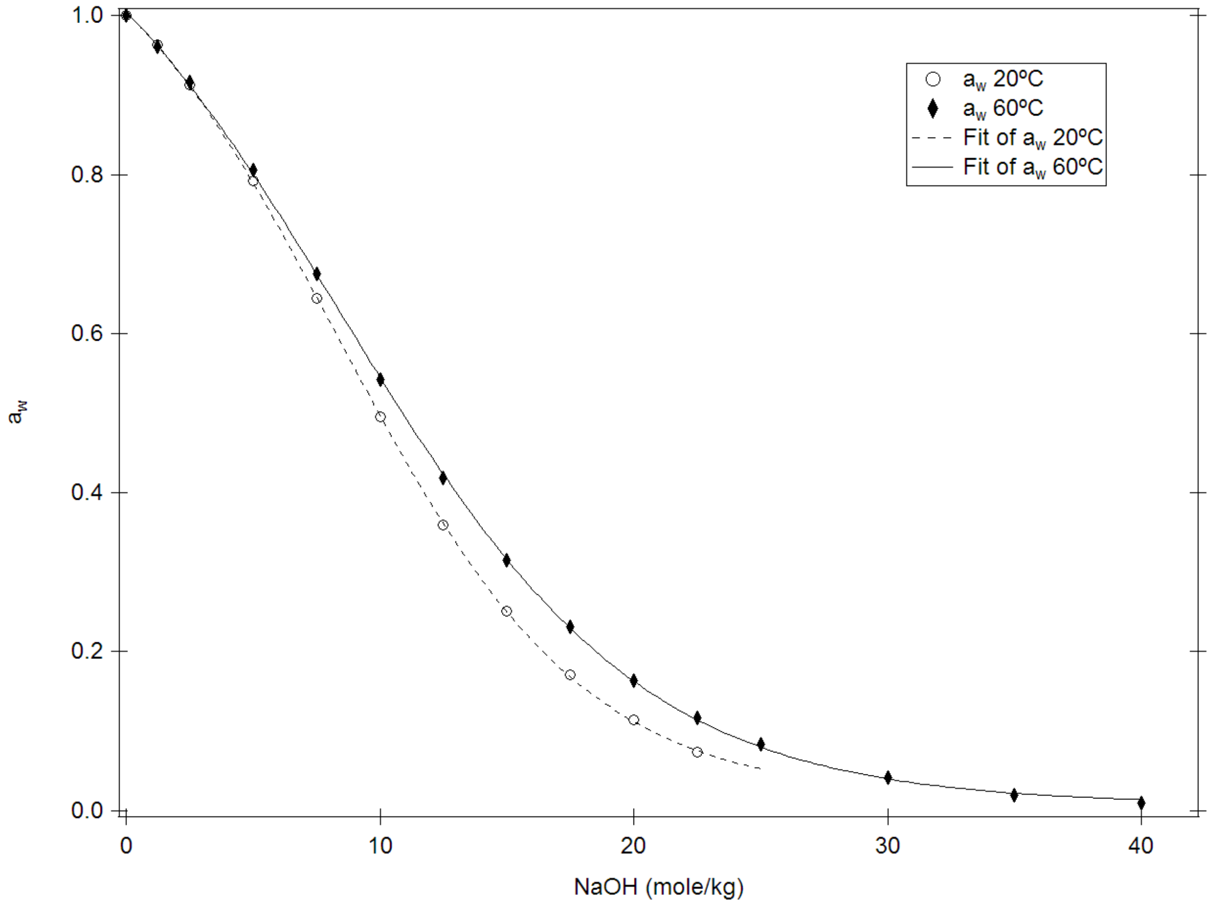
NaOH solutions at various concentrations were used to test the accuracy and precision of the water activity meter. The water activity is strongly affected by the presence of sodium hydroxide ions with nearly the entire range of water activity (0.05-0.80) measurable with NaOH concentrations ranging from 25-5 molal, respectively. Table 3 is a tabulation of water activity of NaOH solutions at the temperatures of 20 °C and 60 °C.

Table 3. NaOH Solution Concentrations and Estimated Water Activity.

NaOH (mole/kg)	a_w at 20 °C	a_w at 60 °C
0.00	1.00	1.00
5.00	0.79	0.80
10.00	0.50	0.55
15.00	0.25	0.32
20.00	0.11	0.16
25.00	0.05	0.08

The water activity for the NaOH solutions in Table 3 were determined from a correlation fit to both 20 °C and 60 °C data originating from RPP-RPT-47795, *Water Activity Data Assessment to be used in Hanford Waste Solubility Calculations,* and "Water vapor partial pressures and water activities in potassium and sodium hydroxide solutions over wide concentration and temperature ranges," (Balej 1985), respectively. Both data sets at 20 °C and 60 °C were fit with a Sigmoid function. The data and the fitted equations are plotted on Figure 2. The equation and fitted parameters are displayed in Equation 9 and Table 4, respectively.

Figure 2. Water Activity Data for Aqueous NaOH Solutions.



Equation 9. Sigmoid Regression Equation.

$$a_w = base + \left[\frac{max}{1 + exp\left(\frac{xhalf - NaOH}{rate}\right)} \right]$$

Where:

a_w = Water Activity

$NaOH$ = NaOH Concentration (mole/kg H_2O).

Table 4. Water Activity Constants for Sigmoid Regression Equation.

Constant	Value at 20 °C	Value at 60 °C
base	1.1825 ± 0.00886	1.2472 ± 0.014
max	-1.1656 ± 0.0114	-1.2391 ± 0.0156
xhalf	8.281 ± 0.0771	8.4124 ± 0.153
rate	4.8474 ± 0.0711	5.9522 ± 0.0962
Quality of Fit		
Chi Squared	5.51378×10^{-5}	1.61845×10^{-4}

Table 5 lists the concentrations of NaOH solutions used in each experiment. The whole number NaOH solutions originated from the Advanced Technologies and Laboratories International, Inc. (ATL) standards laboratory and are noted in Table 5 by ATL book number. These solutions were titrated to determine the standard concentration to one thousandths of a molal in concentration. The other solutions listed in Table 5 were made by mixing two similar masses of a higher concentration solution and a lower concentration solution. For example, the 7.5 molal NaOH solution was made by mixing 29.11 g of 5.097 molal solution with 29.37 g of 9.918 solution for a final NaOH concentration of 7.518 molal. The 2.5 molal solution was made by mixing 34.36 g of 18.2 Mohm water with 45.13 g of 5.097 molal solution for a resulting concentration of 2.203 molal. A National Institute of Standards and Technology traceable balance was used to determine the masses of NaOH solutions used to make the resulting solution.

Table 5. NaOH Solutions Used for Each Experiment.

NaOH Solution	Titrated Concentration (mole/kg H_2O)	ATL Book Number	Mass of Lower NaOH/H_2O Solution (g)	Mass of Upper NaOH Solution (g)	NaOH Concentration (mole/kg H_2O)
2.5			34.36[a]	45.13	2.203
5	5.097	141N22A	-	-	5.097
7.5			29.11	29.37	7.518
10	9.918	143N22A	-	-	9.918
12.5			33.83	39.63	12.57
15	14.837	144N22A	-	-	14.84
17.5			28.92	30.21	16.57
20	18.223	145N22A	-	-	18.22
22.5			34.24	43.75	20.85
25	22.913	146N22A	-	-	22.91

[a]A mass of 18.2 Mohm distilled water containing no NaOH was added.

3. RESULTS

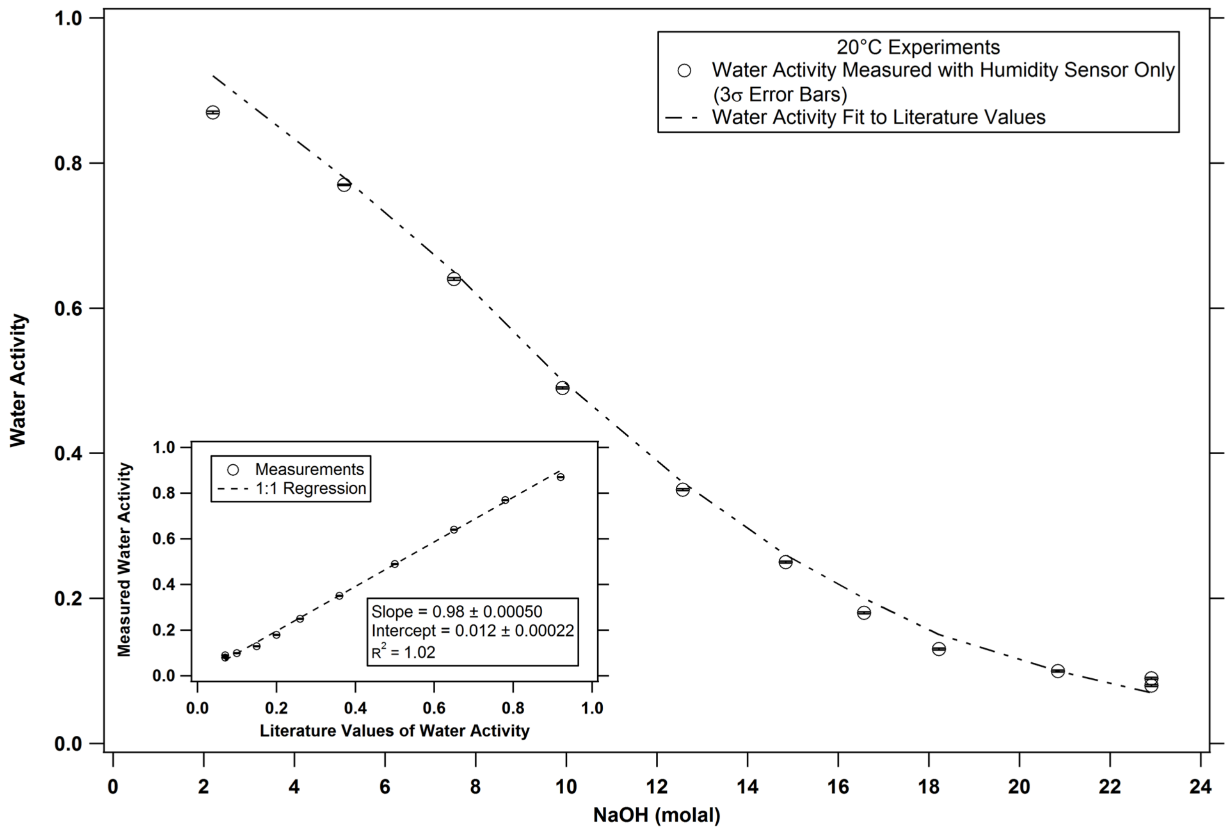
3.1 20 °C RESULTS USING HUMIDITY SENSOR ONLY

The water activity of several NaOH solutions at various concentrations as determined using only the humidity probe at 20 °C is tabulated in Table 6 and displayed in Figure 3. For all NaOH concentrations below 22.5 molal, the system showed a slight negative bias with percent recovery ranging from a low of 89.1% to a high of 99.1%. A positive bias existed for NaOH concentrations of 22.5 and 25 molal. The largest bias was at a NaOH concentration of 25 molal with a percent recovery of 118 to 122%. In general, the accuracy of the water activity measurement was good for NaOH solution concentrations ranging from 2.5-22.5 molal. The regressed 1:1 line showed near perfect agreement with a slope and intercept of 0.98 ± 0.00050 and 0.0012 ± 0.00022 (Inset of Figure 3). The fit was nearly perfect with a coefficient of determination (R^2) value of 1.02. However, an inspection of individual points demonstrated that some deviation from the fit was present with the agreement of water activity data below 0.2. The results of the duplicates also demonstrated that this instrument arrangement at 20 °C showed good precision. Duplicate tests were conducted at NaOH solution concentrations of 5, 15, and 25 molal. The greatest reported percent difference (RPD) of the three duplicates was 3.41% at a NaOH solution concentration of 25 molal, which is within an acceptable limit of ±5%. Generally, this method is both accurate and precise in determining the water activity of electrolyte solutions with a water activity between 0.20 and less than 1.00.

Table 6. Tabulated Water Activity of NaOH Solutions Using Only a Humidity Probe at a Temperature of 20 °C.

Experiment	NaOH (mole/kg)	Mean a_w (3σ)	% Recovery	RPD of Duplicates
2.5	2.20	0.87 ± 0	94.4	-
5	5.10	0.77 ± 0.0011	98.1	0.578
5_Dup	5.10	0.77 ± 0.0014	97.5	-
7.5	7.52	0.64 ± 0.0019	99.1	-
10	9.92	0.49 ± 0.0134	97.4	-
12.5	12.57	0.35 ± 0.0014	96.6	-
15	14.84	0.25 ± 0.0013	95.8	1.23
15_Dup	14.84	0.25 ± 0.0012	97.0	-
17.5	16.57	0.18 ± 0	90.4	-
20	18.22	0.13 ± 0.0013	89.1	-
22.5	20.85	0.1 ± 0.0091	102	-
25	22.91	0.08 ± 0.0012	118	3.41
25_Dup	22.91	0.09 ± 0.0012	122	-

Figure 3. Measured and Literature Values of Water Activity of 20 °C NaOH Solutions at Varying Concentrations Using a Humidity Probe Only.



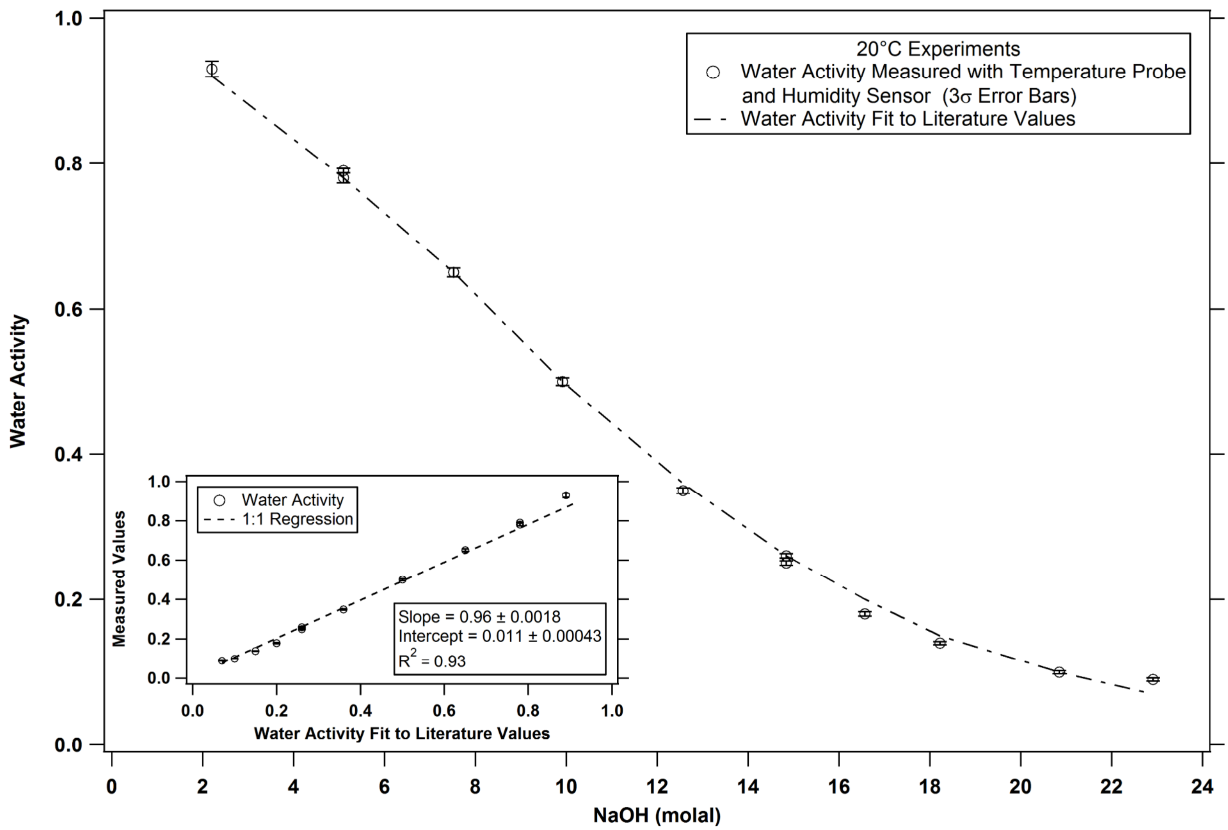
3.2 20 °C RESULTS USING HUMIDITY SENSOR AND TEMPERATURE SENSOR

The water activity was also determined using both a humidity probe and temperature probe. The humidity probe was used to determine the vapor pressure in the head space, and the temperature probe was used to determine the temperature of the NaOH solution, ultimately calculating the saturated water vapor of pure water. The measured water activity of the varying concentrations of NaOH solution demonstrated good agreement with literature values as shown in Figure 4. An inspection of the figure shows little evidence of bias present in the measurement as the data fall in no regular pattern around the literature values (dashed line). This was also confirmed by the 1:1 regression of the measured data plotted against literature values (Inset of Figure 4). It demonstrates good agreement over the range with linear regression having a slope and intercept of 0.96 ± 0.0018 and 0.011 ± 0.00043, respectively. The fit of the regression had an R^2 value of 0.93 showing good fit. The system accurately predicted the water activity of the NaOH solutions varying in concentration from 2.89 to 20.85 molal with the percent recovery not exceeding 100 ± 4 % as tabulated in Table 7. The measured water activity of the NaOH solution at a concentration of 22.91 showed poor results with the percent recovery ranging between 120 and 123%. The RPD determinations of water activity in the duplicate NaOH samples demonstrated good agreement with the RPD never exceeding 3%. These results demonstrate the precision of the instrument is consistent throughout the range of water activity measured. In general, the results suggest that this configuration is accurate and precise when measuring the water activity of electrolyte solutions with a water activity ranging from 0.20 to less than 1.00.

Table 7. Tabulated Water Activity of NaOH Solutions Using Humidity Probe in Conjunction with a Temperature Probe at a Temperature of 20 °C.

Experiment	NaOH (mole/kg)	Mean a_w (3σ)	% Recovery	RPD of Duplicates
2.5	2.20	0.93 ± 0.0112	101	-
5	5.10	0.78 ± 0.0072	99	1.90
5_Dup	5.10	0.79 ± 0.0078	101	-
7.5	7.52	0.65 ± 0.0065	101	-
10	9.92	0.5 ± 0.0097	99	-
12.5	12.57	0.35 ± 0.0097	99	-
15	14.84	0.25 ± 0.003	98	1.91
15_Dup	14.84	0.26 ± 0.0031	100	-
17.5	16.57	0.18 ± 0.0026	92	-
20	18.22	0.14 ± 0.002	92	-
22.5	20.85	0.1 ± 0.0086	102	-
25	22.91	0.09 ± 0.0017	120	2.73
25_Dup	22.91	0.09 ± 0.0017	123	-

Figure 4. Measured and Literature Values of Water Activity of 20 °C NaOH Solutions at Varying Concentrations Using a Humidity Probe and Temperature Probe.



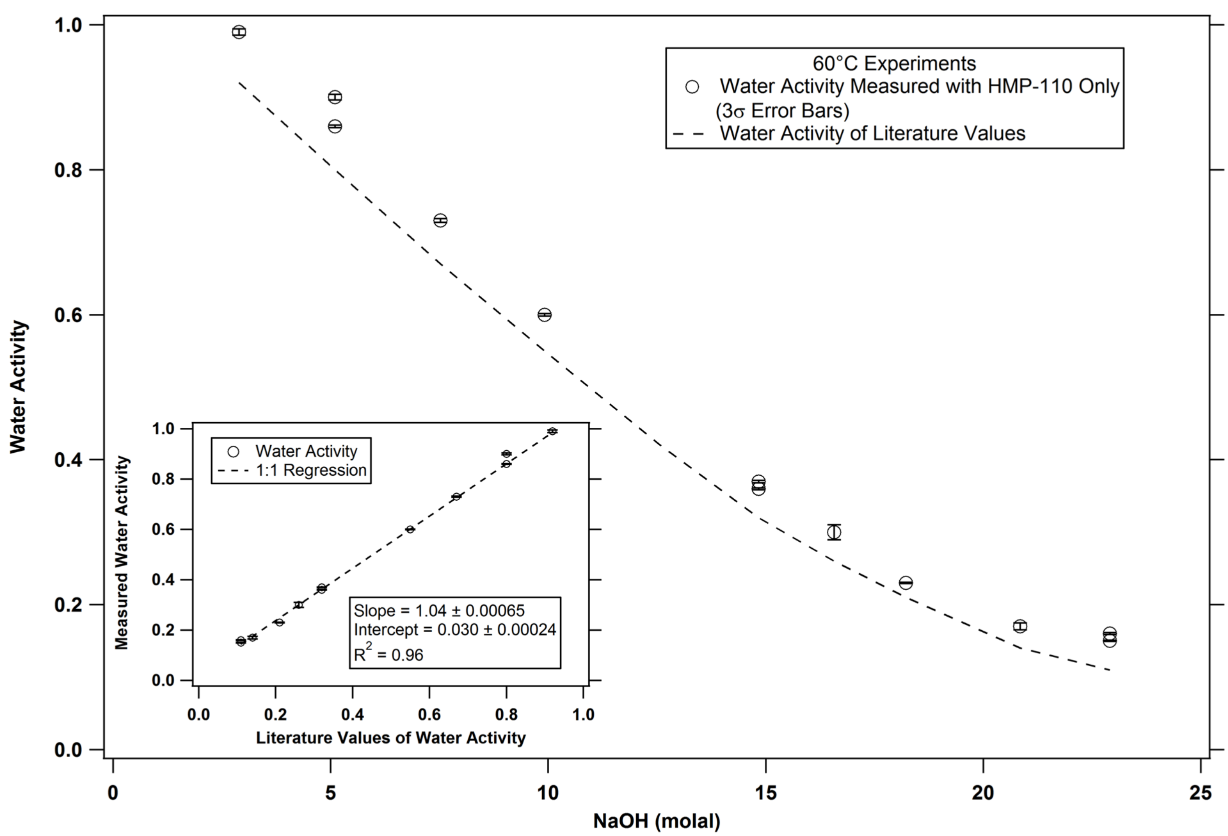
3.3 60 °C RESULTS USING HUMIDITY SENSOR ONLY

The water activity of NaOH solutions of varying concentrations was also determined at a temperature of 60 °C using the humidity probe only. Figure 5 shows the values determined from the experiment (circles) and literature values of these data (dashed line). An inspection of the figure clearly illustrates that the experimentally determined values have a positive bias as compared to the literature values. This is also verified by the 1:1 analysis of the data (inset of Figure 5) as compared to the literature values. A linear regression of the data indicated a positive bias with the slope and intercept having values of 1.04 ± 0.00065 and 0.030 ± 0.00024, respectively. The fit had an R^2 value of 0.96. The percent recovery of each point shows that the water activity was overestimated over the range of NaOH solution with percent recovery ranging from 108 - 146% of the literature values. The percent recovery was the greatest at NaOH solution concentrations of 22.5 and 25.0 molal with percent recoveries of 121 and 146%, respectively. The duplicate analysis ranged from 2.02% to 5.35% indicating good precision. Again this configuration demonstrated good accuracy and precision determining the water activity of electrolyte solutions through a range of 0.20 to less than 1.00.

Table 8. Tabulated Water Activity of NaOH Solutions Using Only a Humidity Probe at a Temperature of 60 °C.

Experiment	NaOH (mole/kg)	Mean a_w (3σ)	% Recovery	RPD of Duplicates
2.5m	2.20	0.99 ± 0.0045	108	-
5m	5.10	0.86 ± 0.0016	107	5.35
5m_Dup	5.10	0.9 ± 0.0038	113	-
7.5m	7.52	0.73 ± 0.0026	109	-
10m	9.92	0.6 ± 0.0017	109	-
12.5m	12.57	-	-	-
15m	14.84	0.36 ± 0.0013	110	5.07
15m_Dup	14.84	0.37 ± 0.0018	116	-
17.5m	16.57	0.3 ± 0.0102	114	-
20m	18.22	0.23 ± 0.001	108	-
22.5m	20.85	0.17 ± 0.0049	121	-
25m	22.91	0.16 ± 0.0013	146	2.02
25m_Dup	22.91	0.15 ± 0.001	143	-

Figure 5. Measured and Literature Values of Water Activity of 60 °C NaOH Solutions at Varying Concentrations Using a Humidity Probe Only.



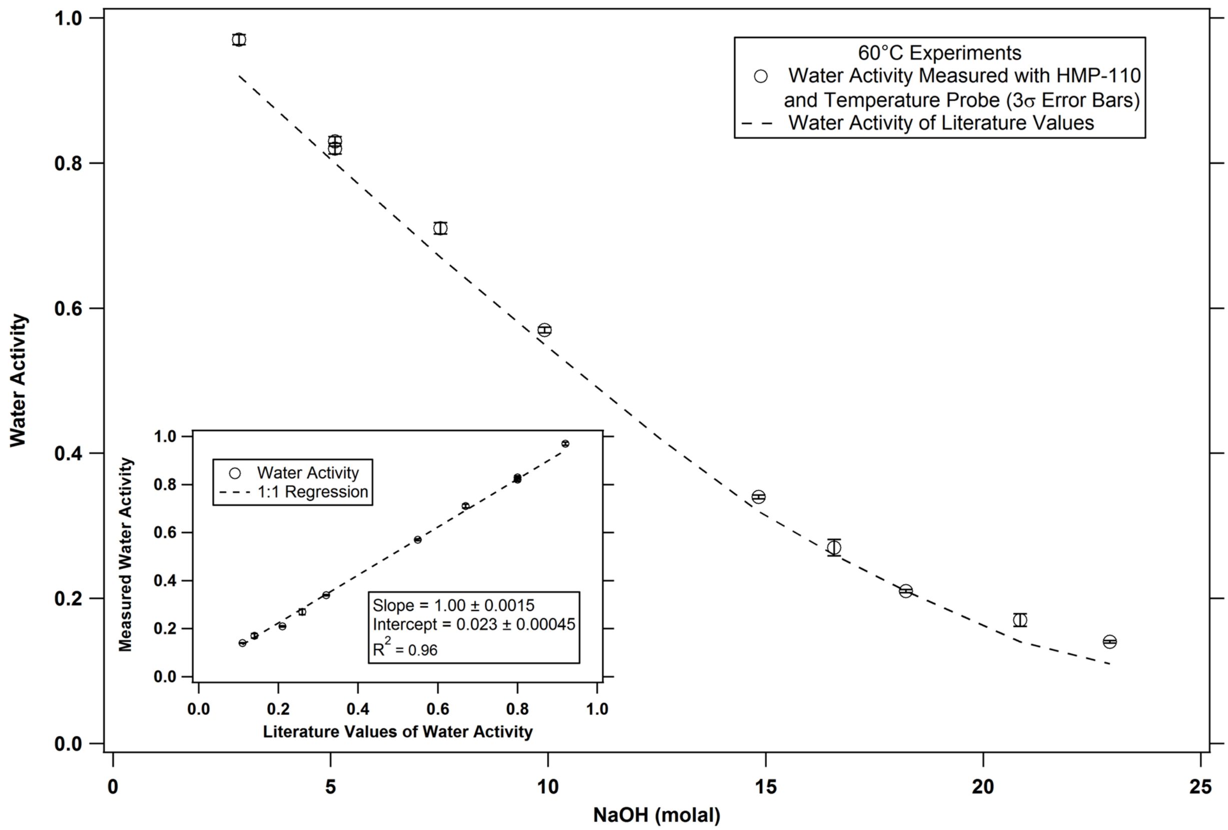
3.4 60 °C RESULTS USING HUMIDITY SENSOR AND TEMPERATURE SENSOR

By incorporating the solution temperature measurement into the calculation of the water activity, the determination of the water activity of the NaOH solution proved more accurate. The results of this experiment are presented in Figure 6. The plot showed that the measured data agree well with the literature values with the possibility of a slight positive bias. However, a 1:1 regression of the data (Figure 6, inset) suggests that the bias is inconsequential with the regression having a slope and intercept of 1.00 ± 0.0015 and 0.023 ± 0.00045, respectively. The R^2 value of the fit was 0.96. Table 9 is a tabulation of the results and shows that in most cases the percent recovery was less than 5%, except for the 2.5, 22.5, and 25 molal solutions. Also, the precision of the measurement was outstanding with RPD of the duplicates at or around 1%. In general, this method was effective when measuring the water activity in the range of 0.20 to less than 1.00.

Table 9. Tabulated Water Activity of NaOH Solutions Using a Humidity Probe and Temperature Probe at a Temperature of 60 °C.

Experiment	NaOH (mole/kg)	Mean a_w (3σ)	% Recovery	RPD of Duplicates
2.5m	2.20	0.97 ± 0.0069	108	-
5m	5.10	0.82 ± 0.0073	103	1.14
5m_Dup	5.10	0.83 ± 0.0064	105	-
7.5m	7.52	0.71 ± 0.0077	105	-
10m	9.92	0.57 ± 0.0041	103	-
12.5m	12.57	-	-	-
15m	14.84	0.34 ± 0.0026	104	0.93
15m_Dup	14.84	0.34 ± 0.0028	105	-
17.5m	16.57	0.27 ± 0.0113	105	-
20m	18.22	0.21 ± 0.0021	102	-
22.5m	20.85	0.17 ± 0.0086	118	-
25m	22.91	0.14 ± 0.0018	134	1.09
25m_Dup	22.91	0.14 ± 0.0016	133	-

Figure 6. Measured and Literature Values of Water Activity of 60 °C NaOH Solutions at Varying Concentrations Using a Humidity Probe and Temperature Probe.



3.5 METHOD ANALYSIS

As explained earlier in this report, the water activity was determined using one of two methods: 1) by humidity probe only and 2) by humidity probe in conjunction with a solution temperature probe. Each method was performed in unison for accurate method comparison. For the purpose of this discussion, the method which implemented the humidity probe only will be referred as Method 1, and the method which used both the humidity probe and temperature probe will be referred to as Method 2.

Some important factors that determined the effectiveness of the method were the percent recovery of the measured data compared to the literature, RPD of the duplicate measurements of identical NaOH solutions, and the linear fit of a 1:1 regression of the measured data compared to the literature data. The percent recovery provides an indication of the accuracy of the method for each experiment performed while the duplicate analysis provides an indication of the precision for three NaOH solutions of a temperature and method of interest. The slope of the 1:1 regression provides an indication of trending bias for a range of NaOH solutions for specific temperature and method. The intercept provides an indication of a general bias for a particular method at a specific temperature.

An inspection of the results of the two methods used to determine the water activity at 20 °C shows that there is no superior method. For the 20 °C experiments using Method 1, the percent recovery ranged between 89 and 122% with a mean percent recovery of 100 ± 9.0% (Table 10) while the percent recovery of the experiments conducted using Method 2 ranged between 102 and 134% with a mean percent recovery of 102 ± 26.8%. These results demonstrate that Method 1 is slightly more accurate than Method 2. However, Method 1 was not as precise as Method 2 as demonstrated by the standard deviation of the mean of the RPD duplicates. Also, the Method 1 slope of the 1:1 regression suggests that the method underestimates water activity with increasing values of water activity.

Table 10. Consolidated Results of 20 °C Water Activity Experiments.

Method	Mean % Recovery (3σ)	Mean RPD of Duplicates (3σ)	1:1 Regression Parameters		
			Slope	Intercept	R^2
1) Humidity Probe Only	100 ± 27.4	2 ± 3.6	0.99 ± 0.0014	0.0054 ± 0.00083	1.00
2) Humidity Probe in Conjunction with a Temperature Probe	102 ± 26.8	2 ± 1.2	1.00 ± 0.0012	0.0029 ± 0.00038	0.96

Method 2 proved to be the more effective method for determining the water activity of NaOH solutions at 60 °C. Both methods had positive bias, but the bias of Method 2 was nearly half the bias of Method 1 with a mean percent recovery of 110 ± 33.4 vice 117 ± 37.7. Also, Method 2 proved more precise with a mean RPD of 1 ± 0.3 vice the Method 1 average RPD of 4 ± 4.5. Method 1 also showed a trending positive bias, which indicated a nonlinear response to varying water activity.

Table 11. Consolidated Results of 60 °C Water Activity Experiments.

Method	Mean % Recovery (3σ)	Mean RPD of Duplicates (3σ)	1:1 Regression Parameters		
			Slope	Intercept	R^2
Humidity Probe Only	117 ± 38.2	4 ± 4.5	1.04 ± 0.00065	0.029 ± 0.00024	0.95
Humidity Probe in Conjunction with a Temperature Probe	110 ± 33.4	1 ± 0.3	1.00 ± 0.0016	0.022 ± 0.0.00045	0.96

4. CONCLUSIONS

The water activity of NaOH solutions ranging in concentration from 2.203 molal to 22.913 molal was determined using a custom water activity meter with a humidity probe only (Method 1) or a humidity probe in conjunction with a temperature probe (Method 2). The water activity of the range of NaOH solutions was determined at equilibrium temperatures of 20 °C and 60 °C. Both methods were effective in determining the water activity through a range of ≈0.20 to 0.93 for a temperature of 20 °C while only Method 2 was effective in determining the water activity though a range of 0.21 to 0.97 at a temperature of 60 °C.

In application, Method 2 should be used to determine the water activity of the tank waste supernates as the solution temperature probe can accurately determine the solution temperature. Using Method 1, the actual solution temperature is not determined, but is assumed to be the same as the head space temperature. However, if cross contamination of samples is of concern then Method 1 can be used as no sensor comes in contact with the sample. Ultimately, the water activity meter configuration implemented during determination of water activity should be based on experimental variables.

5. REFERENCES

Balej, J., 1985, "Water vapor partial pressures and water activities in potassium and sodium hydroxide solutions over wide concentration and temperature ranges," Int. J. Hydrogen Energy, Vol. 10, No. 4, pp 233-243.

LAB-PLN-11-00012, 2011, *Testing and Validation of an Enhanced Acquisition and Control System*, Rev. 0, Washington River Protection Solutions LLC, Richland, Washington.

RPP-RPT-47795, 2011, *Water Activity Data Assessment to be used in Hanford Waste Solubility Calculations*, Rev. 3, EnergySolutions LCC, Richland, Washington.

APPENDIX A

Linear Regressions Engineering Calculation

Title: Multiple Regressions for Water Activity Calculations **Page 1 of 20**
Engineer/Analyst: Jacob McCoskey **Date: 8/29/13**
Checker: Richard Wyrwas **Date: 8/29/13**

Calculation Checklist

Calculation Title/Subject:	Multiple Regressions for Water Activity Calculations		
Scope of Review:	Calculation and Document		
Engineer/Analyst	Jacob K. McCoskey	Date:	8/29/13
Organization Manager	Cary Seidel	Date:	8/29/13

Yes	No*	NA*		
[✓]	[ ]	[ ]	a.	The objective/purpose of the calculation is clearly stated and the problem is completely defined by the purpose statement.
[✓]	[ ]	[ ]	b.	Analytical and technical approaches and results are reasonable and appropriate.
[✓]	[ ]	[ ]	c.	Input data are adequately described, referenced to their source, and checked for consistency with original source information.
[✓]	[ ]	[ ]	d.	Necessary assumptions are reasonable, explicitly stated, and supported. Assumptions requiring verification prior to use are clearly stated and identified/tracked using TBD/HOLD numbers.
[✓]	[ ]	[ ]	e.	For both qualitative and quantitative data, uncertainties are recognized and discussed and the data is presented in a manner to minimize design interpretations.
[✓]	[ ]	[ ]	f.	Mathematical derivations were checked, including dimensional consistency of results.
[✓]	[ ]	[ ]	g.	Calculations are sufficiently detailed such that a technically qualified person can understand the analysis without requiring outside information.
[ ]	[ ]	[✓]	h.	Hand and MathCAD® calculations were verified, including review that correct input data are used, formulae correctly interpret intended expressions, correct units are used, and results are reasonable and appropriate.
[✓]	[ ]	[✓]	i.	Software applications used are identified by the program name and version/release number, both on the calculation cover sheet and in the body of the document.
[✓]	[ ]	[ ]	j.	Software input data is identified and/or attached/included, the input data is correct, and consistent with the calculation document.
[✓]	[ ]	[ ]	k.	Software output is consistent with the input and with the results reported in the calculation document.
[✓]	[ ]	[ ]	l.	Software verification and validation are addressed adequately in accordance with TFC-BSM-IRM_HS-C-01. Software verification documentation is noted on the calculation cover sheet and in the body of the document as included in the calculation document or a reference is provided to separate verification documentation.
[ ]	[ ]	[✓]	m.	Spreadsheets used in the calculation are identified, verified, and documented in accordance with TFC-ENG-DESIGN_C-32. Reference to the corresponding spreadsheet verification form is provided on the calculation cover sheet and in the body of the calculation.
[✓]	[ ]	[ ]	n.	Data or results presented in tables and graphs have been checked against original source.
[✓]	[ ]	[ ]	o.	Unit conversions are correct and consistent.
[✓]	[ ]	[ ]	p.	The number of significant digits is appropriate and consistent.
[✓]	[ ]	[ ]	q.	Limits/criteria/guidelines applied to the analysis results are appropriate and referenced. Limits/criteria/guidelines were checked against references.
[✓]	[ ]	[ ]	r.	Conclusions are consistent with analytical results and applicable limits.
[✓]	[ ]	[ ]	s.	Results and conclusions address all points in the purpose.
[✓]	[ ]	[ ]	t.	Referenced documents are retrievable or otherwise available and the version or revision of each reference is cited.
[✓]	[ ]	[ ]	u.	The document was prepared in accordance with Attachment A, "Calculation Format and Preparation Instructions," of TFC-ENG-DESIGN-C-10.
[✓]	[ ]	[ ]	v.	Impacts on requirements have been assessed and change documentation initiated to incorporate revisions to affected documents, as appropriate.
[✓]	[ ]	[ ]	w.	All checker comments have been dispositioned and the design media matches the calculations.

Richard Wyrwas 8/29/2013
Checker (printed name and signature) Date

* If less than the entire calculation was checked, the scope of the check should be discussed. If any blocks are checked "No" or "NA", an explanation must be provided here or attached

Title: Multiple Regressions for Water Activity Calculations
Engineer/Analyst: Jacob McCoskey **Date:** 8/29/13
Checker: Richard Wyrwas **Date:** 8-29-13

Calculation Review

Subject: Multiple Regressions for Water Activity Calculations
The subject document has been reviewed by the undersigned
The reviewer reviewed and verified the following items as applicable.

Documents Reviewed: Multiple Regressions for Water Activity Calculations

Analysis Performed By: Richard Wyrwas

Sections Verified:

- Design Input
- Basic Assumptions
- Approach/Design Methodology
- Consistency with item or document supported by the calculation
- Conclusion/Results interpretation

Exceptions of Checklist:

- For item h., the checklist was marked NA as the calculations were performed using IGOR Pro and not by MathCAD or hand.
- For item i., the checklist was marked NA as the engineering calculation is embedded in another document and by procedure, a cover sheet is not required.
- For item m., the checklist was marked NA as the calculations were performed using IGOR Pro and not Microsoft Excel.

Reviewer (printed name, signature, and date) Richard Wyrwas 8/29/13

Responsible Manager (printed name, signature, and date) Cary M Seidel 8/29/13

Title: Multiple Regressions for Water Activity Calculations
Engineer/Analyst: Jacob McCoskey **Date:** 8/29/13
Checker: Richard Wyrwas **Date:** 8-29-13

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Title: Multiple Regressions for Water Activity Calculations **Page 4 of 20**
Engineer/Analyst: Jacob McCoskey **Date: 7/22/13**
Checker: Richard Wyrwas **Date: 8-29-13**

Abbreviations and Acronyms

a	Linear Regression Intercept
b	Linear Regression Slope
R^2	Coefficient of Determination
V_r2	Coefficient of Determination as reported by IGOR

Units

°C	Degrees Celsius

Title: Multiple Regressions for Water Activity Calculations **Page 5 of 20**
Engineer/Analyst: Jacob McCoskey **Date: 8/29/13**
Checker: Richard Wyrwas **Date: 8-29-13**

1. CALCULATION OBJECTIVE

1) The first objective of this calculation was to determine the sigmoid regression of water activity at both 20°C and 60°C as a function of NaOH concentration in molality ($aw = f([NaOH])$). This equation will be used to estimate the actual water activity of several NaOH solutions used in the laboratory experiment described in document LAB-PLN-11-00012 Rev. 0, "Testing and Validation of an Enhanced Data Acquisition and Control System." The actual water activity values calculated using the sigmoid function will be compared to measured water activity values collected using the Enhanced Data Acquisition and Control System (EDAQS).

2) The second objective of this calculation document was to determine the slope and intercept of a linear regression of measured sodium hydroxide solution water activity data compared to literature data. The water activity of sodium hydroxide solutions varying in concentration was determined using a water activity meter in two configurations. Configuration 1 included a humidity probe that determined the water vapor pressure of the head space assuming the head space temperature was in thermal equilibrium with the sodium hydroxide solution. Configuration 2 also incorporated the humidity probe to determine vapor pressure of the head space, but also included a temperature sensor to determine the temperature of the sodium hydroxide solution. The water activity of 10 sodium hydroxide solutions ranging from 2.5 to 25 molal in concentration was determined using each meter configuration. Also, the water activity was determined for sodium hydroxide solutions at both 20°C and 60°C using each of the configurations. A total of 4 data sets were compared to literature values using the regression technique described in this document.

2. INPUT DATA

1) The input data for $aw = f([NaOH])$ is published data originated from RPP-RPT-47795, "Water Activity Data Assessment to be Used in Hanford Waste Solubility Calculations," which is a compilation of water activity data for electrolytes in aqueous solutions with corresponding references. The data set is found in Appendix A, NaOH Datasets, part J of RPP-RPT-47795. For our work, data referenced as originating from the International Critical Tables of Numerical Data Physics, Chemistry and Technology, Vol. III was used as it provided a wide range of water activity data with adequate accuracy for translation into a mathematical function. The data is listed in Table 1.

Table 1. Water Activity Literature Data, International Critical tables, 1928

NaOH Molality mol/kg	a_w at 20 °C	a_w at 60 °C
0	1	1
1.25009	0.963567	0.960123
2.50018	0.912253	0.916633
5.00036	0.79252	0.806236
7.50054	0.644278	0.675766
10.0007	0.496037	0.541951
12.5009	0.359199	0.418172
15.0011	0.250869	0.314465
17.5013	0.171047	0.230831
20.0014	0.114032	0.163923
22.5016	0.074121	0.117088
25.0018	0.051314	0.083634
30.0022		0.042152
35.0025		0.020072
40.0029		0.010036

2) The input data for each of the four regressions is outlined in Table 2. Each data set includes the mean measured water activity and associated standard deviation of the ten sodium hydroxide solutions. It also includes the actual water activity calculated using $aw = f([NaOH])$ for each of the ten sodium hydroxide solutions at the given temperature.

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Table 2. Data Values for 1:1 Regression Calculation

	HMP-110 Only at 20°C			HMP-110 and Temperature Sensor at 20°C			HMP-110 Only at 60°C			HMP-110 and Temperature Sensor at 60°C		
Experiment	**Exp. aw**	**Exp. Stdev (1σ)**	**Lit. aw**	**Exp. aw**	**Exp. Stdev (1σ)**	**Lit. aw**	**Exp. aw**	**Exp. Stdev (1σ)**	**Lit. aw**	**Exp. aw**	**Exp. Stdev (1σ)**	**Lit. aw**
2.5	0.87	0.0009	0.92	0.93	0.0037	0.92	0.99	0.0015	0.92	0.97	0.0023	0.92
5	0.77	0.0004	0.78	0.78	0.0024	0.78	0.86	0.0005	0.80	0.82	0.0024	0.80
5_Dup	0.77	0.0005	0.78	0.79	0.0026	0.78	0.90	0.0013	0.80	0.83	0.0021	0.80
7.5	0.64	0.0006	0.65	0.65	0.0022	0.65	0.73	0.0009	0.67	0.71	0.0026	0.67
10	0.49	0.0045	0.50	0.50	0.0032	0.50	0.60	0.0006	0.55	0.57	0.0014	0.55
12.5	0.35	0.0005	0.36	0.35	0.0032	0.36	-	-	0.42	-	-	0.42
15	0.25	0.0004	0.26	0.25	0.0010	0.26	0.36	0.0004	0.32	0.34	0.0009	0.32
15_Dup	0.25	0.0004	0.26	0.26	0.0010	0.26	0.37	0.0006	0.32	0.34	0.0009	0.32
17.5	0.18	0.0005	0.20	0.18	0.0009	0.20	0.30	0.0034	0.26	0.27	0.0038	0.26
20	0.13	0.0004	0.15	0.14	0.0007	0.15	0.23	0.0003	0.21	0.21	0.0007	0.21
22.5	0.10	0.0030	0.10	0.10	0.0029	0.10	0.17	0.0016	0.14	0.17	0.0029	0.14
25	0.08	0.0004	0.07	0.09	0.0006	0.07	0.16	0.0004	0.11	0.14	0.0006	0.11
25_Dup	0.09	0.0004	0.07	0.09	0.0006	0.07	0.15	0.0003	0.11	0.14	0.0005	0.11

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3. METHOD OF ANALYSIS

The sigmoid regression and linear regression was performed using a macro that is included in the IGOR Pro Version 6.21 copyrighted by WaveMetrics, Inc.

1) The sigmoid regression is menu driven and is performed using the following steps.

    1. Open the IGOR program.
    2. Load all data arrays in Table 2 as waves into an IGOR table.
    3. Pull up the **"Curve Fitting"** pop-up window by accessing the **Curve Fitting...** option of the Analysis drop down menu.
    4. Select the **Function and Data** tab of the pop up window.
    5. Select sigmoid under the **"Function"** drop down menu of the **Function and Data** tab.
    6. Select the measured data wave for the experiment of interest in the **"Y Data"** drop down menu of the **Function and Data** tab.
    7. Select the literature data wave for the experiment of interest in the **"X Data"** drop down menu of the **Function and Data** tab.
    8. Press the "Do It" button of the "Curve Fitting" pop-up window.

    The result of the sigmoid regression is printed in the "Command Window." Several values are reported in the results, but the values of interest are chi squared, base, max, xhalf, and rate. The values are labeled in the IGOR results of the "Command Window" as "V_chisq", "base", "max", "xhalf", and "rate", respectively.

2) The linear regression is menu driven and is performed using the following steps.

    1. Open the IGOR program.
    2. Load all data arrays in Table 2 as waves into an IGOR table.
    3. Pull up the **"Curve Fitting"** pop-up window by accessing the **Curve Fitting...** option of the Analysis drop down menu.
    4. Select the **Function and Data** tab of the pop up window.
    5. Select line under the **"Function"** drop down menu of the **Function and Data** tab
    6. Select the measured data wave for the experiment of interest in the **"Y Data"** drop down menu of the **Function and Data** tab.
    7. Select the literature data wave for the experiment of interest in the **"X Data"** drop down menu of the **Function and Data** tab.
    8. Select the **Data Options** tab of the pop up window.
    9. Select the data wave containing the standard deviation of the measured data in the **"Weighting"** drop down menu.
    10. Ensure the **"Standard Dev."** option is selected in the **Wave Contains** box of the **"Weighting"** drop down menu box.

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11. Press the "Do It" button of the "Curve Fitting" pop-up window.

The result of the linear regression is printed in the "Command Window." Several values are reported in the results, but the values of interest are the coefficient of determination (R^2), the regression intercept (a) and the regression slope (b). The values are labeled in the IGOR results of the "Command Window" as "V_r2", "a" and "b", respectively.

4. COMPUTER SOFTWARE

IGOR Pro , version 6.02, was used to conduct these calculations and is registered in HISI under HISI # 2910. It is graded as N/A software and was approved for use on 8/06/2013.

5. RESULTS

The results of the sigmoid fit to the literature NaOH water activity data is displayed in Table 3.

Table 3. Results of Sigmoid Regression of Literature NaOH Solution Water Activity Data

Constant	Value at 20 °C	Value at 60 °C
Base	1.1825 ± 0.0204	1.2472 ± 0.014
Max	-1.1656 ± 0.0263	-1.2391 ± 0.0156
Xhalf	8.281 ± 0.178	8.4124 ± 0.153
Rate	4.8474 ± 0.164	5.9522 ± 0.0962
Quality of Fit		
Chi Squared	5.51378×10^{-5}	1.61845×10^{-4}

Table 4 contains the results of the 1:1 regressions for each of the four experiments.

Table 4. Experiment Results of 1:1 Regressions

Experiment	a	b	R^2
HMP-110 Only at 20°C	0.0012 ± 0.00022	0.98 ± 0.00050	1.02
HMP-110 and Temperature Sensor at 20°C	0.011 ± 0.00043	0.96 ± 0.0018	0.93
HMP-110 Only at 60°C	0.030 ± 0.00024	1.04 ± 0.00065	0.96
HMP-110 and Temperature Sensor at 60°C	0.023 ± 0.00045	1.00 ± 0.0015	0.96

6. CONCLUSIONS

Engineer/Analyst: Jacob McCoskey Date: 8/29/13
Checker: Richard Wyrwas Date: 8-29-13

IOGR Pro successfully fitted a sigmoid function to the water activity of various NaOH solutions at both 20 °C and 60 °C. The results of the IGOR fit were compared to the results of an OriginPro fit and the outputs from each of the programs were nearly identical.

IGOR accurately calculated the slope and intercept of the 1:1 regression of the four experiments. Also, the output was compared to a similar regression completed using Origin Pro and the data outputs were nearly identical. Also, the coefficient of determination was reported. The determined values are of expected magnitude

7. REFERENCES

IGOR Pro Version 6.2, WaveMetrics, Inc., Lake Oswego, Oregon, 2010

LAB-RPT-13-00006, 2013, *Instrument Qualification of Custom Fabricated Water Activity Meter for Hot Cell Use*, Washington River Protection Solutions LLC, Richland, Washington.

RPP-RPT-47795 Rev. 3, 2011, Water Activity Data Assessment to be used in Hanford Waste Solubility Calculations, Washington River Protection Solutions LLC, Richland, Washington.

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APPENDIX 1. IGOR OUTPUT OF SIGMOID REGRESSIONS

Water Activity of NaOH Solutions at 20°C

```
CurveFit/NTHR=0 Sigmoid  aw_20_NaOH[0,11] /X=NaNO3_NaOH /D /F={0.950000, 4}
  Fit converged properly
  Curve fit with data subrange:
        aw_20_NaOH[0,11]
  fit_aw_20_NaOH= W_coef[0] + W_coef[1]/(1+exp(-(x-W_coef[2])/W_coef[3]))
  W_coef={1.1825,-1.1656,8.281,4.8474}
  V_chisq= 5.51378e-005;V_npnts= 12;V_numNaNs= 0;V_numINFs= 0;
  V_startRow= 0;V_endRow= 11;
  W_sigma={0.00886,0.0114,0.0771,0.0711}
  Fit coefficient confidence intervals at 95.00% confidence level:
  W_ParamConfidenceInterval={0.0204,0.0263,0.178,0.164,0.95}
  Coefficient values ± 95% Confidence Interval
        base    =1.1825 ± 0.0204
        max     =-1.1656 ± 0.0263
        xhalf   =8.281 ± 0.178
        rate    =4.8474 ± 0.164
```

Water Activity of NaOH Solutions at 60°C

```
CurveFit/NTHR=0 Sigmoid  aw_60_NaOH /X=NaNO3_NaOH /D
  Fit converged properly
  fit_aw_60_NaOH= W_coef[0] + W_coef[1]/(1+exp(-(x-W_coef[2])/W_coef[3]))
  W_coef={1.2472,-1.2391,8.4124,5.9522}
  V_chisq= 0.000161845;V_npnts= 15;V_numNaNs= 0;V_numINFs= 0;
  V_startRow= 0;V_endRow= 14;
  W_sigma={0.014,0.0156,0.153,0.0962}
  Coefficient values ± one standard deviation
        base    =1.2472 ± 0.014
        max     =-1.2391 ± 0.0156
        xhalf   =8.4124 ± 0.153
        rate    =5.9522 ± 0.0962
```

APPENDIX 2. IGOR OUTPUT OF LINEAT REGRESSIONS

HMP-110 Only at 20°C

CurveFit/NTHR=0 line Water_Activity_Avg__Vapor_ /X=Modeled_Water_Activity /W=Water_Activity_Std_1sig__Vapor_ /I=1 /D
 fit_Water_Activity_Avg__Vapor_= W_coef[0]+W_coef[1]*x
 W_coef={0.0012344,0.97585}
 V_chisq= 8333.85;V_npnts= 13;V_numNaNs= 0;V_numINFs= 0;
 V_startRow= 0;V_endRow= 12;V_q= 0;V_Rab= -0.781291;
 V_Pr= 0.933607;V_r2= 1.01824;
 W_sigma={0.000219,0.000502}
 Coefficient values ± one standard deviation
  a =0.0012344 ± 0.000219
  b =0.97585 ± 0.000502

HMP-110 and Temperature Sensor at 20°C

CurveFit/NTHR=0 line Water_Activity_Avg__Solution_ /X=Modeled_Water_Activity /W=Water_Activity_Std_1sig__Soluti /I=1 /D
 fit_Water_Activity_Avg__Solutio= W_coef[0]+W_coef[1]*x
 W_coef={0.0113,0.96245}
 V_chisq= 2354.56;V_npnts= 13;V_numNaNs= 0;V_numINFs= 0;
 V_startRow= 0;V_endRow= 12;V_q= 0;V_Rab= -0.732706;
 V_Pr= 0.903335;V_r2= 0.933553;
 W_sigma={0.000429,0.00184}
 Coefficient values ± one standard deviation
  a =0.0113 ± 0.000429
  b =0.96245 ± 0.00184

HMP-110 Only at 60°C

CurveFit/NTHR=0/TBOX=769 line Mean_HMP110 /X=Actual_Water_Activity /W='1s_StDev_HMP110' /I=1 /D
 fit_Mean_HMP110= W_coef[0]+W_coef[1]*x
 W_coef={0.029802,1.0385}
 V_chisq= 6710.35;V_npnts= 12;V_numNaNs= 0;V_numINFs= 0;
 V_startRow= 0;V_endRow= 12;V_q= 0;V_Rab= -0.789862;
 V_Pr= 0.860334;V_r2= 0.963943;
 W_sigma={0.000238,0.000647}
 Coefficient values ± one standard deviation
  a =0.029802 ± 0.000238
  b =1.0385 ± 0.000647

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HMP-110 and Temperature Sensor at 60°C

CurveFit/NTHR=0/TBOX=769 line 'Mean_HMP&Temp' /X=Actual_Water_Activity /W='1s_StDev_HMP&Temp' /I=1 /D

'fit_Mean_HMP&Temp'= W_coef[0]+W_coef[1]*x
W_coef={0.023432,0.99815}
V_chisq= 1647.84;V_npnts= 12;V_numNaNs= 0;V_numINFs= 0;
V_startRow= 0;V_endRow= 12;V_q= 0;V_Rab= -0.779027;
V_Pr= 0.911342;V_r2= 0.963254;
W_sigma={0.000447,0.00154}
Coefficient values ± one standard deviation
a =0.023432 ± 0.000447
b =0.99815 ± 0.00154

Title: Multiple Regressions for Water Activity Calculations **Page 15 of 20**
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Checker: Richard Wyrwas **Date:** 8-29-13

APPENDIX 3. RESULTS OF SIGMOID REGRESSION CHECK USING ORIGIN PRO VERSION 9.00

Figure A-1. Origin Pro check of sigmoid regression of NaOH water activity at 20 °C

Nonlinear Curve Fit (CopyOfBoltzmann (User)) (8/28/2013 08:28:42)

Parameters

		Value	Standard Error
aw at 20C	A1	-1.16564	0.01146
	A2	1.1825	0.00889
	x0	8.28068	0.0771
	dx	4.8478	0.07173
	span	2.34814	0.02024
	EC50	3946.86686	304.31085

Reduced Chi-sqr = 6.89342724224E-6
COD(R^2) = 0.99996224262886
Iterations Performed = 10
Total Iterations in Session = 10
Fit converged. Chi-Sqr tolerance value of 1E-9 was reached.
span, EC50 are derived parameter(s).

Statistics

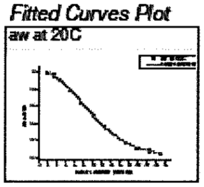
	aw at 20C
Number of Points	12
Degrees of Freedom	8
Reduced Chi-Sqr	6.89343E-6
Residual Sum of Squares	5.51474E-5
Adj. R-Square	0.99995
Fit Status	Succeeded(100)

Fit Status Code :
100 : Fit converged. Chi-Sqr tolerance value of 1E-9 was reached.

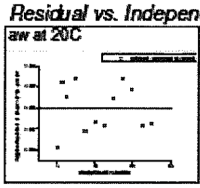
ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
aw at 20C	Regression	4	4.29219	1.07305	155662.52452	0
	Residual	8	5.51474E-5	6.89343E-6		
	Uncorrected Total	12	4.29225			
	Corrected Total	11	1.46058			

Fitted Curves Plot



Residual vs. Independent Plot



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Engineer/Analyst: Jacob McCoskey **Date: 8/29/13**
Checker: Richard Wyrwas **Date: 8-29-13**

Figure A-2. Origin Pro check of sigmoid regression of NaOH water activity at 60 °C

Nonlinear Curve Fit (CopyOfBoltzmann (User)) (8/28/2013 08:40:19)

Input Data

	Dep/Indep	Data	Range	Weight Type
aw at 60C	x Indep	[Book5]Sheet1!A"NaOH Molality"	[1*:15*]	No Weighting
	y Dep	[Book5]Sheet1!C"aw at 60C"	[1*:15*]	No Weighting

Parameters

		Value	Standard Error
aw at 60C	A1	-1.23929	0.01566
	A2	1.24738	0.01399
	x0	8.41087	0.15278
	dx	5.95329	0.09673
	span	2.48666	0.02957
	EC50	4495.66115	686.83421

Reduced Chi-sqr = 1.47141923383E-5
COD(R^2) = 0.99991447157045
Iterations Performed = 10
Total Iterations in Session = 10
Fit converged. Chi-Sqr tolerance value of 1E-9 was reached.
span, EC50 are derived parameter(s).

Statistics

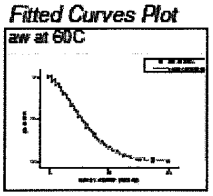
	aw at 60C
Number of Points	15
Degrees of Freedom	11
Reduced Chi-Sqr	1.47142E-5
Residual Sum of Squares	1.61856E-4
Adj. R-Square	0.99989
Fit Status	Succeeded(100)

Fit Status Code :
100 : Fit converged. Chi-Sqr tolerance value of 1E-9 was reached.

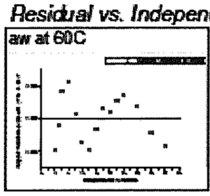
ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
aw at 60C	Regression	4	4.53917	1.13479	77122.34103	0
	Residual	11	1.61856E-4	1.47142E-5		
	Uncorrected Total	15	4.53933			
	Corrected Total	14	1.89242			

Fitted Curves Plot



Residual vs. Independent Plot



APPENDIX 4. RESULTS LINEAR REGRESSION CHECK USING ORIGIN PRO VERSION 9.00

Figure A-3. **HMP-110 Only at 20°C**

Linear Fit with X Error (8/21/2013 13:28:46)

Notes

Description	Perform Linear Fitting
User Name	h3390899
Operation Time	8/21/2013 13:28:46
Equation	y = a + b*x
Report Status	New Analysis Report
Method	FV
Special Input Handling	

Input Data

Input X Data Source	Input Y Data Source	Range	Weight Data
[Book3]Sheet1!D	[Book3]Sheet1!A"20oC Method 1"	[1*:13*]	[Book3]Sheet1!B

Masked Data - Values Excluded from Computations

Notes
No Masked Data

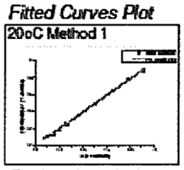
Bad Data (missing values) -- Values that are invalid and thus not used in computations

Notes
No Missing Data

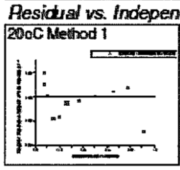
Parameters

		Value	Standard Error
20oC Method 1	Intercept	0.00123	2.18692E-4
	Slope	0.97585	5.01822E-4

Fitted Curves Plot



Residual vs. Independent Plot



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Checker: Richard Wyrwas **Date: 8-29-13**

Figure A-4. **HMP-110 and Temperature Sensor at 20°C**

Linear Fit with X Error (8/21/2013 13:29:38)

Notes

Description	Perform Linear Fitting
User Name	h3390899
Operation Time	8/21/2013 13:29:38
Equation	y = a + b*x
Report Status	New Analysis Report
Method	FV
Special Input Handling	

Input Data

Input X Data Source	Input Y Data Source	Range	Weight Data
[Book4]Sheet1!D	[Book4]Sheet1!A"20oC Method 2"	[1*:13*]	[Book4]Sheet1!B

Masked Data - Values Excluded from Computations

Notes
No Masked Data

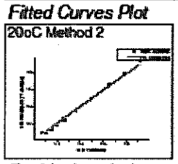
Bad Data (missing values) -- Values that are invalid and thus not used in computations

Notes
No Missing Data

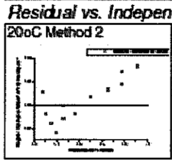
Parameters

		Value	Standard Error
20oC Method 2	Intercept	0.0113	4.28741E-4
	Slope	0.96245	0.00184

Fitted Curves Plot



Residual vs. Independent Plot



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Engineer/Analyst: Jacob McCoskey **Date: 8/29/13**
Checker: Richard Wyrwas **Date: 8-29-13**
Figure A-5. **HMP-110 Only at 60°C**

Linear Fit with X Error (8/21/2013 11:15:36)

Notes

Description	Perform Linear Fitting
User Name	h3390899
Operation Time	8/21/2013 11:15:36
Equation	y = a + b*x
Report Status	New Analysis Report
Method	FV
Special Input Handling	

Input Data

Input X Data Source	Input Y Data Source	Range	Weight Data
[Book1]Sheet1!D	[Book1]Sheet1!A"60oC Method 1"	[1*:12*]	[Book1]Sheet1!B

Masked Data - Values Excluded from Computations

Notes
No Masked Data

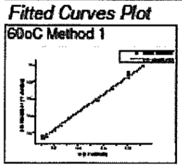
Bad Data (missing values) -- Values that are invalid and thus not used in computations

Notes
No Missing Data

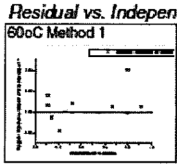
Parameters

		Value	Standard Error
60oC Method 1	Intercept	0.0298	2.37787E-4
	Slope	1.03847	6.47219E-4

Fitted Curves Plot



Residual vs. Independent Plot



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Engineer/Analyst: Jacob McCoskey Date: 8/29/13
Checker: Richard Wyrwas Date: 8-29-13

Figure A-6. **HMP-110 and Temperature Sensor at 60°C**

Linear Fit with X Error (8/21/2013 13:24:59)

Notes

Description	Perform Linear Fitting
User Name	h3390899
Operation Time	8/21/2013 13:24:59
Equation	y = a + b*x
Report Status	New Analysis Report
Method	FV
Special Input Handling	

Input Data

Input X Data Source	Input Y Data Source	Range	Weight Data
[Book2]Sheet1!D	[Book2]Sheet1!A"60oC Method 2"	[1*:12*]	[Book2]Sheet1!B

Masked Data - Values Excluded from Computations

Notes
No Masked Data

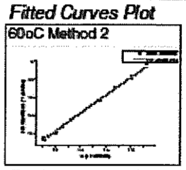
Bad Data (missing values) -- Values that are invalid and thus not used in computations

Notes
No Missing Data

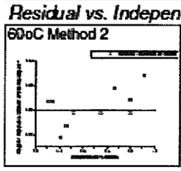
Parameters

		Value	Standard Error
60oC Method 2	Intercept	0.02343	4.47138E-4
	Slope	0.99815	0.00154

Fitted Curves Plot



Residual vs. Independent Plot



Electronically Approved by:

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Title:
Date: Thursday, 09 January 2014, 07:54 AM   Pacific Time
Meaning: Approved by the author or delegate
==

UserName: Cooke, Gary (h0410221)
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Date: Tuesday, 14 January 2014, 05:01 PM   Pacific Time
Meaning: Approved by the Group Manager or delegate
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