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Factors Influencing Moisture Analysis in the 3013 Destructive Examination Surveillance Program

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DISCLAIMER

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EXECUTIVE SUMMARY

Thermogravimetric analysis of a solid sample with mass spectrometry (TGA-MS) of the evolved gas is used in the destructive examination (DE) portion of the Integrated Surveillance Program to quantify the moisture content of the material stored in a 3013 container. As with any measurement determined from a small sample, the collection, storage, transportation, and handling of the sample can affect its ability to represent the properties of the bulk material.

During the course of the DE program, questions have periodically arisen concerning the ability of the moisture sample to reflect reliably the actual moisture content of the entire material stored in the 3013 container. Most concerns are related to the ability to collect a representative sample and to preserve the moisture content of the sample between collection and analysis. Recent delays in analysis caused by maintenance issues with the TGA-MS instrument presented a unique opportunity to document and quantify the effects various factors have on the TGA-MS moisture measurement.

This report will use recent data to document the effects that current sample collection and handling practices have on the TGA-MS moisture measurement. Some suggestions will be made which could improve the current sample collection and handling practices for the TGA-MS moisture measurement so that the analytical results more accurately reflect the moisture content of the material stored in the 3013 container.

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LIST OF ABBREVIATIONS

3013 container	A container conforming to DOE-STD-3013
CPD	Can Puncture Device
DE	Destructive examination
FTIR	Fourier transform infrared spectrometry
IM	Initial Moisture
KIS	K-Area Interim Surveillance
LOI	Loss on ignition
MS	Mass Spectrometry
RH	Relative humidity
RP	Representative
SRNL	Savannah River National Laboratory
TGA	Thermogravimetric Analysis

1.0 Introduction

In the destructive examination (DE) portion of the Integrated Surveillance Program, the moisture content of the material in a 3013 storage container at the time of DE is estimated by analyzing a sample removed from the 3013. Thermogravimetric analysis of a solid sample with mass spectrometry (TGA-MS) of the evolved gas is used to quantify the moisture content of the sample. Thermogravimetric analysis (TGA) is used to measure the amount of mass change of a sample while being heated and mass spectrometry (MS) is used to identify and quantify certain species in the off-gas stream. The moisture content is determined by the integration of the mass 18 signal of the MS, with confirmatory indications from the mass 17 signal and the total mass loss of the sample. As with any measurement determined from a small sample, the collection, storage, transportation, and handling of the sample can affect its representativeness of the bulk material.

Samples from each DE are sent to SRNL for analysis. The Initial Moisture (IM) sample is used to determine the moisture content of the bulk material when the 3013 container is opened and the Representative (RP) sample is used for most other analyses. The samples from a single DE are sent to SRNL at one time. The IM sample is collected immediately after the inner container is opened while other samples are collected a few days later.

Packaging moisture measurements made prior to loading the 3013 containers were primarily intended to determine if the material met the requirement of less than 0.5 weight percent moisture. Some packaging moisture methods, such as TGA with Fourier transform infrared spectrometry (TGA-FTIR) and TGA-MS, had the capability to provide accurate moisture content measurements, while other methods did not, such as TGA and loss on ignition (LOI). Packaging moisture measurements were often viewed as a go – no go test rather than an accurate quantitative measurement. The packaging moisture values tended to be conservative (i.e. the measurement values were biased higher than the actual values). Berg, Crowder, and Almond developed a methodology to provide a better estimate of the moisture content at the time of packaging, generally referred to as "best" moisture.[1] This method is useful when packaging moisture was measured with TGA, but does not provide an improved estimate when LOI was used. The original intention of making the DE IM sample was to get a reliable measurement of the moisture content at the time of examination, which should also be representative of the moisture content at the time of packaging.

During the course of the DE program, questions have periodically arisen concerning the ability of the IM sample to reflect reliably the actual moisture content of the entire material stored in the 3013 container. The lack of correlation between the measured moisture and the best moisture at packaging is shown in Figure 1-1; the data is from a recent query of the DE database covering the years FY2007 to FY2015. It cannot be definitively stated which value is more accurately reflect the actual moisture content of the material; while IM measurement can be affected by sample management issues (as described in this document), the best moisture values are derived from reanalysis of various measurement methods, each of which had its own sample management program and inherent biases.

Recent delays in analysis caused by maintenance issues with the TGA-MS instrument presented a unique opportunity to document and quantify the effects various factors have on the TGA-MS moisture measurement for the 3013 DE program. The concerns with the IM sample moisture measurement and sample management fall into broad categories: exposure to the glovebox atmosphere during sample collection, collection of a potentially non-representative sample, and moisture gain over time by the samples after collection.
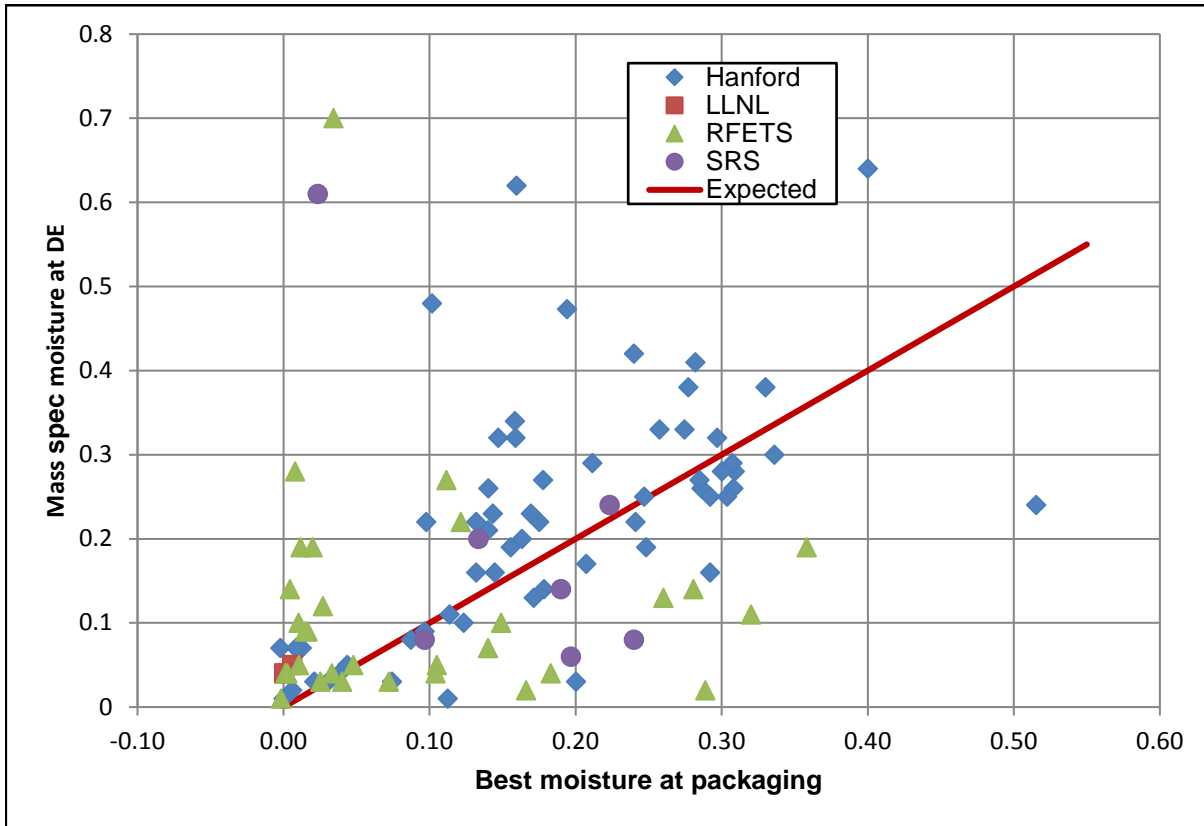
Figure 1-1. Mass Spectrometer moisture at DE vs. best moisture at packaging

2.0 Background

To begin the destructive examination process, the can is punctured and a sample of the headspace gasses is taken using the Can Puncture Device (CPD). At the end of the gas sampling process, the container is purged and backfilled with dry gas several times prior to removal from the can puncture device. This process has the potential to remove some loosely bound water from the material.

Once the 3013 is removed from the CPD, the material inside is exposed to the atmosphere via the puncture hole and begins to exchange moisture. The can is then cut open and de-nested. Although the holes made by the CPD are covered with tape as they are exposed, there is still some small exposure to the atmosphere during the cutting and de-nesting process.

The IM sample is scooped from the top of the material as soon as possible after the convenience can has been opened. There is a significant tradeoff between obtaining a sample representative of the moisture content of the material in the container and minimizing the potential to exchange moisture between the sample and the atmosphere. It has been the practice of the DE program not to take a truly representative sample but to quickly take a potentially non-representative sample and minimize sample contact with the atmosphere.

After collecting the IM sample, the equilibrium humidity of the headspace gas in the convenience can is measured. The convenience can is then emptied and the RP sample is collected. Other samples may also be collected at this time.

It is important to protect the IM sample from exchanging moisture with the environment between collection and analysis. Since the equilibrium humidities of the material in the 3013 containers are rather

low, usually less than 10% relative humidity (RH), care must be taken to ensure the sample does not gain moisture from the atmosphere in the glovebox, which is usually between 25% and 55% RH.[2] It is possible that an occasional sample could lose moisture to the atmosphere, but unlikely due to the relatively high humidities in the gloveboxes at the Savannah River Site.

After collection, the IM sample is loaded into a B-vial, which is a small stainless steel vessel, and sealed using a Buna-N o-ring. The sample then is stored until it is shipped to the Savannah River National Laboratory (SRNL) for analysis. Once at SRNL, the sample is moved to the lab module with the TGA-MS and it is analyzed. In beginning years of the 3013 DE program, it was possible to analyze the IM samples shortly after receipt, but in the past few years, there have been significant delays between receipt of the sample and analysis.

During the period from FY2013 to FY2016, frequent maintenance and subsequent calibration runs created delays in processing samples. The samples could adsorb moisture from the atmosphere during the delays, biasing the moisture measurement to the high side when it was finally made. An earlier report documented volatile halide salt deposition as a major contributor to the increase in instrument downtime and proposed lowering the final TGA temperature to lessen that problem.[3] That modification was implemented and the downtime due to instrument maintenance has been significantly reduced. Some maintenance delays still occur due to the age and condition of the instruments, as certain spare parts are no longer readily available.

While the sample collection, transportation, and storage processes have been designed to provide little opportunity for moisture exchange between the sample and environment, recent events have shown that these precautions may have been less than adequate.

3.0 Data from FY2015 DE measurements

Much of the data presented in this report come from FY2015. In FY2015, SRNL made equilibrium humidity measurements on the IM and RP samples as soon as possible after receipt, in hopes that an SRNL humidity measurement could replace the humidity measurement in K-Area. While the humidity measurements in SRNL could not replicate the data taken in K-Area, useful information on sample handling was incidentally obtained during this effort. The measured humidities are shown in Figure 3-1; the data are presented as relative humidity to compensate partially for the temperature differences between the K-area measurement and the SRNL measurement. The SRNL standards lab typically finds the error (2σ) for the types of instruments used is ±1% to ±1.5% RH.

The effect of taking a representative sample on moisture levels is also illustrated in Figure 3-1. While the measurement of the humidity of the SRNL samples never matched the KAC measurement, the equilibrium humidity of the RP sample was always higher than that of the IM sample. The increase in the moisture level is likely caused by the current method of collecting a representative sample. The time required to collect a representative same exposes the RP sample to the relatively high humidity in the glovebox for a significantly longer period than the IM sample. In general, the RP humidity was measured on the day following the measurement of the IM humidity, so increased storage time would not be a significant factor.

An instrumented cap was used to make the humidity measurement, so it was not necessary to remove the sample from the B-vial to measure the equilibrium humidity. As part of the SRNL measurement, careful weights of the B-vials were made before and after the measurement. The purpose of the weighings was to ascertain if a measureable amount of moisture was adsorbed by the sample during the period of time the humidity probe was attached to and then detached from the B-vial. The operation of swapping the lid and the humidity probe adapter was accomplished in under 60 seconds in all cases. An analytical balance with readability of 0.1 mg was used for these measurements; in contrast, the balance used to load the samples in K-Area had readability of 0.1 gram.
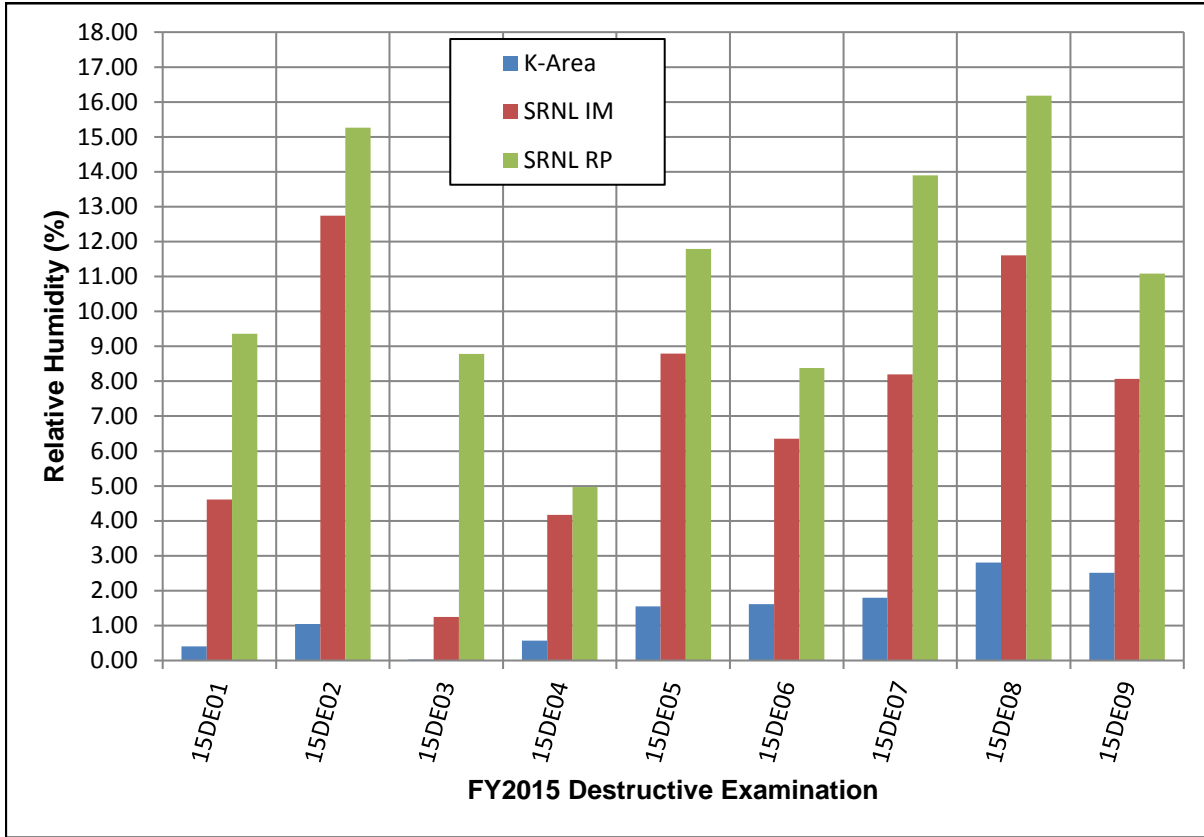
**Figure 3-1. Relative humidities for FY2015 DE bulk material in K-Area,
and IM and RP Samples in SRNL**

[Note: The relative humidity of 15DE03 measured in K-Area was 0.03%.]

Unfortunately, the amount of material lost during the opening of the B-vial always overwhelmed any weight gain due to moisture adsorption. The material loss is caused by the design of the B-vial. The B-vial was not originally designed to be used with an o-ring. Without an o-ring, there would have been a tight fit between the top of the B-vial and the bottom of the cap. When an o-ring is used, it is placed in the thread relief at the end of the threads on the B-vial. The o-ring thus prevents the cap from contacting the body of the B-vial, and allows particles of the oxide powder to become trapped in the threads. This trapped material is usually not recoverable when the B-vial is opened.

As part of material accountability in the 3013 program, B-vials were also weighed on an analytical balance immediately prior to being opened to remove material for TGA-MS analysis. Although these weighings were not intended for that purpose, it was possible to track weight gain of the material in the B-vial between the humidity measurement and the TGA-MS measurement.

After the TGA-MS measurement of the 15-07 IM sample, the TGA-MS instrument was out of service for over nine months for repairs. During this interval, periodic measurements were made of the weights of 15-08-IM and 15-09-IM to track any mass gain or loss. The weight changes of the B-vials and samples are shown in Figure 3-2, presented as a percentage of the measured sample weight. The weight gains of 15-01 and 15-03 through 15-07 averaged 10 mg, and final weight gains of 15-08 and 15-09 were both close to 66 mg.
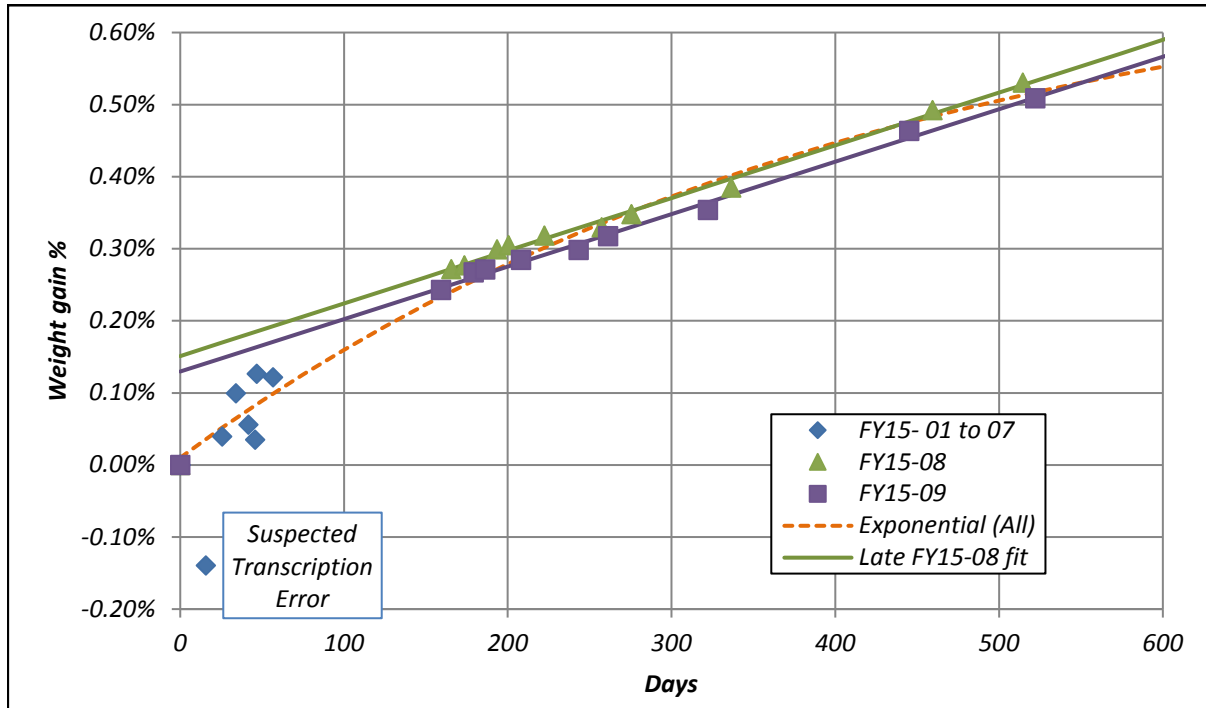
Figure 3-2. FY2015 IM sample weight gain after receipt in SRNL

3.1 Changes in moisture content due to delays prior to TGA-MS measurement

The B-vials were not originally designed to use an o-ring, and therefore the B-vial may not always seal as well as if a properly designed seal was used. Previous observations have shown that the o-ring material used allows measurable permeation of moisture; other o-ring materials would allow less permeation, but their use is not approved under the current SRNL safety basis.

Ideally, the samples are sent to SRNL within two weeks from can puncture, and the TGA-MS measurement is made within two weeks of receipt at SRNL. The ideal schedule is not always met, often due to instrument maintenance or reduced staffing availability during holiday periods. When the TGA-MS is operating properly, three samples in duplicate could be run every two weeks.

Significant delays to the TGA-MS analysis of the IM samples occurred during the FY2013 – FY2016 period, caused by lack of TGA / MS availability due to maintenance and recalibration. In particular, there were unusually long delays due to TGA-MS maintenance for FY2015 samples. Figure 3-3 shows the breakdown of the elapsed time in the TGA-MS measurement of each sample from the time of can puncture in K-Area. Three maintenance delays between 15-01 and 15-07 totaling 142 days and the first 180 days after the analysis of 15-07 were to correct problems caused by the condensation of volatile salts. Ideally, these measurements should be no more than 14 days after receipt of the sample and no more than 28 days after can puncture. The dashed line in Figure 3-3 shows the 28 day target for making the TGA-MS measurement. After the analysis of 15-07, the instrument was unavailable for operation for over nine months. At that point, the FY2016 IM samples were run first, before 15-08 and 15-09. This decision allowed more time to track the weight gain of 15-08 and 15-09.

3.2 Correction for measured moisture for weight gain during delay

The consequence of a delay in sample analysis is that the sample gains weight during the delay. The weight gain is primarily from moisture diffusing through (or possibly leaking around) the o-ring seal and adsorbing on the sample. A small amount of carbon dioxide may diffuse through the o-ring and be
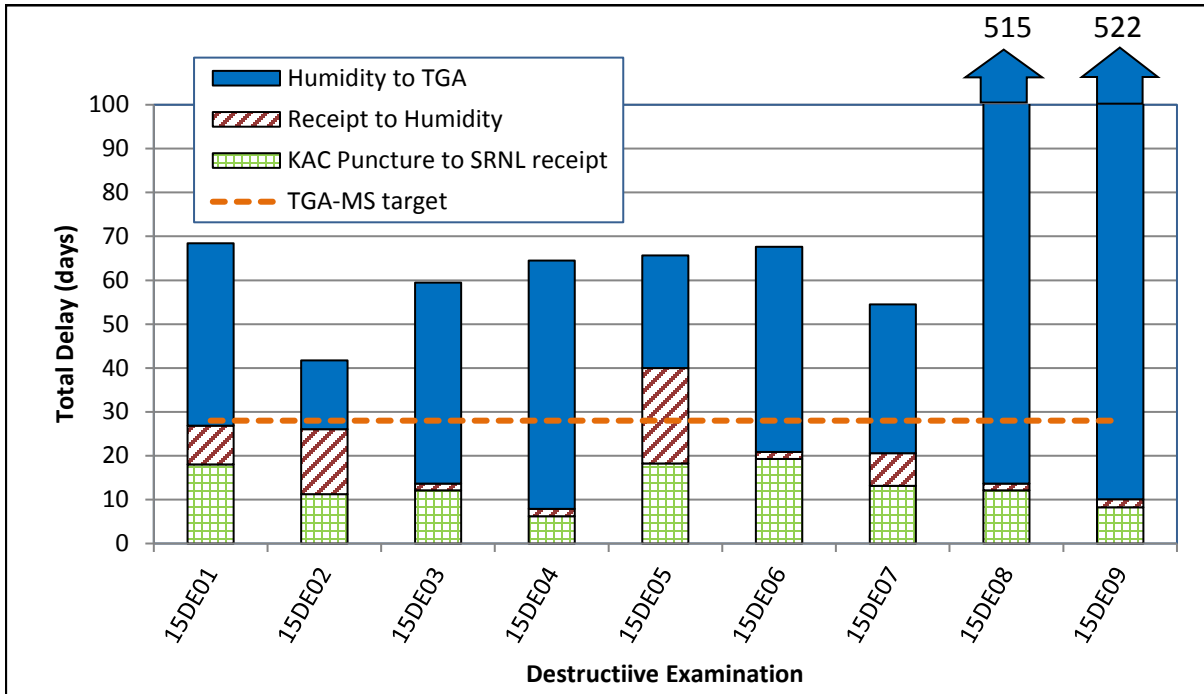
Figure 3-3. FY2015 DE - Lag in days between can puncture and TGA-MS analysis

adsorbed on the sample, but the diffusion rate of CO_2 through the o-ring is an order of magnitude lower than that of moisture.[4] It is reasonable to assume, therefore, that much of the weight gain is due to adsorbed moisture on the sample. This assumption was validated by the final TGA-MS analyses of 15-08 and 15-09, which showed typical levels of CO_2.

Using the weights recorded for the equilibrium humidity measurement and for accountability, it is possible to estimate what portion of the TGA-MS moisture measurement can be attributed to moisture gained during storage. The attribution of the moisture measurement is shown in Figure 3-4. The "X" at the top of each bar is TGA-MS moisture measurement. The solid blue area is the amount of measured weight gain due to the time between the humidity and TGA-MS measurements (assuming all the weight gain was moisture). Although the sample containers were weighed in K-Area after they are filled, this weighing is only made with a readability of 0.1 g, which is not sufficient precision to track weight gain of a small sample. Since weight change between sample collection in K-Area and the humidity measurement in SRNL could not be directly measured, it has been estimated using the slope at time zero of the exponential trend shown in Figure 3-2. This estimated weight gain is shown by the diagonally hatched area. Finally, the grid hatched region shows the remaining amount of moisture that would have been in the sample at the time of can puncture. The "best" packaging moisture is shown as a "+". The uncertainties in these estimates are not large, and it is clear that adsorbed moisture due to the lag between collection and analysis can become a significant fraction of the moisture content as measured by the TGA-MS. It is also worthy of note that in most cases, the estimated IM moisture content and the "best" moisture at packaging are in reasonable agreement.

3.3 Representativeness of the IM sample

No attempt is made to take an IM sample that was representative. Often the parent material contains hard chunks, which presents challenges when coring to obtain a representative sample. Any operation to divide and recombine the sample would increase the time the material is exposed to the glovebox atmosphere, thus increasing the opportunity for the sample to adsorb moisture. To limit the ability of the
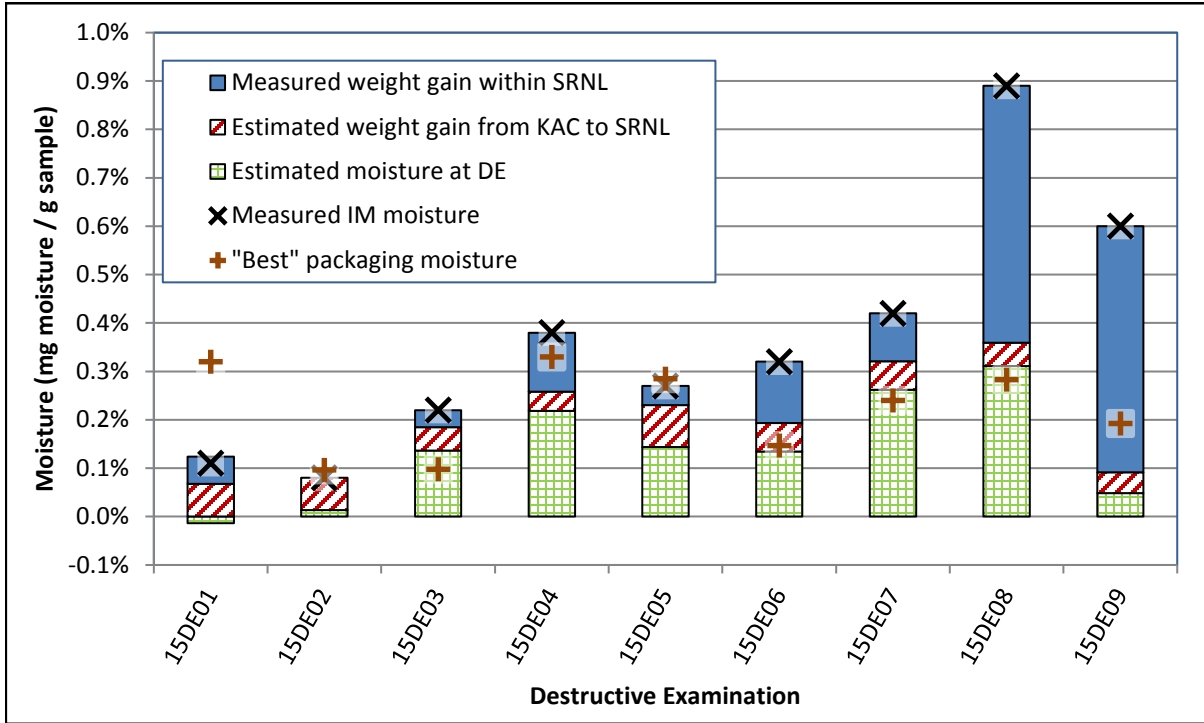
Figure 3-4. Attribution of MS moisture based on weight gain

sample to adsorb atmospheric moisture, the initial moisture samples are simply scooped off the top of the material. Since the top of the material is cooler that the center, it is likely that the sample contains higher than average moisture at the time of sampling.[5]

There are certainly other approaches to collection of the IM sample than quickly scooping material from the top of the container. However, the surveillance program has historically decided that it is better to collect a potentially non-representative sample with little atmospheric exposure than to obtain a representative sample that has had an opportunity to exchange moisture with atmosphere.

One potential method to test if a sample is representative would be to measure the equilibrium humidity of the sample immediately after it is taken. If the sample had a different equilibrium humidity than the bulk material, then one could conclude that sample was not truly representative of the bulk material. Unfortunately, this test has not been performed in K-Area. However, it may be possible to use the concepts of this test to determine if the differences between the equilibrium humidities measured in K-Area and SRNL may partially be due to non-representative sampling rather than moisture adsorption after collection. The two samples 15-06 and 15-07 are very similar materials; they have similar isotopic content, similar impurities, and have the same categorization under the 3013 surveillance program. Assuming that the moisture attribution from the measured and estimated weight gain is roughly correct, then 15-06 would have had a slightly lower moisture content at the time of the humidity measurement in SRNL than 15-07 did at the time of collection. If the samples at SRNL remained representative of the bulk material, it would be expected that the SRNL humidity measurement for 15-06 would be close to the K-Area humidity measurement for 15-07. However the SRNL humidity for 15-06 (6.35% RH) is over three times that of the K-Area humidity of 15-07 (1.8% RH). An explanation for this result is that the moisture content of the 15-06 IM sample after collection was not representative of the bulk material. It is also possible that a small amount of moisture adsorbed during sample collection would have a greater impact on the small sample than a similar amount of moisture would have on the bulk material. If the high SRNL humidity for 15-06 was due to non-representative sampling or handling during collection,

then it is reasonable to suspect that the other high humidities may also be the result of non-representative sampling, creating a bias in the SRNL TGA-MS moisture measurement.

4.0 Discussion and Identification of Potential Actions

The two problems with the measurement of moisture content of 3013 DE materials may be addressed in a number of various ways. Some potential actions are presented below to address the problem of the representativeness of the initial moisture sample or the weight gain (assumed to be moisture gain) in the interval between collection and analysis. Almost all the suggestions below can be implemented either singly or with others. The first two actions are associated with collecting or verifying the IM sample is a representative sample. All the rest of the actions, except for the last, are focused on reducing the delay or slowing the rate of moisture adsorption of the IM sample. The actions are summarized in Table 1 below.

1. Test IM sample for representative humidity

   Before being removed from the K-Area Interim Surveillance (KIS) glovebox, the humidity of the IM sample could be measured, using the same type of device SRNL used in FY2015 to measure IM humidities. The SRNL devices are still available and the humidity probe and meter are the same type currently used in K-Area. A small heating device may be needed to increase the temperature of the IM sample to match the temperature of the bulk of the material in the convenience container. The relationship between moisture content and equilibrium humidity is not well established for most 3013 materials so equilibrium humidity is not a quantitative measurement of moisture. If the humidity measurement of the IM sample differed from the bulk measurement, it would potentially indicate that the IM sample was no longer completely representative of the bulk material. However, humidity measurements that were closer may not be an indication that the IM sample is representative of the moisture content in the bulk material.

2. Improved IM sample collection

   There are commercial and custom tools that are designed to take deep core samples of powders. HB-Line uses a custom designed tool to sample material quickly for moisture measurement. The 3013 DE program could employ a similar strategy. After the convenience container was opened, an attempt would be made to take a sample quickly using a coring tool or similar device. If the first attempt was not successful, the traditional scooping method would be used. This technique could potentially improve sample collection while still keeping the opportunity for moisture in-leakage low. It has been difficult in the past to find a tool that would work with the wide variety of materials stored in 3013 containers. If it is not possible to obtain a tool that works with all materials, the use of alternate sampling processes may complicate data collection.

3. Improvements in SRNL processes

   Improvements to the process in SRNL to move the IM sample to the lab module with the TGA-MS have been made. While not a significant source of the delay between collection and measurement, the movement of the sample did occasionally contribute a day or two of delay. Now the IM sample is moved to the lab module with the TGA-MS the same day of the receipt or the following day.

4. Correct moisture measurement with precision measurement of sample weight gain

   Weight gain of the IM sample could be monitored closely by performing a precision measurement of the IM sample B-vial shortly after collection. An analytical balance with a readability of 0.1 mg could be used to weigh the B-vial in the KIS glovebox, or the B-vial and bag could be weighed after being bagged out of the glovebox. The weight would also be measured in SRNL before the TGA-MS analysis to determine the weight gain of the sample. This process would be an improvement of the method used to assign moisture content used for the FY2015 samples above, as the weight gain from after sampling in K-Area would be actually measured, rather than estimated.

Assuming that all weight gain is adsorbed moisture, (a reasonable assumption based on the 15-08 and 15-09 TGA-MS data) the measured moisture could be corrected for weight gain during the delay between collection and measurement. This method does not account for adsorption of species other than water and or radiolytic hydrolysis, but merely provides a means to somewhat correct the moisture measurement.

5. Moisture Barrier Bags

After removal from the glovebox, the IM sample could be packaged in a moisture barrier bag. These are typically heat sealable Mylar bags that have a layer of aluminum foil to reduce moisture permeation. HB-Line uses moisture barrier bags to ship oxide samples to SRNL for analysis, and to store dried desiccant assemblies. The bags do not provide perfect barriers, but could significantly reduce the amount of moisture adsorbed in a given time.

6. All metal seal sample containment

The IM sample would be placed in a container with metal seals, such Conflat seals or VCR seals. While this is a seemingly simple solution to virtually eliminate moisture permeation through the container, the current SRNL safety basis makes implementation of a "robust" container of plutonium powder difficult. SRNL has developed a preliminary design but some details remain to be worked out. A soldered plug is planned to provide pressure relief at elevated temperatures. A small test program would be needed to select solder with suitable corrosion resistant properties, and to demonstrate proper relief at temperature. It would likely take a year to develop and approve such a container for use in SRNL.

7. Conditioned sample

Take a representative sample using normal techniques, and then prior to TGA-MS analysis, condition the moisture level of the sample so that it has the same humidity at temperature as the bulk measurement of the convenience can. Available commercial equipment exists which can readily perform this adjustment. Some models of TGA are able to pre-treat samples in this manner.

While equipment exists to condition the sample, there are severe problems with this approach. First, a method has to be chosen to select what is a reasonable temperature of the bulk material, as significant temperature gradients exist in the convenience can. There is also the problem of hysteresis in the adsorption and desorption on moisture. The amount of adsorbed moisture to achieve a given equilibrium humidity may be different depending on whether moisture is being desorbed or being adsorbed to reach the desired humidity. Finally, there is the issue of hydrated salts causing large plateaus of constant humidity over a wide range of adsorbed moisture. If the observed humidity is that of a plateau, it would be impossible to choose a single value for the adsorbed moisture of the bulk material. The method also does not account for other reactive processes that might affect the equilibrium humidity.

8. Procure new TGA-MS instruments

A significant impact of using old equipment is the downtime and expense of repair and maintenance. Over the past three years, more money, effort, and time have been expended in repair and maintenance of the current TGA-MS systems than would have been needed to procure and install a new instrument. While no instrument will be free of maintenance or repair problems, a new instrument could be expected to provide a reasonable period of reliable service. A new instrument may offer other advantages that could reduce the labor hours required to make moisture measurements. Auto-loading instruments could potentially speed the development of instrument calibration curves, and improved electronics could provide more stability, requiring fewer calibrations over multiple runs. Other possibilities for a new instrument include instruments coupled with FTIR spectroscopy that could be used to detect condensing gas species that are not currently seen.

Procurement of a new TGA-MS has the potential to reduce the lag between sample collection and analysis and to reduce the cost to make the measurement.

The above actions all offer ways to improve the TGA-MS moisture measurement. However, if the 3013 surveillance program has reached a point where there is no value even to an improved TGA-MS moisture measurement, the measurement could be discontinued. Discontinuing the TGA-MS moisture analysis would eliminate all costs currently associated with the measurement. Unfortunately, it places SRNL in a position where the capability to perform TGA-MS measurements may atrophy and not be available after just a few years. Once the current HB-Line oxide production campaign ends, there will no longer be any regular users of TGA-MS other than 3013 DE. Without steady customers, it is possible that the instruments will fall into poor condition and eventually become unrepairable. Should the 3013 DE program later need TGA-MS moisture analysis, it may no longer be available at SRNL.

5.0 Conclusions

Concerns that the IM sample may not reliably reflect the moisture level of the material stored in the 3013 container are partially based on the lack of correlation between the data at packaging and at DE. Major contributors to this lack of fidelity are exposure during sample collection, the potentially non-representative nature of the collection of the IM sample, and weight gain of the sample during the lag time between collection and analysis. While the representativeness or lack thereof of the IM sample has not been experimentally quantified, it is expected to have higher moisture levels than the bulk material in the container due to temperature gradients in the container. Non-homogeneity of the material could also affect the moisture content of IM sample compared to the bulk material. Data presented in this report experimentally quantify weight gain during the lag period, at least for a subset of samples.

6.0 Recommendations

It is recommended that the 3013 DE program should either make improvements to the process of collection and storage of the sample so that it more reliably reflects the moisture level of the bulk material or give serious consideration to discontinuing the measurement.

If TGA-MS is continued in FY2018, it is highly recommended that moisture correction by weight gain using a high precision weight measurement in K-Area (action 4) and packaging of the IM sample in a moisture barrier bag (action 5) both be implemented. These inexpensive measures can be quickly implemented and will have significant positive impact on the quality of the IM sample results.

It is also recommend that an equilibrium humidity measurement of the IM sample be performed in K-Area (action 1). This will aid in determining if the IM sample is a good representative of the moisture level in the container. If the IM sample is not representative, then work could begin on making future IM sample more representative (action 2) in later years if TGA-MS analysis is continued.

If TGA-MS analysis is to continue for more than one year, then work should begin to finalize the design and approval of a metal sealed container that can be used in SRNL to store powders (action 6). Additionally, the procurement of a new TGA-MS instrument (action 8) must also be considered, as it would reduce the costs and manpower required for the moisture measurement.

7.0 References

1. Berg, J. M.; Crowder, M. L.; Almond, P. M., Relationship Between Reported, As-Packaged Moisture and Moisture Measurements Made During Surveillance of 3013 Containers. *J. Nucl. Mater. Manage.* **2010,** *38* (3), 7.
2. Nguyen, B. *Relative Humidity and Temperature Measurements*; SRNS-STI-2017-00142; Savannah River National Laboratory: Aiken, SC, January 31, 2017, 2017.
3. Scogin, J. H. *Technical Basis for the Reduction of the Maximum Temperature TGA-MS Analysis of Oxide Samples from the 3013 Destructive Examination Program*; SRNL-STI-2016-00126, Rev 0; Savannah River National Laboratory: Aiken, SC, 2016.
4. Strum, P.; Leuenberger, M.; Sirignano, C.; Neubert, R. E. M.; Meijer, H. A. J.; Langenfelds, R.; Brand, W. A.; Tohjima, Y., Permeation of atmospheric gases through polymer O-rings used in flasks for air sampling. *J. Geophys. Res.* **2004,** *109* (D4).
5. Berg, J. M.; Gupta, N. K.; Nguyen, B.; Narlesky, J.; Prenger, F. C.; Traver, L.; Veirs, D. K., Thermal Gradients and the Potential to Form Liquids in 3013 Containers. *J. Nucl. Mater. Manage.* **2010,** *38* (3), 10.

Appendix A. Summary of Proposed Actions

Table A-1. Summary of Proposed Actions

	Action	Difficulty	Effect	Cons	Earliest operation	Recommended Priority
1	Measure IM sample humidity	Low to Medium	• Potential to detects non-representative IM sample	• Does not produce representative sample • Additional equipment in KIS Glovebox (heater for B-vial)	FY2018	**2**
2	Improve IM sample collection	Medium to High	• Potential collection of representative IM sample	• Requires some development • May not work in all cases	FY2019	**3**
3	Improve SRNL processes	Low	• Reduce lag	• None	Completed	**N/A**
4	Correct measurement with weight gain	Low	• Corrects moisture measurement by subtracting sample weight gain	• Does nothing to reduce moisture adsorption • Additional equipment outside KIS glovebox (balance)	FY2018	**1**
5	Moisture barrier bags	Low	• Reduces moisture adsorption of sample	• May require additional equipment outside KIS glovebox (heat sealer)	FY2018	**1**
6	Metal sealed container	High	• Eliminates moisture adsorption by sample	• Requires container development and approval	FY2019	**2**
7	Conditioned sample	Very High	• Returns sample to conditions measured in convenience can	• Requires development • Requires new instruments	FY2021	**Not recommended at this time**
8	New TGA-MS	High	• Reduces lag between collection and measurement • Reduces cost of measurement • Could offer other improvements in measurement	• Requires instrument selection • Requires significant one time procurement • Requires installation	FY2020	**3**

Appendix B: Best Moisture and TGA-MS Moisture for DEs FY2007 to FY2014

Table B-1. Best Moisture and TGA-MS Moisture for DEs FY2007 to FY2015 DE 07

Container	Site	DE	Best Moisture	MS Moisture
H001181	Hanford	2015-04	0.33	0.38
H001191	Hanford	2016-01	0.31	0.00
H001209	Hanford	2012-01	0.28	0.38
H001236	Hanford	2013-01	0.40	0.64
H001513	Hanford	2012-03	0.31	0.29
H001916	Hanford	2008-11	0.00	0.07
H001941	Hanford	2009-04	0.01	0.02
H001979	Hanford	2015-03	0.10	0.22
H001992	Hanford	2008-07	0.07	0.03
H002088	Hanford	2008-12	0.14	0.23
H002195	Hanford	2009-19	0.00	0.01
H002200	Hanford	2009-10	0.02	0.03
H002447	Hanford	2010-05	0.04	0.04
H002496	Hanford	2010-02	0.21	0.17
H002509	Hanford	2009-06	0.31	0.26
H002534	Hanford	2008-15	0.25	0.19
H002554	Hanford	2009-03	0.24	0.22
H002565	Hanford	2009-07	0.29	0.25
H002567	Hanford	2010-09	0.04	0.05
H002573	Hanford	2008-14	0.27	0.33
H002574	Hanford	2012-02	0.14	0.26
H002592	Hanford	2011-03	0.03	0.03
H002636	Hanford	2014-09	0.01	0.07
H002657	Hanford	2009-08	0.17	0.22
H002667	Hanford	2009-11	0.16	0.19
H002715	Hanford	2009-12	0.31	0.28
H002728	Hanford	2010-10	0.16	0.20
H002750	Hanford	2008-17	0.01	0.07
H002786	Hanford	2010-11	0.25	0.25
H003052	Hanford	2014-04	0.19	0.47
H003064	Hanford	2014-02	0.30	0.28
H003077	Hanford	2010-12	0.09	0.08
H003119	Hanford	2009-18	0.10	0.09
H003157	Hanford	2008-08	0.12	0.10
H003181	Hanford	2015-05	0.28	0.27

H003258	Hanford	2015-06	0.15	0.32
H003307	Hanford	2014-03	0.17	0.23
H003328	Hanford	2010-13	0.52	0.24
H003337	Hanford	2011-04	0.11	0.01
H003343	Hanford	2011-06	0.17	0.13
H003367	Hanford	2010-13	0.13	0.22
H003371	Hanford	2011-07	0.18	0.14
H003390	Hanford	2012-04	0.11	0.11
H003409	Hanford	2008-13	0.21	0.29
H003443	Hanford	2011-01	0.30	0.32
H003526	Hanford	2011-08	0.13	0.16
H003565	Hanford	2011-09	0.16	0.32
H003625	Hanford	2011-11	0.14	0.21
H003650	Hanford	2010-08	0.29	0.16
H003655	Hanford	2010-04	0.26	0.33
H003704	Hanford	2010-14	0.28	0.41
H003710	Hanford	2010-03	0.34	0.30
H003737	Hanford	2015-07	0.24	0.42
H003898	Hanford	2014-05	0.16	0.62
H003900	Hanford	2010-07	0.30	0.25
H004012	Hanford	2012-06	0.14	0.16
H004048	Hanford	2012-07	0.10	0.48
H004099	Hanford	2009-01	0.20	0.03
H004111	Hanford	2009-02	0.29	0.26
H004219	Hanford	2014-08	0.16	0.34
H004251	Hanford	2010-01	0.18	0.27
L000075	LLNL	2012-05	0.00	0.04
L000178	LLNL	2011-12	0.01	0.05
H000898	RFETS	2008-03	0.00	0.04
R600719	RFETS	2007-04	0.10	0.04
R600885	RFETS	2007-01	0.10	0.05
R601285	RFETS	2007-07	0.15	0.10
R601318	RFETS	2008-02	0.17	0.02
R601722	RFETS	2007-02	0.18	0.04
R601957	RFETS	2007-03	0.03	0.04
R602498	RFETS	2009-05	0.26	0.13
R602731	RFETS	2008-01	0.07	0.03
R610156	RFETS	2015-01	0.32	0.11
R610298	RFETS	2008-05	0.00	0.14
R610324	RFETS	2008-06	0.01	0.10
R610327	RFETS	2008-04	0.00	0.04

R610558	RFETS	2009-16	0.00	0.01
R610573	RFETS	2009-15	0.12	0.22
R610578	RFETS	2008-10	0.02	0.19
R610584	RFETS	2008-09	0.14	0.07
R610627	RFETS	2010-06	0.02	0.09
R610679	RFETS	2008-16	0.04	0.03
R610697	RFETS	2007-06	0.28	0.14
R610700	RFETS	2009-13	0.03	0.03
R610735	RFETS	2007-05	0.36	0.19
R610764	RFETS	2009-14	0.05	0.05
R610785	RFETS	2010-15	0.01	0.19
R610806	RFETS	2009-17	0.11	0.27
R610826	RFETS	2010-16	0.01	0.28
R610853	RFETS	2010-17	0.03	0.12
R610960	RFETS	2012-08	0.03	0.70
R610996	RFETS	2014-01	0.01	0.05
R611131	RFETS	2011-10	0.01	0.09
R611398	RFETS	2009-09	0.29	0.02
S001105	SRS	2011-05	0.20	0.06
S001721	SRS	2010-18	0.19	0.14
S002116	SRS	2014-07	0.13	0.20
S002129	SRS	2011-02	0.24	0.08
S002162	SRS	2015-02	0.10	0.08
S002250	SRS	2012-10	0.02	0.61
S002277	SRS	2014-06	0.22	0.24

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Appendix C: FY2015 IM Sample Data

Table C-1. FY2015 IM Sample Weight Gains

Sample	Sample mass (KAC) (g)	Weighing Date	Days from Initial	Measured Weight (g)	Weight Gain (mg)	wt% Gain
15-01-IM	12.9	2014-12-11	-	119.9580	-	-
		2015-01-22	41.5	119.9652	7.2	0.06%
15-02-IM	12.7	2014-12-30	-	119.7971	-	-
		2015-01-15	15.7	119.7794	-17.7	-0.14%
15-03-IM	12.8	2015-01-23	-	119.8550	-	-
		2015-03-10	45.8	119.8595	4.5	0.04%
15-04-IM	10.1	2015-02-12	-	117.2368	-	-
		2015-04-10	56.6	117.2491	12.3	0.12%
15-05-IM	12.9	2015-03-25	-	119.6550	-	-
		2015-04-20	25.7	119.6601	5.1	0.04%
15-06-IM	12.8	2015-05-07	-	119.0275	-	-
		2015-06-23	46.7	119.0437	16.2	0.13%
15-07-IM	12.8	2015-05-27	-	120.0163	-	-
		2015-06-30	33.9	120.0290	12.7	0.10%
15-08-IM	12.7	2015-06-18	-	119.9945	-	-
		2015-12-01	165.4	120.0290	34.5	0.27%
		2015-12-09	173.4	120.0297	35.2	0.28%
		2015-12-29	193.4	120.0325	38.0	0.30%
		2016-01-05	200.4	120.0332	38.7	0.30%
		2016-01-27	222.4	120.0349	40.4	0.32%
		2016-03-02	257.4	120.0364	41.9	0.33%
		2016-03-20	275.4	120.0387	44.2	0.35%
		2016-05-20	336.4	120.0434	48.9	0.39%
		2016-09-20	459.4	120.0570	62.5	0.49%
		2016-11-14	514.4	120.0619	67.4	0.53%
15-09-IM	12.8	2015-07-02	-	120.1085	-	-
		2015-12-09	159.2	120.1396	31.1	0.24%
		2015-12-29	179.2	120.1427	34.2	0.27%
		2016-01-05	186.2	120.1432	34.7	0.27%
		2016-01-27	208.2	120.1449	36.4	0.28%
		2016-03-02	243.2	120.1467	38.2	0.30%
		2016-03-20	261.2	120.1491	40.6	0.32%
		2016-05-20	322.2	120.1538	45.3	0.35%
		2016-09-20	445.2	120.1678	59.3	0.46%
		2016-12-06	522.2	120.1736	65.1	0.51%

Table C-2. FY2015 Humidity Data

DE	Can Humidity Date	K-Area RH (%)	K temp (°C)	K partial pressure (Pa)	IM RH Date	IM RH (%)	IM Temp (°C)	IM partial pressure (Pa)	RP RH Date	RP RH (%)	RP Temp (°C)	RP partial pressure (Pa)
15-01	2014-11-14 22:41	0.40	25.0	12.7	2014-12-11 19:01	4.61	25.08	146.8	2014-12-29 16:00	9.36	23.08	264.4
15-02	2014-12-04 17:29	1.05	30.6	46.2	2014-12-30 18:00	12.74	22.54	348.3	2014-12-31 16:19	15.26	23.35	438.1
15-03	2015-01-09 21:30	0.03	27.8	1.1	2015-01-23 12:50	1.25	22.78	34.7	2015-01-23 18:25	8.78	22.75	243.1
15-04	2015-02-04 19:20	0.57	25.2	18.2	2015-02-12 17:07	4.17	22.55	114.1	2015-02-17 21:48	4.97	21.62	128.5
15-05	2015-02-13 17:20	1.55	29.0	62.2	2015-03-25 16:37	8.79	24.20	265.6	2015-03-26 15:49	11.79	23.51	341.8
15-06	2015-04-16 17:20	1.61	28.6	62.9	2015-05-07 14:50	6.35	20.69	155.0	2015-05-06 18:45	8.38	20.58	203.2
15-07	2015-05-06 21:21	1.80	29.3	73.5	2015-05-27 11:05	8.20	22.99	230.4	2015-05-28 09:26	13.90	22.65	382.5
15-08	2015-06-04 21:42	2.81	27.3	101.8	2015-06-18 13:28	11.61	23.66	339.6	2015-06-24 09:30	16.18	24.04	484.3
15-09	2015-06-22 17:03	2.51	27.4	91.4	2015-07-02 18:57	8.07	23.33	231.4	2015-07-07 18:19	11.08	23.45	320.1