Loss-on Drying and Other Moisture Mysteries

by Art Gatenby

Chapter One:
Loss-On Drying

One quiet night, I was musing over moisture analysis and how easy it is to do using loss-on drying. Little did I know what was in store.

Of course, everybody knows that all you do is:

1. Weigh a sample,
2. Dry it out, and then
3. Weigh it again.

However, I decided that a modicum of research about drying would be prudent before I started. As I got into it, this small inquiry into moisture testing expanded into a lot more about evaporation, vapor pressure, water content complexities and – *SPOOKIEST OF THE BUNCH* – water activity, all just to determine the effects of drying something.

Do I talk about it all at once or break it into individual mysteries? I found the former approach overwhelming, but with respect to the latter – where to start?

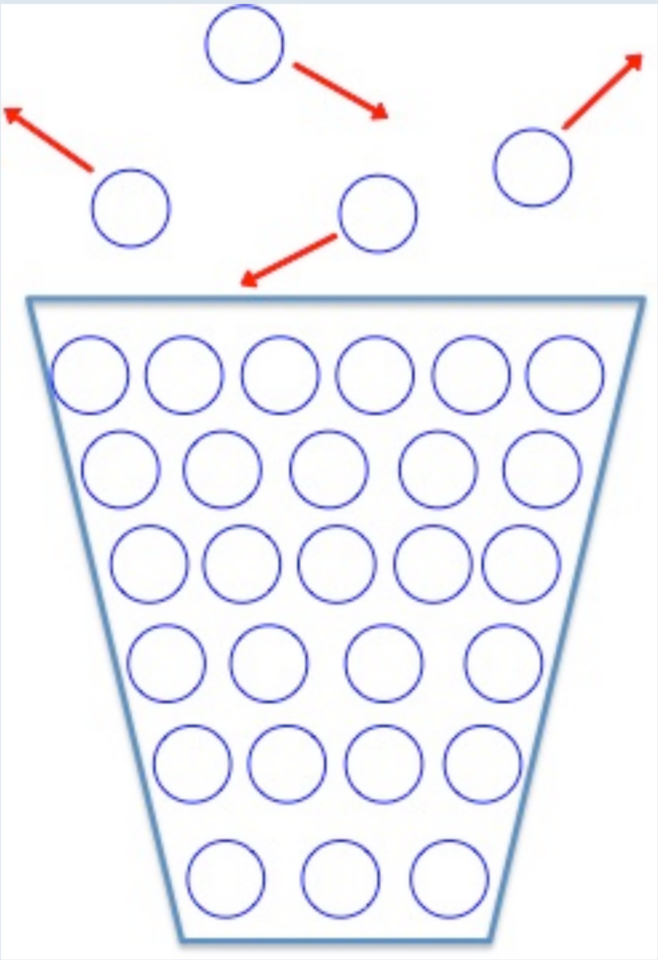
After brooding for a while, I concluded that evaporation was an important aspect to the loss-on drying process; simple in concept and easy to understand. Consequently, I start with evaporation because it is elementary (as long as you don't consider the influence of vapor pressure, atmospheric pressure, temperature and humidity, but we'll consider some of those influences later).

It seems that evaporation is all about water molecules bumping into each other. If they are highly agitated by an energy source, they fly away from their neighbors and transform a closely packed liquid into a loosely packed gas or vapor. At various times, the flow balances: some switch to vapor, some switch back to liquid (or as we know it, water). Changing the ambient pressure, temperature or humidity changes this balance, requiring more or less energy to affect the evaporation volume.

When things settle into equilibrium, the gas molecules sit at the liquid surface and exchange positions with the liquid molecules. At this gas-liquid boundary, vapor pressure increases with heat and decreases when cooled. The more the vapor pressure, the more flying gas molecules are generated, thus resulting in more evaporation.

The energy, usually heat, gets the highly agitated molecules to fly out of the liquid. These hot ones leave behind the cooler ones, cooling the liquid. This is how perspiration evaporating from your brow cools you on a hot, dry summer day.

All of these influence loss-on drying tests. I thought it was “just turn on the heat and wait”, with no consideration for bouncing molecules, seasonal temperature fluctuations, or weather-related variables to confuse and change evaporation rates. Now we know some of the reasons that loss-on drying tests sometimes take longer or shorter than normal.



Chapter Two:
Vapor Pressure

Let’s start with a definition:

> *Vapor Pressure is the equilibrium pressure of a vapor above its liquid, or the pressure of the vapor resulting from evaporation of a liquid above the sample.*

To refresh the image from the previous chapter, evaporation is molecules bouncing out of a liquid into a gas. When the evaporation settles down rather than flying off into the vapor, the molecules above the liquid in the vapor or gas ,continuously exchange places with the molecules at the surface of the liquid, the liquid and vapor are in equilibrium. That is when you have Equilibrium – Vapor Pressure.

This vapor pressure is a unique characteristic of a pure liquid. The molecular bonding of the pure liquid defines its unique vapor pressure.

- Weak bonding high vapor pressure.
- Strong bonding low vapor pressure.

To see how it works you have to look at the dynamics. For any pure liquid, dynamics fortunately are only related to temperature. We stated that each pure liquid has a unique vapor pressure, but that value changes with temperature. Unique, but changing – can that be accurate? Yes, because a unique vapor pressure is defined at a each temperature. It goes up as the temperature rises and goes down as the temperature declines.

Fortunately for our understanding, the surface area of a liquid has zero effect on Vapor Pressure. I'm not 100% sure why I even mention this except that if this was not a constant, it would confuse the energy issues related to getting evaporation, which is why we started this whole rant.

Because we are rambling about moisture, the liquid we refer to will be water. To generate evaporation and get the water out, which we need to do when we conduct Loss On Drying Tests, energy needs to be added to the test sample. The energy is some form of heat, which increases the Vapor Pressure; the molecules start bouncing around and move from the liquid state to gas. With loss-on-drying moisture test equipment, the gas or water vapor is moved away from the sample so that the water vapor has no chance to get back to the water surface and start an equilibrium exchange with the water.

That's how Vapor Pressure relates to a loss-on drying moisture test.

Chapter Three: Free and Bound Water

The easy part of the loss-on drying concept is free [or unbound] water. This is water in or on the surface that will evaporate with a moisture balance.

Things get tricky when we consider bound water, which may be caught in *capillaries, fibers or held onto via chemical reactions.*

You may recall that when water vapor pressure is at equilibrium, nothing evaporates. When the sample is heated, the vapor pressure rises and the water will begin to evaporate – which does a neat job of reducing the sample's weight. This weight stops changing when all of the water is gone, allowing us to determine the amount of water via the attendant weight change.

But wait! *All of the water may not be gone*. Bound water – which, it turns out, has a lower vapor pressure than the pure water we just removed – did not evaporate. A paradox, perhaps: we seemed to have gotten rid of all the water, but maybe did not because the bound water still remained.

How do we know if there is any of this bound water left? The answer depends upon the test material's hydro-characteristics. **Hygroscopic** materials attract water and find ways to bind the moisture while non-hygroscopic [or **hydrophobic**] materials keep water out of the capillaries, the fibers and the chemical reactions.

Some examples of hygroscopic materials are biological materials, sugar, and some engineered polymers. Examples of hydrophobic materials are hydrocarbons, fats and lipids.

There are exotic ways to determine if and how much bound water remains. There also are intricate techniques to remove most of this residue.

Before attacking these, a question should be asked: *should we care about the presence and amount of bound water?*

Chapter Four: Water Activity

Loss-On-Drying moisture analysis seemed like a simple process until, in a naïve state of bliss, I promised to consider the effects of evaporation, vapor pressure and bound water. While I was otherwise occupied with these realities, I offered to enter the world of witchcraft and folklore: also known as water activity.

I offer what will hopefully be an uncomplicated definition of water activity:

> *Water Activity: the energy or escaping tendency of water.*

I would be happy if I could leave it at that, but I am compelled to relate water activity to good old Loss-On-Drying. Unfortunately, the concept begins in the complex world of Boyle, Charles and Dalton and their gas laws. These populate the Ideal Gas Law with considerations of pressure, partial pressure, temperature (at Kelvin no less) volume, molecules and moles.

Herein is my attempt to integrate these physics/chemistry phenomena to formulate a comprehensible description of water activity.

Let us first reflect upon a question I recently posed: “Should we care about the presence and amount of bound water?”

The answer is very often yes, and the reason frequently involves water activity. There are many reasons water activity – also know as a_w – is important. If it is too high, it can cause spoilage, browning, mold growth, clumping and a host of other unpleasant effects. In fact, excessive water activity can screw up a perfect blend of fruit and breakfast cereal (with dried up fruit and soggy corn flakes).

It seems that water has an energy quotient that can lead it to enhance chemical reactions, cause bad things like bacteria growth or mix with other materials to mess up a good combination of components. Moisture content alone is not a predictor of this energy, however.

Each material has a natural relationship between moisture content and water activity, called its Moisture Sorption Isotherm (MSI) defined as:

> *The relationship at equilibrium between water content and the equilibrium humidity of a material.*

This is effectively a moisture fingerprint. These isotherms change with temperature so it is not a static attribute.

The implications of water activity in the food industry are related to shelf-life, contamination, health, texture and taste issues. Thus, the a_w measurement is becoming an ever-increasing factor in food product design and food process quality control.

Also, water activity is becoming a serious consideration in the development and production of pharmaceutical products. It is water activity and its relationship to moisture content [not moisture content alone] that determines whether microorganisms can access water in a system, adding an important dimension to production process control.

The relationship of a_w to moisture content is likewise of growing importance in other products where water action affects either the production process or a product's physical characteristics.

Water activity measurement is a relative humidity technique; a comparison of a sample's vapor pressure at equilibrium to that of pure water. The measurement consists of placing a sample in a closed space, waiting for equilibrium to be reached and then measuring the resulting relative humidity in the air space. This is done using a calibrated capacitance cell or a chilled mirror (a technique that gets a dew point and converts that to relative humidity). The a_w number is the percentage of relative humidity divided by 100.

Knowing the MSI of a product, you can convert moisture content measurements to water activity. Loss-On-Drying results can be converted to water activity for many products. When the Loss-On-Drying process removes only -- and all -- of the water, a conversion of the moisture percentage to a_w can be made with the MSI for the product.

In my musings and reflections on the science of the gas laws and mystical scientific witchcraft of water activity, I decided that to get you past a superficial understanding of water activity, you need a more expert source.

To get in-depth understanding about the action of water activity and how the measurements are used, I recommend Dr. Ted P. Labuza (tplabuza@umn.edu) at the University of Minnesota. He is an internationally recognized expert on water activity. You can find a bio of Dr. Labuza and a link to his publications at this site.

Chapter Five:
Drying

This voyage has taken me down mysterious paths through spooky theories, back to age-old chemistry concepts and into the vagaries of thermodynamics related to evaporation, vapor pressure, bound water and water activity. I have come full-circle: back to explaining loss-on drying – a form of drying that I had assumed would be the simplest of all.

I thought the first four topics (evaporation, vapor pressure, bound moisture, water activity) were tough, complex, and confounding. Drying – defined as “the mass-transfer process of removing water (or other solute) by evaporation from a solid, semi solid or liquid” – seemed easy.

As is often the case, reality makes “easy” a non-operative word. Such has turned out to be so with respect to the issue of drying.

To begin with, there is the process in which heat is transferred to create a temperature in a solid that evaporates moisture from the surface and causes it to migrate from the inside outward. This internal migration occurs through several mechanisms such as diffusion, capillary action and the internal pressure created by shrinkage. It is not as simple as hanging laundry on a clothesline to dry on a breezy, sunny day.

First, there is the initial and underlying issue of product classification. Here are some examples:

- Non-hygroscopic Capillary Porous Solids: These are materials such as sand, crushed minerals, certain crystals, polymer particles and some ceramics. They have recognizable pore space filled with liquid, little bound moisture and do not shrink on drying.
- Hygroscopic Porous Solids: Clay, molecular sieves, wood, textiles, silica gels, alumina and zeolites are examples. They are characterized by clearly seen pore space, physically bound moisture and shrinkage in the early stages of drying.
- Colloidal (non Porous) Solids: Examples include soap, glue, polymers like nylon and various food products. There is no pore space and all moisture -- *except that on the surface* -- is physically bound.

There are other less-common classifications and combinations as well.
In the drying process, the rate of moisture removal varies widely between these classifications. In some, the rate is linear throughout. In others, the removal-rate is high at the beginning and diminishes as drying progresses [as illustrated in the dreaded drying-rate curves]. The principles of evaporation, equilibrium pressure, vapor pressure, partial pressure, temperature, relative humidity, dew point, moisture

sorption isotherms and ideal gas laws all apply. As you may remember, some of these concepts have effect in other sections of the Moisture Mysteries Series. They all apply to this concluding phenomenon of drying, to which in the beginning I naively referred as just plain drying.

Most products from today's industry undergo drying at some stage. For example, drying is an important element in a wide range of products such a food, pharmaceuticals, lumber, paper, fiberboard and a host of chemical products. In fact, approximately 10% of the energy consumption in the US and Canada is directly related to production drying.

All of the issues that stretched my thought process are present with the development of production systems. Consequently, dryer designs are not universal across product classifications because of the inherent complexities in the drying process. Production drying systems are developed for specific products. These include convection, belt, fluid bed, rotary, spray, flash and drum dryers.

One of the more difficult issues is to get at is the bound water. Among other techniques to deal with this is freeze-drying. Additionally, there are mechanical methods of removing moisture [e.g. centrifuging] that are referred to as dewatering rather than drying.

A compromise is often sought between the cost of transportation (lower moisture) and the cost of drying. Further, the level of drying is often a measure of a product’s suitability for market -- i.e. color, flavor, shrinkage, palatability and cracking. To check the effectiveness of these processes in meeting the diverse objectives, the moisture content after drying needs to be determined. The most frequently used technique of moisture determination is Loss-on Drying. That was the reason for this series of articles that sought to explain the factors of drying.

The loss-on drying moisture measurement process involves all issues and considerations concerned with production drying. People regularly ask us, “at what temperature should we run the test and for how long?” This discussion of drying should help them understand why we reply, “it depends”.