



WHITE PAPER:



Sample Drying for Freeze Point Tests

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The purpose of the various ASTM/EI methods for measuring freeze point of jet fuels is to determine the freeze point caused by the hydrocarbon components in the base fuel, not the water in jet fuel. Removing water from the sample prior to freeze point testing is useful in improving the precision of freeze point results. For a single operator using one piece of apparatus, he/she will find the results more consistent; in other words more repeatable. If drying is practiced by more operators and laboratories, the results will be more agreeable among those parties. That means reproducibility can also be improved.

By removing water, the occurrence of ice crystals and the haziness caused by free water in a freeze point test is minimized; hence the appearance and disappearance of hydrocarbon crystals become the dominant, if not the only events that take place during the cooling and warming of the sample. These events become more distinct and easier to identify as there are fewer or even no observable ice crystals in the sample to confuse the operator or the instrument.

For wet samples such as those coming directly out of a process (for example, a steam stripper), the use of a drying step is prudent, and often indispensable regardless of which ASTM/EI method is used for determining freeze point. Very often, stream samples have a milky appearance at room temperature, especially when they are freshly taken from the process. Without a drying step, the freeze point of such samples could be very unrepeatable, due to the excessive amount of ice crystals in the sample that could obscure the observation on the melting behavior of the hydrocarbon crystals. Not drying such a sample prior to freeze point test is imprudent. For the same reason, online analyzers that are commonly used to monitor freeze point depend on the efficiency of a good sample conditioner to remove water from the sample prior to analysis.

For jet fuel that is already dried – such as finished products – there is usually no benefit in freeze point results if one tries to dry further. However, there is no harm in drying an already dried sample either. It is just unnecessary. Regardless, some laboratories choose to dry all samples to ensure good repeatability, as moisture level in a jet fuel sample cannot be reliably judged based on visual inspection. Also, some samples – such as hydrocracked jet stocks – are known to be interfered by moisture at low levels that are beyond visual inspection. On that basis, laboratories that demand high freeze point precision justify drying all samples prior to freeze point testing.

Samples can also pick up water from the air if left exposed. Therefore, even if a sample is dry to begin with, if no additional precautions (for instance, sealed in air-tight containers or kept by nitrogen purging) are used to prevent moisture intrusion, the fuel can still be vulnerable to interference by moisture over an extended period.

Fuels used as QC references are continually used for a long period of time, so it is prudent to maintain a drying procedure for them.

A minimum requirement of any water removal technique is that it removes water only. It should not remove anything that would change or affect the hydrocarbon freeze point. Filtration is commonly used to dry jet fuel. We are not aware of any concern with filtration having an effect in changing the hydrocarbon freeze point. The general complaint with filtration is the work involved in setting up the apparatus: funnel, filter paper and receiving beaker, etc. Also, all the utensils have to be cleaned afterwards, causing more work, and consuming and disposing solvent. The method is not particularly environmentally friendly.

In the past 40 years, molecular sieves (DrySac) are also widely used in laboratories and in process to dry organic liquids (Notes 1,2). Molecular sieves are used in the form of small beads (or pellets). Drying is effected by adsorption of water molecules on the bead surface. In addition to the exterior surface of the bead, there is a much larger (in the order of many thousand times) interior surface that can be accessed only by the water and other similarly small-sized molecules through pores on the exterior surface. These pores lead into a massive network of channels. The surface of these channels is responsible for almost all the adsorption activity.

The hydrocarbon molecules in jet fuels are much larger than the pore diameter (Note 3); consequently, they cannot get into the interior surface and be adsorbed. Also, molecular sieves are selective in their adsorption activity; only polar chemicals such as water are adsorbed. Non-polar chemicals such as paraffins, which are known to be responsible for wax crystals (solute phase) in jet fuel freezing, are not attracted to the molecular sieve.

One may ask, “How about the polar components in jet fuel? Would they get adsorbed and change freeze point?” These are very valid questions. One needs to have a reasonable and balanced perspective of the situation.

There are three reasons why we believe the effects are negligibly small. First, the total amount of polar chemicals – such as those that bear an oxygen, sulfur or nitrogen group – in jet fuel is low, typically below fraction of a percentage in finished products (though could be a little higher in stream components). Secondly, these molecules are also too large to be adsorbed into the interior surfaces of the molecular sieves. They could be adsorbed onto the exterior surface, which is proportionately a much smaller area. But they would have to compete with water, which is strong in polarity and more agile. Thirdly, even if one were to assume that all the polar hydrocarbons are adsorbed, which is an unreasonable and pessimistic assumption, the impact of such a scenario on freeze point is still expected to be low and most likely negligible. This is because not only

the total concentration of polar chemicals is low, but also they are typically not the solute phase that is responsible for crystallization in jet fuel. Based on our experience, a concentration difference of the magnitude in discussion is not likely to produce a measurable change in freeze point.

There are additional important facts that we can consider.

1. Molecular sieve would not be as important today as a drying agent for organic liquids if it favors adsorption of organics (or hydrocarbons) over water to the extent that an important property is compromised.
2. A number of studies by ASTM, Phase Technology and other oil companies have supported the observation that molecular sieve has no impact on jet fuel freeze point (see Dr. Gordon Chiu's presentation to EI in July 2007 and ASTM in December 2007)
3. Molecular sieve in the form of DrySac is used by many petroleum laboratories around the world to dry jet fuel samples. It would be hard to imagine that the chemists and technologists in these laboratories would, for over ten years, use DrySac if (a) it does not improve precision, and more importantly; (b) it significantly changes the hydrocarbon freeze point of their samples when compared to, say, results from a referee method.
4. We treat our samples, particularly the very precious validation samples, with molecular sieve (DrySac) prior to freeze point testing. We do this not just because of the reported functions of molecular sieve; but also because of our good experience with it for over twenty years. Some of our validation samples are old; but they are still giving the same freeze point as they were years ago in round robin tests.

We have also, in many occasions, tested old samples without any pretreatment with DrySac. Some of those results had shifted away from the original round robin values. With subsequent treatment with DrySac, the results often returned to the original targets. While we are not claiming that molecular sieve is always effective in improving precision; but in the interest of "playing safe", we use it regularly.

5. Speaking purely by experience, our technical staff conduct hundreds of freeze point tests every working day, many of those tests are done for research purposes. Maintaining the integrity of test samples is of paramount importance. The last thing that we want is an unintentional change in freeze point caused by an external factor such as the drying agent. It would be very hard to convince any of our technical staff not to use DrySac on their samples. They would quote both their positive experience and the complete lack of negative experience to justify its use.

Science is only as good as our observations and the limitation of human intelligence in interpreting the observations. If one were to put a lot of effort into finding a system that behaves differently from what is being discussed, one could possibly find such an exception(s). But then, one should also ask, "How useful are these systems in representing the fuels that are processed and

handled by the petroleum industry?" and "Is the loss of accuracy on these selected (most probably rare) samples significant enough to warrant an industry-wide ban on sample drying and thus forgo the ability to test stream samples and with good precision on other samples?"

In conclusion, there is no data that convinces us to change methodologies. We believe the decision on sample drying should be left with the individual laboratories.

They are in the best position to understand their own requirements. If they are not sure what to do, they could conduct their own experiments and decide for themselves whether or not drying is needed.

NOTE

1. See for example, an industry brochure "on the use of molecular sieves (www.axens.net/pdf/products/Axens_adsorbents.pdf) listing "Jet fuel drying" as a principal application of molecular sieves in the refining industry.

2. Many academic studies (see for example, N. Foster *et al.*, *Sensors and Actuators*, **B77** (2001), p. 620-4, section 2.1) use molecular sieves to remove water from transmission, hydraulic, and engine oils, some of which containing even heavier cuts (higher boiling components) than in jet fuels.

3. For example, the hydrocarbon species adsorbed by molecular sieve type 4A, besides water H₂O, are limited to light molecules and small carbon number members such as "SO₂, CO₂, H₂S, C₂H₄, C₂H₆, and C₃H₆." (ref: www.sigmaldrich.com/Brands/Aldrich/Tech_Bulletins/AL_143/Molecular_Sieves.html, www.asge-online.com/pdf/MSieves.pdf, or www.emersonprocess.com/valveautomation/Bettis/download_files/product_brochures/MolecularSieve.pdf).

Another reference (www.tower-packing.com/Dir_molecular_sieve.htm) lists the order of adsorption rate as "argon, krypton, xenon, ammonia, carbon monoxide, C₂H₄, C₂H₂, CH₃OH, C₂H₅OH, CH₃CN₂, CS₂, CH₃Cl, CH₃Br, and carbon dioxide", and states that molecules of effective diameter > 4Å, e.g., C₃H₈ (propane) are excluded.

In contrast, typical jet fuel (kerosene) has a carbon number distribution between 6 and 16 carbon numbers (ref: 2006 Chevron Aviation Fuels Technical Review (www.chevronglobalaviation.com/docs/aviation_tech_review.pdf)). Hence the probability that hydrocarbon components in the jet fuel would be removed by molecular sieves is diminishingly small.