Karl Fischer Analysis of Strong Acid Samples

Aliquots of strong acid (concentrated H2SO4) were analyzed to establish the optimum method and determine reproducibility. Following titrant standardization and minor method development, five samples were analyzed. The average determined moisture content was 4.851%. The population standard deviation was 0.16%.

Instruments: Schott Titroline KF Karl Fischer titrator, Mettler AE160 analytical balance.

Reagents: GFS WaterMark Titrant Catalog Number 99661 (1 L: nominal 5.0 mg/mL titer. Lower titer may be substituted for low moisture content samples.) GFS WaterMark KF Buffer Solution Catalog Number 99801 (A buffered solvent is required for strong acid analysis) Water Standard: Riedel de Hahn 10 mg/mL or equivalent.

Pre-analysis: The Titroline KF was assembled per manufacturer's instructions. The KF titrant titer was determined using the automated "Standardize using Solution" method and determined on repetitive analyses to be 5.17 mg/mL.

Procedure:

1. 1. Following the manufacturer's instructions, choose the sample analysis mode. Default system settings may be used. Only two changes were made to the default system settings: the extraction time and endpoint hold times were each raised from 10 to 15 seconds.
2. 2. Using the "fill" arrow on the stirring assembly, add approximately 75 mL of buffered solvent to the titration vessel. To make subsequent analysis more consistent, mark the front of the vessel with a permanent marker to establish a volume "target." The precise volume is not critical: it is important that a consistent volume be used, and that the volume is sufficient to buffer the acid that is to be added in the analysis. Stirring is important, and for these analyses was set at approximately 3.5 on the scale. See Note 1.
3. 3. Press the "Start" button and allow the system to come to equilibrium. That should require approximately one minute, which allows time for the sample to be prepared. (In this series, the sulfuric acid was introduced by syringe. Appropriate sample introduction will depend on the sample type.) When the vessel is at equilibrium, the solvent should be a clear yellow to brown color. See Note 2.
4. 4. When the vessel has reached equilibrium, press the "Start" key a second time. A sample number will appear. Press "F1" to accept the sample number. This number is important only if the data is being printed, or if you wish to re-calculate sample data later (if a sample weight is incorrectly entered, for example).
5. 5. The system will now prompt for a sample weight. Pre-weigh the sample container. Introduce the sample into the titration vessel in an appropriate manner. The solution in the vessel will lose its yellow color and should be completely clear (with the exception of any color introduced by the sample itself). It is very important to minimize the entry of moisture from the air into the cell. The sample must be introduced without opening the reaction cell to ambient air if at all possible. A needle entry through the septum is preferred to opening the septum, if it possible. See Note 3.
6. 6. When the sample has been introduced, re-weigh the sample container. Using the directional arrows on the front panel, input the sample weight. When the weight is correct, press "F1" to

begin the titration. Following a delay (set in the system settings, currently 15 seconds), the titration will begin. The system will first add small aliquots of titrant to determine the relative nearness of the endpoint. The addition rate will accelerate to quickly approach the endpoint, then slow again to avoid overshooting. The titrant should mix easily in the solvent/sample mix. If the sample has introduced too much acid and overcome the buffer capacity, the titrant may form distinct droplets and not mix well. In addition to this visible evidence, a less distinct endpoint may be developed, and the "correct" endpoint may be overshot, resulting in excess use of titrant and high results. These problems are avoided by using the correct amount of solvent (to provide buffer) and adjusting the sample size (to avoid exceeding the buffer capacity). Results from samples run when the buffer capacity has been exceeded should be suspect.

7. 7. When the sample is complete, the results will appear on the display. The results should be recorded at this time, although they are available for review or recalculation at a later time if needed.
8. 8. Lower the Teflon tube that removes solvent to the bottom of the titrant vessel. It may interfere slightly with the stir bar, which is not a problem at this point. Press the "Empty" button (arrow pointing to the back of the titrant vessel stand) until all solvent is removed from the vessel. A small volume of fresh solvent may enter from the inlet tube, which is normal. See Note 4.
9. 9. When the vessel is empty, pull the solvent drain tube up until its end is above the level of the solvent in a "filled" vessel.
10. 10. Refill the vessel and go back to Step 3.

Notes:

1. 1. The Karl Fischer reaction is pH dependent. It is important that the pH not be allowed to enter a strongly acidic range, as erratic results will result. The required solvent will buffer 5 millimoles of acid per mL of solvent. Using (approximately) 75 mL of fresh solvent each analysis, 375 mm of acid can be adequately buffered. The molecular weight of HF is 36.5. Therefore, approximately 13.5g of acid could be introduced before the buffer is exceeded. 10g of sample as a practical maximum is recommended. The sample size may be varied. If it is practical, a total weight of water in the introduced sample of 10 to 75mg is recommended. This would result in a titrant volume of 2 to 15 mL, using the recommended titrant. This allows for both rapid and accurate analyses. The volume of solvent, sample size and titrant may all be adjusted to achieve optimum results.
2. 2. The final endpoint is somewhat arbitrary. The important feature is not the precise color or final current reading, but that the color or current reading is accurately reproduced. 20 microamps is a common endpoint reading. If you desire a "darker' endpoint, the final current reading may be adjusted in the system settings to a higher number. It will result in a darker color. However, since the color (and current) present at the initial conditioning step is repeated at the endpoint, the volume of titrant used in the sample analysis is unaffected.
3. 3. In order to determine the effects of excess acid on the titration, I intentionally added excess acid in some cases: I titrated multiple samples without changing the vessel solution. There were several obvious effects. First, in samples using fresh solution, the liquid became completely clear and colorless on the addition of the sample. In an over-acidified sample, the solution became quite cloudy upon sample addition. In fresh samples, the titrant mixed virtually instantly in the stirred solution. It simply "tailed" into the clear solution, with the deep brown/red color of the titrant dispersing evenly. In over-acidified solutions, the titrant broke up into small "balls' and

took several seconds to disperse. It appeared to be oily, and there was a distinct separation of what looked like organic and aqueous layers for a short time. At the endpoint, the solution was cloudy, rather than clear, yellow. In most, but not all cases, the over-acidified samples used more titrant. Their average calculated moisture content was approximately 5.3%, rather than the 4.85% of the properly buffered samples. These tests were performed with sulfuric, rather than hydrofluoric acid, so the physical appearance may not be consistent. However, you should expect that sample that exceed the buffering capacity of the solvent may exhibit unusual physical, as well as analytical results. There are several reasons that the system must be properly buffered. The first and most obvious is that the accuracy of the results depends on it. Also, HF will strongly attack the vessel and electrode. Buffering the system will reduce the speed of that attack. The vessel should be emptied promptly at the end of each analysis. It would add to the cost of analysis in general, but I recommend that, if a second sample is not to be analyzed immediately, the vessel should be filled, then emptied without titration. That would serve to rinse any residual acid from the vessel, potentially extending the life of the electrode.

4. 4. There are two Teflon tubes that enter the top of the titration vessel. One introduces fresh solvent into the vessel, the other drains the vessel following a completed titration. The entry tube may be "permanently" set, in that it is not necessary to change the depth that the tube is placed in the vessel. It should be set so that the tip is approximately 1 - 1.5" below the top of the vessel: it will never be in contact with the solution in the vessel. The drain tube may be moved. For complete solvent removal, it should be touching the bottom of the vessel near one edge. However, when the vessel has been fully drained, I recommend pulling the tip of the tube up until it is above the level that the liquid will achieve when fresh titrant is added. The front of the titrant vessel has a "Schott" logo. The "fill line" will be approximately halfway between the logo and the taper at the bottom of the vessel. When the vessel is being filled, and when the titration is being conducted, I recommend raising the drain tube to the same height as the fill tube, i.e., approximately to the level of the "Schott" logo. By doing that, it is possible to fill the vessel and bring it to the conditioned mode awaiting a sample without the possibility of having the solution siphon from the vessel to the waste jar, which reduces the buffer volume and wastes buffer. When the vessel is first filled, there may be a slight over-pressure from the addition of the solvent, which could initiate the siphoning. Raising the tube will absolutely prevent that possibility.

Technical information provided by Kevin Lackey.