# Thermo. Titr. Application Note No. H-101

| **Title:** | **Determination of Water Content of Mineral Acids** |
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| ***Scope*:** | Determination of water in concentrated mineral acids such as phosphoric, hydrochloric, nitric and sulfuric acids with triethyl orthoformate (TEOF) |
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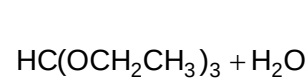
| ***Principle*:** | A sample of concentrated mineral acid is dissolved in anhydrous acetonitrile, and the water content titrated with a solution of TEOF in acetonitrile<br>  <br>The TEOF reacts exothermically with water in the presence of a strong acid (acting as a catalyst).<br><br>*Notes:*<br>*1.Determination of water in phosphoric and hydrochloric acids was carried out in anhydrous 2-propanol, but this solvent is unsuitable for use with concentrated nitric and sulfuric acids. In these cases, acetonitrile was used as the solvent. For uniformity, it is recommended that anhydrous acetonitrile be used for all water determinations in concentrated mineral acids and their mixtures.*<br><br>*2. Because phosphoric acid proved to be insufficiently acidic in this medium to sufficiently catalyze the reaction, methane sulfonic acid was added prior to the titration. The other mineral acids do not require addition of the methane sulfonic acid catalyst.*<br><br>*Reference:* J. Chen and J. S. Fritz (1991). Gas chromatographic determination of water after reaction with triethyl orthoformate. *Anal. Chem.* **63**, 18, 2016-2020 |
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| ***Reagents:*** | *1.16 mol/L triethyl orthoformate (TEOF)*(CAS 122-51-0, Sigma-Aldrich cat. no. 304050, anhydrous, M=148.20, d=0.89, purity=98%) Pipette 100mL TEOF by bulb pipette into a perfectly dry 500mL volumetric flask, and make to volume with anhydrous acetonitrile. |
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| | *Solvent:* Anhydrous acetonitrile (e.g., Sigma-Aldrich, cat. no. 271004) protected from atmospheric moisture using a guard tube with 3A molecular sieve<br>*Methane sulfonic acid („$MeSO_3H$“)*, 99.5+% (CAS 75-75-2, Aldrich cat. no. 471356) |

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| ***Method:*** | *Basic Experimental Parameters:*<br>Titrant delivery rate (mL/min.) 6<br>Data smoothing factor 70<br>Stirrer speed 8<br>*Sample Analysis.*<br>*1. Phosphoric acid .*Weigh accurately approximately 0.5-0.6g 85% w/w concentrated phosphoric acid into a completely dry 10-90mL titration vessel. Add 250µL methane sulfonic acid by air pipette. The titration program commences by adding 30mL of anhydrous solvent to the vessel. The titration program then starts the stirrer, and after a programmed 10 second delay, titrant addition commences.<br>*2. Hydrochloric acid.* Weigh accurately approximately 2.5g concentrated hydrochloric acid into a perfectly dry 200mL volumetric flask. Make to volume with anhydrous solvent and mix well. Take a 10mL aliquot by bulb pipette, and dispense into a perfectly dry titration vessel. Add 20mL of anhydrous solvent and titrate. Each 10mL aliquot contains approximately 0.125g of hydrochloric acid.<br>*3. Nitric acid.* Weigh accurately approximately 5g concentrated nitric acid into a perfectly dry 200mL volumetric flask. Make to volume with anhydrous acetonitrile and mix well. Take a 10mL aliquot by bulb pipette, and dispense into a perfectly dry titration vessel. Add 20mL of anhydrous acetonitrile and titrate. Each 10mL aliquot contains approximately 0.25g of nitric acid.<br>*4. Sulfuric acid.* Weigh accurately approximately 1.5g concentrated sulfuric acid directly into a perfectly dry titration vessel. Add 30mL anhydous acetonitrile and titrate. Dispensing via an air pipette set to 0.85mL will deliver approximately 1.5g.<br>*Notes:*<br>*1. The solvent may be added using a Dosino, with the vent tube protected with 3A molecular sieve.*<br>*2. 98% purity TEOF is approximately 5.9 mol/L. If it is desired to analyze acids with a greater water content (e.g., hydrochloric or nitric acids) by weighing directly* |

*without a serial dilution, then a more concentrated titrant solution may employed. This might also result in higher analytical precision.*

*Standardization and blank determination*. Prepare a standard water solution by pipetting 20mL DI water into a 500mL volumetric flask and make to volume with anhydrous solvent. At 25ºC, this water solution may be calculated to have a strength of 2.2138 mol/L $H_2O$. Connect a Dosino to deliver this water solution to the Titrotherm system. Construct a two-step pre-dose titration program which adds water solution and make-up anhydrous solvent in the following amounts:

| *Std. $H_2O$ soln., mL* | *solvent, mL* | *Total, mL* |
|---|---|---|
| 1 | 29 | 30 |
| 1.5 | 28.5 | 30 |
| 2 | 28 | 30 |
| 2.5 | 27.5 | 30 |
| 3 | 27 | 30 |

After adding 250µL methane sulfonic acid to a perfectly dry 10-90mL titration vessel, titrate each of the above combinations of standard water solution and solvent in turn.

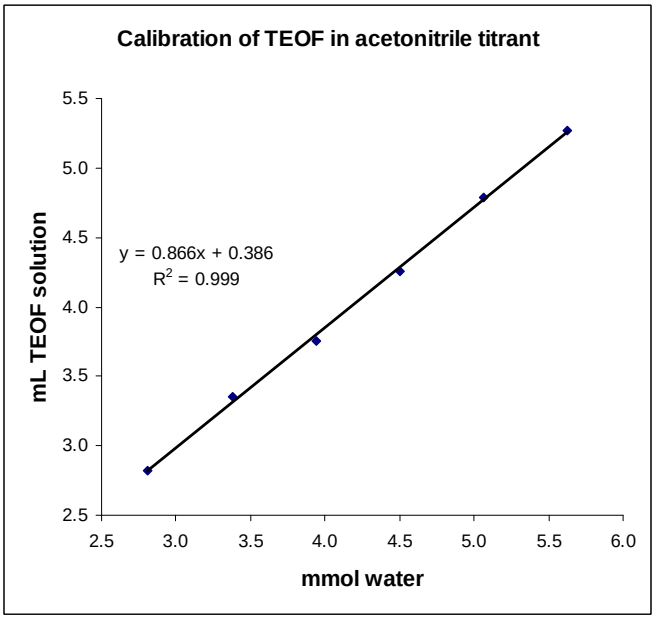
Perform a regression analysis of the results, plotting mmol H2O (x-axis) against mL of TEOF titrant dispensed (y-axis). Compute the TEOF molarity from the reciprocal of the gradient. The titration blank is equivalent to the y-intercept value.

***Results:*** *Analysis of commercial A.R. reagent acids*

** The bottle of $H_3PO_4$ had been opened many years ago.*

| **Acid** | **% $H_2O$ w/w** |
|---|---|
| *Phosphoric, ~85% w/w | 15.63±0.10 (n=7) |
| Hydrochloric, ~32% w/w | 67.5±0.38 (n=5) |
| Nitric, ~70% w/w | 29.70±0.10 (n=6) |
| Sulfuric, ~96% w/w | 4.13±0.03 (n=6) |

## *Standardization of TEOF:*

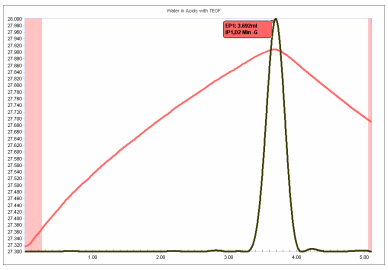



TEOF molarity = 1/gradient = 1/0.8655 = 1.1533 mol/L

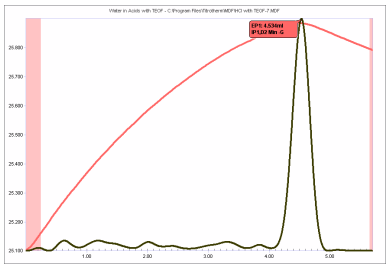
Titration blank = y-intercept value = 0.386mL

## *Thermometric Titration Plots:*

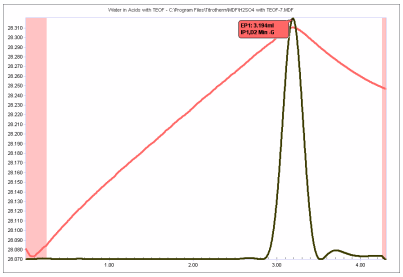
*Note: $MeSO_3H$ was added to enhance endpoint sharpness with analysis of $H_3PO_4$. This was not done in the case of the other three acids tested. However, in the case of analysis of the HCl (and to a lesser extent, HNO3), use of a greater sample mass with concomitant increase in TEOF strength might have led to better analytical prescision.*



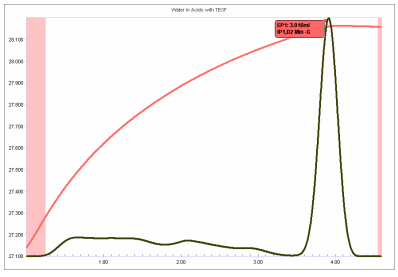
$H_2O$ in $H_3PO_4$



$H_2O$ in HCl



$H_2O$ in $H_2SO_4$



$H_2O$ in $HNO_3$

**Legend:**

Red = temperature curve

Black = second derivative curve