Determining water without Karl Fischer

Method Development for quantitative measurement of water concentration by Gas Chromatography.

Executive Summary

There are many examples where water is a serious contaminant in chemical manufacturing processes. Such unwanted contamination can result in poor performance of final products or may even generate hazardous situations. The possible sources of water can be raw materials such as solvents, the atmosphere or decomposition of unstable compounds during the production process.

The classical routine method for quantitative water measurement is a Karl Fischer titration, but some organic matrices are not suitable for water analysis by this titration method. This White Paper describes the method development of quantification of water in highly reactive matrices down to ppm level with the use of Gas Chromatography.

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Key facts

>100	Analytical Techniques
>1000	Customer Requests per year
>10000	Samples Analyzed per year

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Highly reactive compounds can behave differently when they are contaminated by water. Due to hydrogen bonding it is difficult to separate the residual water from the organic molecule. It can be necessary to determine water content down to ppm level. Karl Fisher titration is the most commonly used technique but can be interfered by the reactive decomposition products and therefore giving incorrect results. One possible alternative is thermometric titration which makes use of the strong endothermic reaction of 2,2-dimethoxypropane with water to acetone and methanol. However this equipment is not always available in the laboratory.

The challenge was to choose the right replacement analytical technique to accurately determine water in reactive matrices. After exploring different analytical methods (HPLC, spectroscopic methods), Gas Chromatography (GC) was chosen as an optimal alternative method. GC has also some challenges but deep analytical knowledge of both the analyte and the behavior of the complex matrix enabled us to fine-tune all the parameters and develop a reliable method.

How to develop a technique for quantitative water analysis when Karl Fischer fails?

Identification of the chemical and physical characteristics of water

Water is a small molecule with relatively high boiling point. Also, due to hydrogen bonding the energy required for evaporating water is much higher than in analogous compounds (figure 1), making it difficult to analyze by GC.

Hydrogen bonding also makes the separation of water and any other polar molecules very challenging.

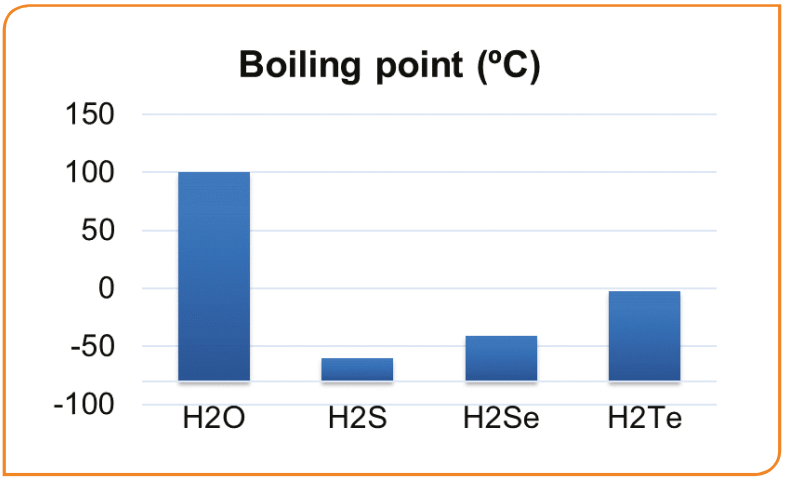

Figure 1: Influence of hydrogen bonding on boiling point

Sample preparation:
Due to possible hygroscopic nature of these challenging samples the preparation for analysis should be done in nitrogen atmosphere. The solvents should be pre-dried to remove traces of water frequently present in organic solvents.

Column protection
Injecting water onto a GC column can oxidize the column. For this measurement a special column has been used which is resistant to oxidization by water.

Calibration
To correct the error related to injection with GC, Diethyl ether is used as an internal standard. As there is always some water in the blank, the calibration line has been corrected for this.

Detector
A suitable detector choice would be thermal conductivity detector.

Final result
The method described above resulted in a clear sharp peak well separated from the main component and degradation products (Figure 2).

Calibration curve with the use of internal standard has a good linear fit with low variance (Figure 3).

Conclusion
The ECCD successfully developed an effective and accurate method to measure water concentrations in complex organic matrices down to ppm level using commonly available equipment.

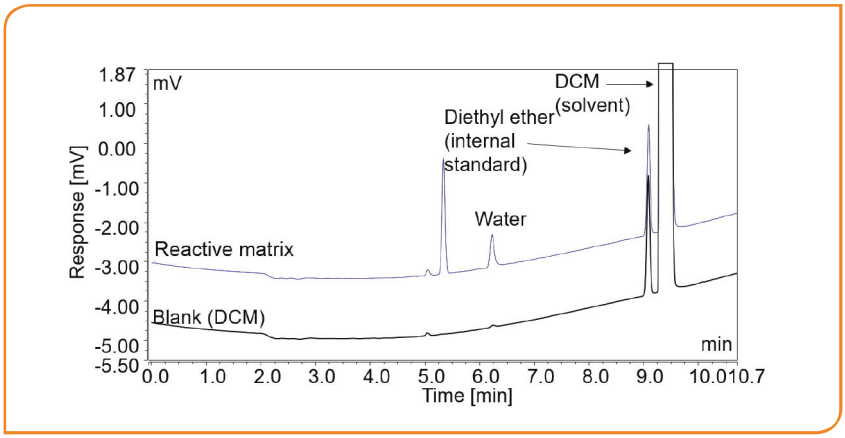

Figure 2: GC chromatogram of a reactive sample containing 0.5 mass % of water

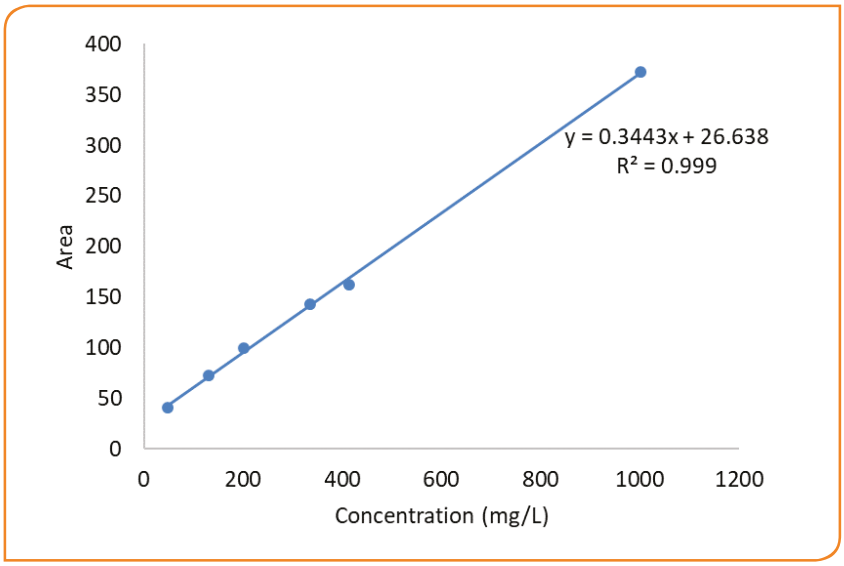

Figure 3: Calibration line of water; with Diethyl Ether as internal standard

References
1) http://highschoolenergy.acs.org/content/hsef/en/how-can-energy-change/energy-of-evaporation.html (hydrogen bond photo)

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