

Application News

No. A551

Spectrophotometric Analysis

Analysis of Minor Components in Water Using the IRSpirit

Water absorbs strongly in the mid-infrared region, which makes it difficult to detect and identify solutes in low concentration aqueous solutions. The water bands simply overwhelm spectral contributions of minor components. Several processing and sampling techniques have been developed to get around this issue. For meaningful results however, these methods require both stability and sensitivity of the FTIR instrument.

This article describes a difference spectrum method and sample condensation technique using the compact IRSpirit, a stable and sensitive compact FTIR instrument.

S. Iwasaki

■ Aqueous Solution Analysis via FT-ATR

Pollution load monitoring is utilized increasingly in industry, and not only to prevent the release of regulated pollutants (downstream monitoring). Water used in manufacturing processes can impact the quality of finished products, so upstream monitoring to characterize water quality (as a process parameter) is also important. Online TOC (Total Organic Carbon) is commonly employed for water monitoring, providing rapid quantification of organic carbon. It cannot however, perform chemical identification of the organic compounds contributing to the increased load.

This is where FTIR is useful, as it can perform chemical identification of organic substances in wastewater. If on-line TOC measurements detect an increase of organic substances, FTIR may be able to identify the source of contamination, leading to resolution of the problem. FTIR is not ideal for trace contaminants though, typically higher concentrations >5 % are required for good spectral quality. The minimum detection level is highly sample dependent. This article uses sucrose solutions of varying concentrations to explore the level at which an organic compound may be detectable with the application of processing and sampling techniques.

■ QATR-S Dedicated ATR Accessory

The sample condensation measurements were performed with the QATR-S single bounce ATR accessory, newly designed specifically for the IRSpirit. This accessory mounts in the sample compartment of the IRSpirit, flush on all sides, creating a wide top-sampling surface that can easily accommodate large samples without having to cut them down (Fig. 1). Both diamond and germanium crystals are available, and easily user-swappable. The swing clamp mechanism that pushes the sample against the crystal incorporates a torque limiter, preventing damage to the crystal from over-tightening. The QATR-S can be mounted only in the IRSpirit.



Fig. 1 QATR-S Accessory Installed in IRSpirit Sample Compartment

■ ATR Spectrum of Water

Fig.2 shows an ATR spectrum of water. Measurement conditions are detailed in Table 1. Water has strong absorption from 3800 – 2800 cm^{-1} (OH stretch), 1800 – 1500 cm^{-1} (OH bend), and <1000 cm^{-1} (molecular libration). These spectral features overlap OH and NH, C=O and CH_2 , and the molecular fingerprint region, making it difficult to detect minor organic components in aqueous solution.

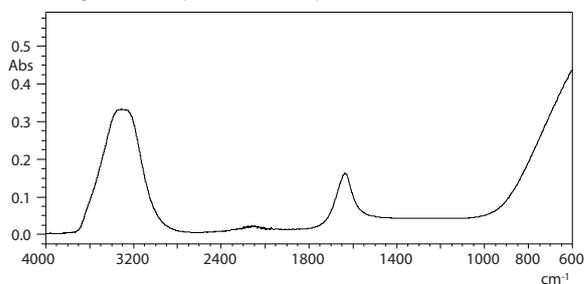


Fig. 2 ATR Spectrum of Water

Table 1 Measurement Conditions

Instrument	: IRSpirit-L (KBr window) QATR-S (Wideband diamond disk)
Resolution	: 4 cm^{-1}
Accumulation	: 45
Apodization	: Sqr Triangle
Detector	: LiTaO ₃

Difference Spectrum Processing Method

A difference spectrum is obtained by subtracting an infrared spectrum of water from the mixture (water plus solute) spectrum. It allows for the detection of spectral features of solute molecules, if the concentration of the solute is high enough. Fig. 3 (a) and 3 (b) show the measurement results of aqueous solutions of sucrose at 0.5 and 5 % concentrations, respectively. The water and sucrose solution spectra are represented by black and red traces, whereas the difference spectra are shown in blue. The 0.5 % concentration of sucrose is too low to provide meaningful spectral features even after the subtraction of the water contribution. The difference spectrum of the 5% concentration solution does show peaks in the fingerprint region though, in the range from 1200 – 900 cm^{-1} . These features are assigned to C-O stretch in alcohols, and C-C stretch in aliphatic ethers (> 1000 cm^{-1}) and CH₂ deformation modes (<1000 cm^{-1}).

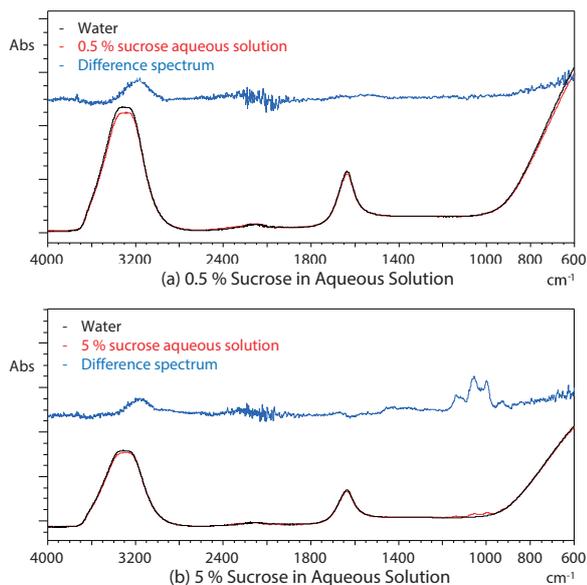


Fig. 3 Difference Spectra Processing Method, Concentration Dependence of Sucrose ID

Condensation Sample Preparation Technique

In this sampling technique, evaporation over time is used to increase solute concentration in aqueous solutions. This is accomplished by placing a small amount of aqueous solution on an ATR crystal, and evaporating the water to leave behind an increasingly concentrated solution (Fig.4). This technique is better for chemical ID rather than quantitation, as the concentration level will be changing over the course of the experiment.

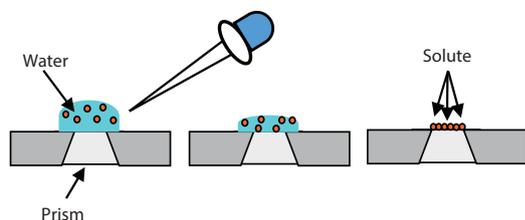


Fig. 4 Schematic of Condensation Method – Solute Concentration Increasing with Time

10 μL of sucrose solution was measured onto the ATR crystal. The surface tension of the aqueous solution maintains the sample as a drop. The FT-ATR spectrum was measured initially, and then again at 20 and 22 minutes elapsed time. Three different sucrose concentrations were investigated in this manner: 0.1, 0.5 and 5 %.

Fig.5 (a), (b), and (c) show the resulting spectra from these measurements, with the $t=0$ measurement in black, the $t=20$ min measurement in red, and the $t=22$ minute data in blue. Not surprisingly, as time progresses and water evaporates, the spectral features of the sucrose grow more prominent. Also, the sucrose features are stronger for the more concentrated solutions.

In contrast to the difference spectrum processing method described first, the sucrose component of the 0.1 % concentration solution was ultimately resolvable, albeit after 22 minutes had elapsed and water evaporated. As this measurement was taken with a single bounce ATR configuration, it is possible that a multi-bounce accessory may enable the analysis of even lower concentration solutions, provided enough of the sample is available to ensure adequate coverage of the crystal.

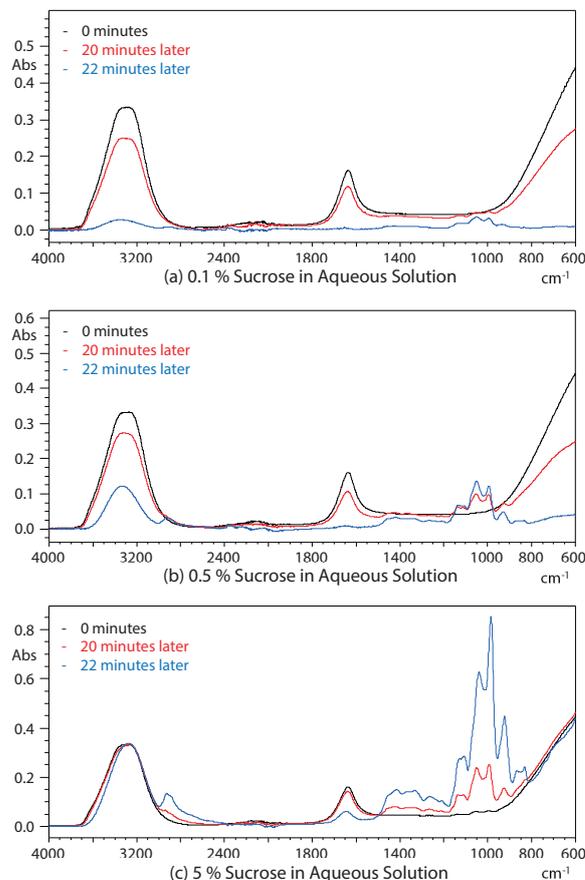


Fig. 5 Condensation Sampling Method – Time and Concentration Dependence of Sucrose ID

Conclusion

This article demonstrates the application of processing and sampling methods to detect low-level solutes in aqueous solutions. The superior stability and sensitivity of the IRSpirit allow these techniques to successfully ID sucrose in low concentration solutions.