Process Analytical Systems

Application Note - Tetramethylammonium Hydroxide in Water

Statement of Problem

For semiconductor wafer processing, the level of tetramethylammonium hydroxide in water is critical in the developer blend system. The solution of tetramethylammonium hydroxide must be kept at 2.38%.

Summary of Conclusions

The concentrations of tetramethylammonium hydroxide can be easily measured at 2.38% by near-infrared (NIR) spectroscopy with a fiber optic coupled NIR Model 412 Process Analyzer to better than ±0.1 % v/v. Analysis time is under 50 seconds. This study did not investigate the effect of varying bath temperature on the results. Water is a highly polar molecule, hence its spectrum is very temperature sensitive. Since the bath is 98% water, temperature will be a factor in any on-line installation. Experience indicates that it can be corrected spectroscopically. (See Low Levels of Organics in Water; Saccharin— Guided Wave Publication #3014)

Background Information

Modern NIR spectrometers have extremely high signal-to - noise ratios and superb long-term stability plus multi-channel capability thus making them ideal for monitoring of chemicals in process applications. Fiber optics permits the probe to be located remotely from the analyzer. Probes may be inserted directly into the process (insertion probes) or located in sidestreams (flow cells). In most cases, sample conditioning is not required thus eliminating the need for costly and failure prone sample conditioning systems. Coupled with modern high-speed personal computers, these systems are fast and reliable.

Previous Guided Wave studies have shown that low levels of organics can be measured in water. GWI demonstrated Low Levels of Organics in Water: Saccharin in Guided Wave publication #3014. that soluble sodium saccharin could be measured to 60-ppm g/g saccharin by taking into account the temperature effect on the water spectrum from 16 to 32°C. In the saccharin study, we demonstrated that water spectra are about 10 times more sensitive to water temperature then PtRTDs. Hence the temperature can be inferred from the spectra, eliminating the need for costly temperature control or accurate thermometers.

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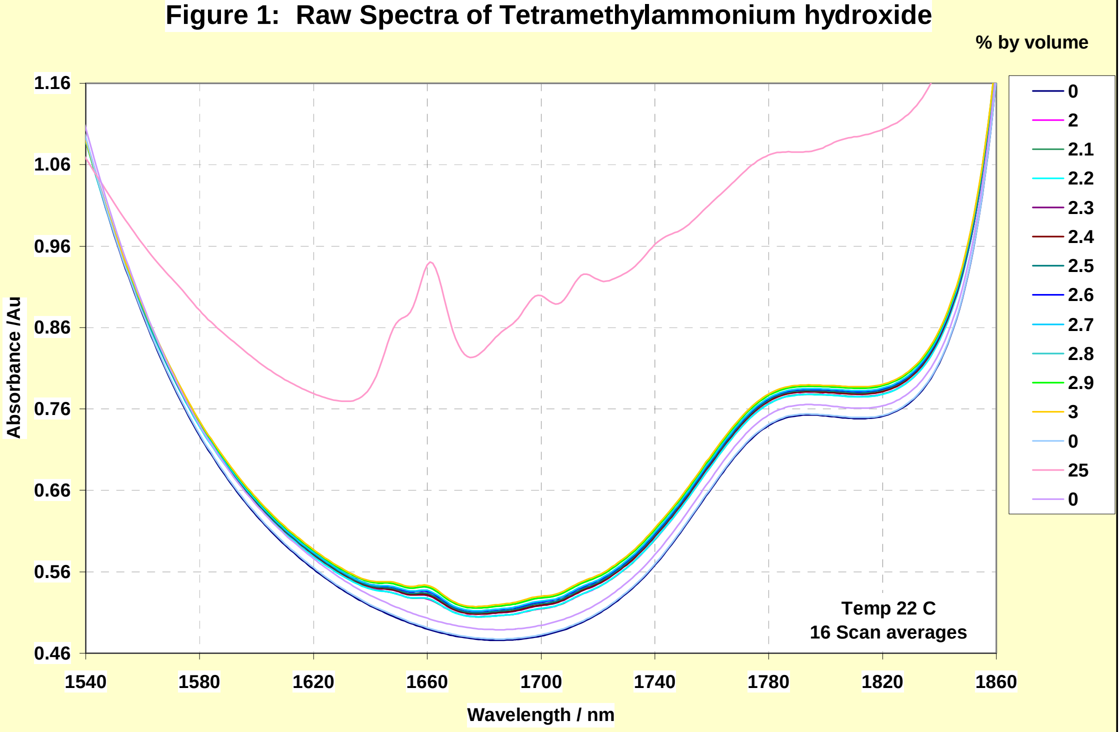
Experimental Design

Samples of 13 solutions of $(CH_3)NOH$ were made by diluting tetramethylammonium hydroxide, 25% Aqueous Solution, Electronic Grade 99.9999 % (metal basis) in DI water by volume. The samples were placed into a beaker, which was immersed in a temperature controlled circulating bath. A Guided Wave 2-mm path SST probe was inserted into the sample along with a Pt-RTD temperature sensor. Spectral data were collected over 40 m of 500 µm diameter single strand low-OH fused silica fiber on an extended range (1000 nm-2100 nm) **Guided Wave 412 Process Analyzer.** All spectra were collected at an average of 22.0°C with less than a range of 0.15°C over a 3-hour period. Each spectrum consisted of an average of 16 scans for a total data collection time of 47s (Figure 1).

Figure 1: Raw Spectra of Tetramethylammonium hydroxide



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Literature: 3044-07-01

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Data Analysis

The raw spectra were baseline corrected at 1625 and 1795 nm (5 pt averages) and the spectrum of DI water was subtracted (Figures 2 & 3) The peak height at 1660 nm was correlated to the percent tetramethylammonium hydroxide (Figure 4). Figure 5 shows this correlation extended out to 0 and 25%. The zero point fits well on the linear regression but the 25% point does not. This is due to density changes in the sample with increasing concentration. In Table I the predictions based on this single wavelength analysis are given. Note that when the prediction for 25% is multiplied by its density, the prediction improves significantly. No corrections were made on these spectral data for temperature changes, which could impact the accuracy of the predictions.

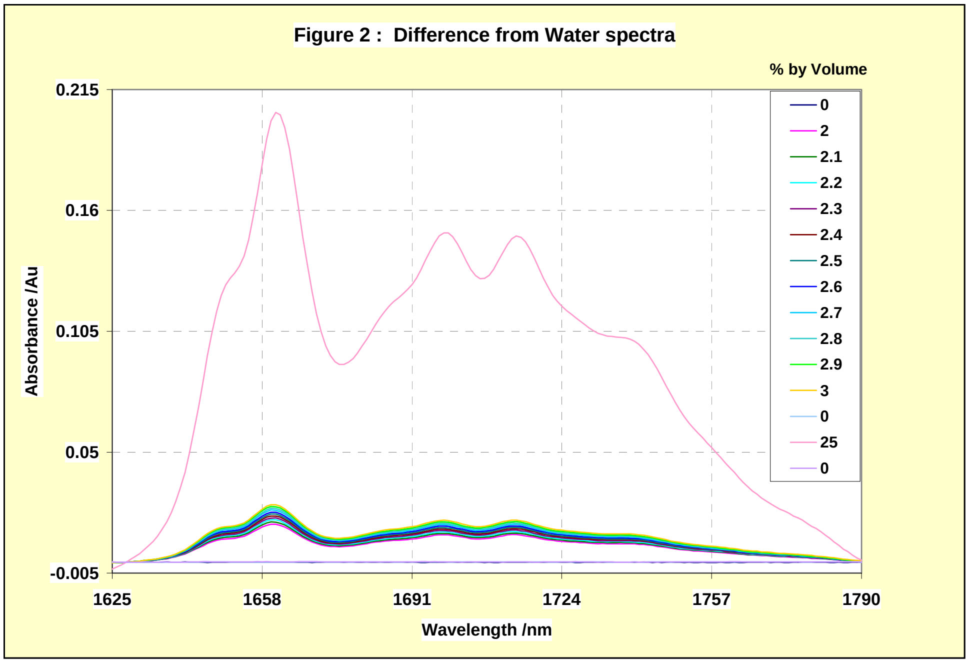

Figure 2 : Difference from Water spectra

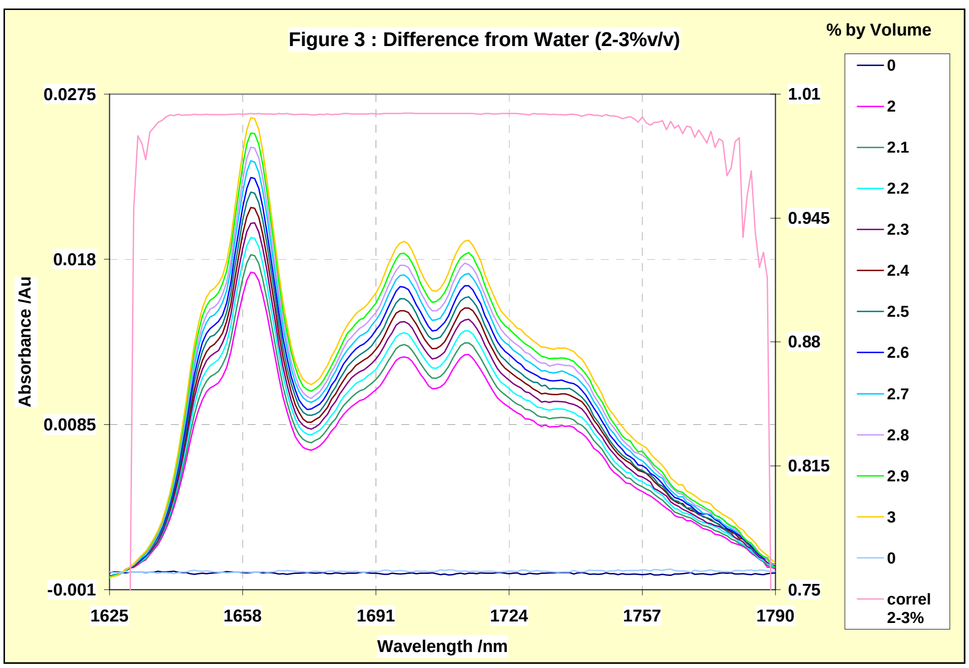

Figure 3 : Difference from Water (2-3%v/v)

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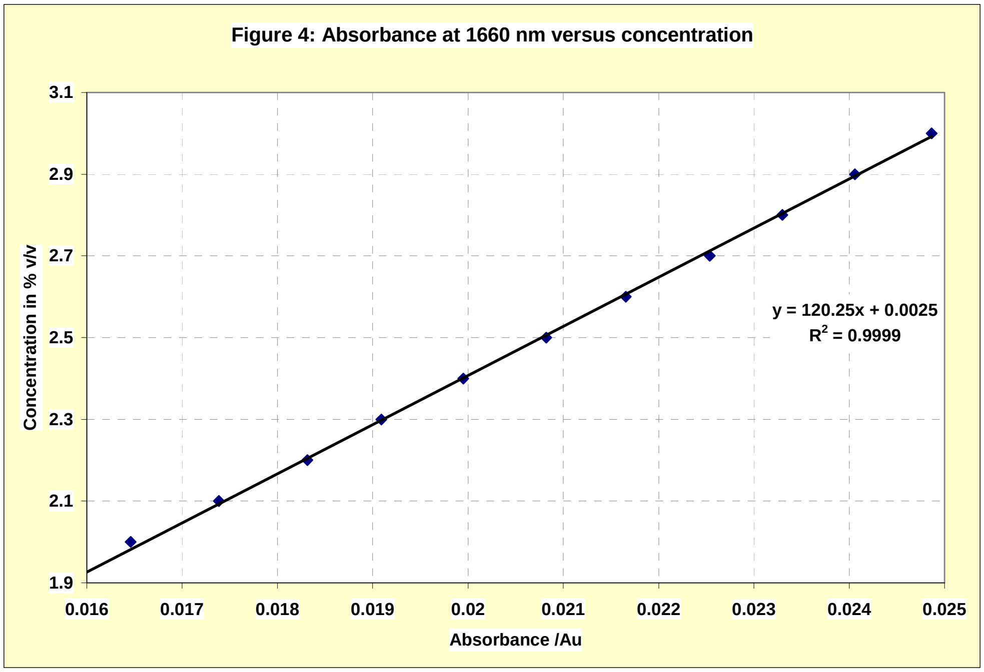

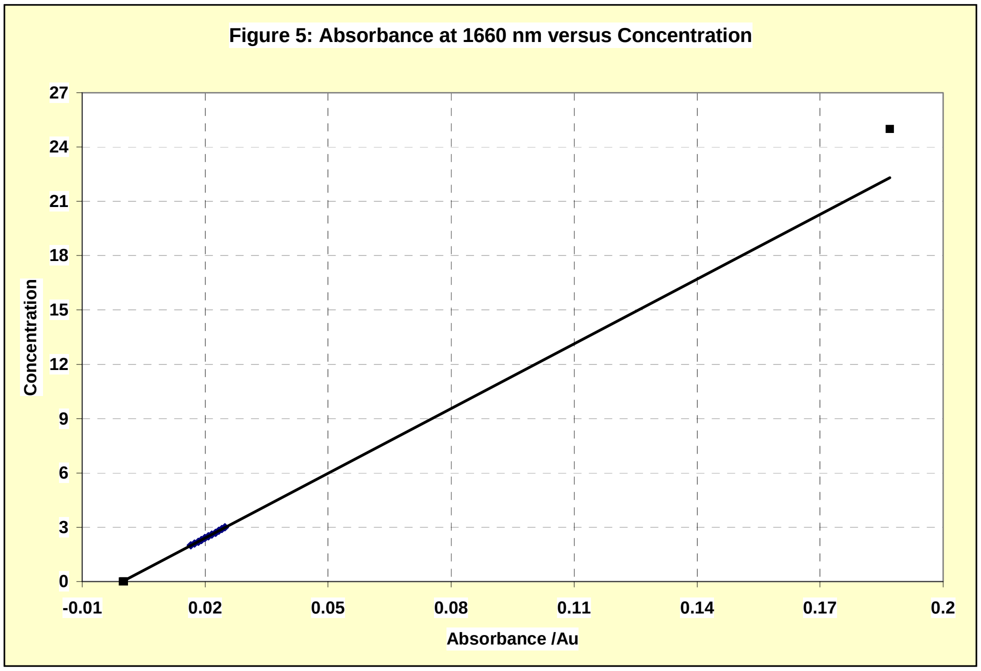

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Table 1

Prepared in % V/V	Prediction	Error
0	0.001	0.001
2	1.982	-0.018
2.1	2.093	-0.007
2.2	2.205	0.005
2.3	2.298	-0.002
2.4	2.402	0.002
2.5	2.506	0.006
2.6	2.607	0.007
2.7	2.712	0.012
2.8	2.804	0.004
2.9	2.896	-0.004
3	2.992	-0.008
0	0.004	0.004
25	22.490	
Prediction for 25% * density	24.829	
St Dev of Errors		0.008

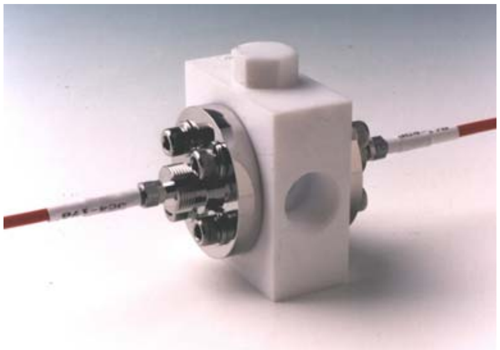
Conclusions and Recommendations

Measuring tetramethylammonium hydroxide in water using NIR spectroscopy is quite feasible. We have shown measurements levels equal to ±0.008% for one standard deviation. This yields a 95% confidence level (3x) of about ±0.03% and a conservative lower detection limit (10x) of 0.08% v/v.

From our experience, we know temperature will have a significant impact on the spectroscopy. Also from experience, we have learned that controlling the temperature, or even measuring it, is not accurate enough by about a factor of ten. Fortunately, the thermal information is accurately recorded in the spectra, hence it is sufficient to measure the spectra and deduce directly from it, the proper corrections for the thermal changes.

Commercial Design

Since semiconductor processes are very sensitive to metals contamination, Guided Wave recommends using our mechanically stabilized Teflon Flow Cell. With sample wetted components of synthetic sapphire optics and Teflon, no metals are exposed so metal contamination is eliminated. The cell is seen below with its front entry port exposed with an optics access and cleaning port on top. Stainless steel metal parts stabilize the unit against thermal distortion.



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