Airborne Urea Sampling and Analysis

By Dr. Dan Cowles, Dr. Mary Havlicek, Lynn Vanatta, Piyamit Chitrathorn

Introduction

Balazs^{TM} Analytical Services developed a method for capture and analysis of airborne urea. Urea is a problematic contaminant in fabs, first because it is a reactive amine, and secondly because it can decompose to ammonia. Amines generally, and ammonia in particular, are critical impurities for photolithography. Although a method is already in place at Balazs to quantify urea in water, a sampling method for airborne urea provides further control and quantification of this semi-volatile contaminant for the fabs.

Urea is a ubiquitous environmental contaminant that enters fabs through the water supply (1). Unfortunately, urea is only partially removed in the production of ultra-pure water (UPW). For example, samples of water were collected from various stages of a DIW production facility and analyzed for urea. Table 1 displays the urea results. Purification reduces the urea concentration from about 40 ppbw in incoming city water to around 3 ppbw in the final delivery DIW. Historically, semiconductor DIW samples analyzed by Balazs have contained up to 20 ppbw urea (1).

Sample #	Description	Bottle#	Urea (ppb)
1	City water	S011	41
2	Post carbon bed	A017	8.5
3	Post RO	A002	8.9
4	Post storage tank after deaeration	S025	3
5	Post 1st UV	S012	2.7
6	Post Cation and Anion beds	S032	2.9
7	Post 2nd UV, before mixed ion beds	A019	3.2
8	Post mixed beds	A027	3
9	Water leaving TIME to Fabs	S016	2.7
Blank	Distilled water blank (Sparkletts)	S014	<0.5

Table 1: Urea Concentrations in UPW Purification Process.

Wafers-in-process can be exposed to urea directly in any fabrication step utilizing UPW. In addition, urea in UPW can potentially migrate to the cleanroom air supply via the humidity-control mechanism. Fab humidity control typically involves steam generation from DIW, which, as demonstrated above, often contains low-ppb concentrations of urea.

Finally, urea can conceivably enter the cleanroom from outside as a particle or vapor in the make-up air. Airborne urea itself, or its decomposition byproduct, ammonia, can negatively impact photolithography processes, for example by neutralizing photoresist acids.

Therefore, although a method has already been established by Balazs for direct quantification of urea in water, there is additionally a need to measure urea in air.

Method

Urea is a solid at room temperature, however it possesses a sublimation-pressure sufficient to form ppb-level concentrations in air. The sublimation-pressure is known to vary sharply with temperature.

In our experimental apparatus, humidified clean-dry-air (CDA), or alternatively UHP nitrogen, flows through a cartridge filled with urea crystals (>99.5%). The CDA flow-rate through the cartridge ranges from 0.3 to 3 LPM. Relative humidity in the CDA exiting the cartridge is controlled at around 50 %. A fraction (or sometimes all) of the CDA exiting the cartridge is sampled using a conventional Balazs impinger train. The sample flow-rate to the impingers varies from 500-900 cc/min and the impinger is loaded with an aqueous solution which has been previously verified to be free of urea (i.e. urea <DL of IC-MS).

Analysis for urea was performed on a Dionex DX600 ion chromatograph with a Finnigan MSQ mass spectrometer. The instrument was calibrated by analyzing (in replicate) multiple urea standards that spanned the concentration range of interest. At the 95% confidence level, the uncertainty in the reported results is ± 2 ppbw.

Results

Capture Efficiency Test

The most important aspect of ensuring method success was to check the capture efficiency of urea in air with the Balazs sampling system. Different experimental setups were made to check this capture efficiency in a variety of conditions. Urea capture efficiency was measured for three carrier gases: UHP nitrogen, clean-dry-air (CDA), and CDA humidified to 50% R.H. In the initial tests, three impingers were arranged in series. However, after breakthrough of urea beyond the first impinger was found to be undetectable, a single impinger was used. Capture efficiencies are shown in Figure 1 below.

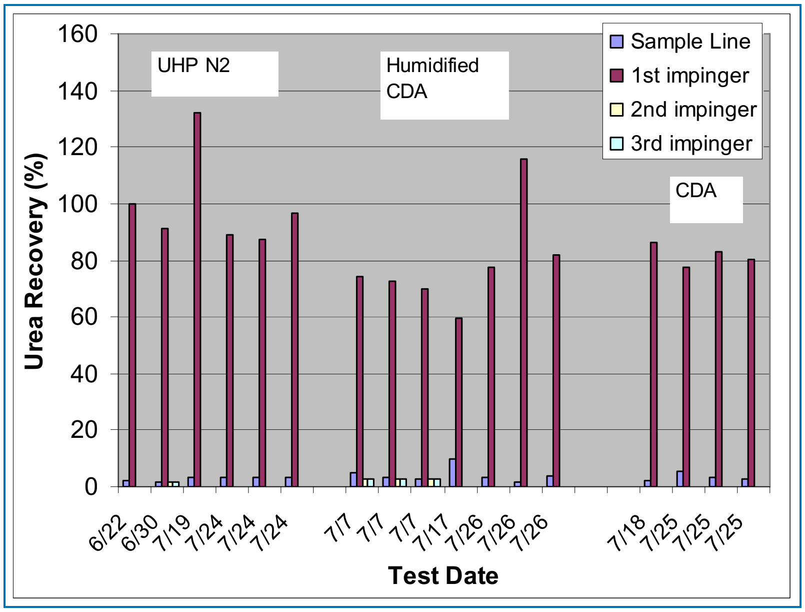

Figure 1: Urea Recovery Test Summary.

The calculated capture efficiency is typically 90-100% when UHP N_2 is used as the carrier gas, ~80% when CDA is the carrier, and 70-80% when 50% relative humidity CDA is used. Although we have not analyzed our CDA for moisture, CDA often contains >100 ppm H_2O. We believe moisture adsorbed on the urea crystals can depress the sublimation-pressure, due to the strong attraction of urea for moisture.

Conclusions

Balazs has shown that the urea capture efficiency in air with the Balazs impinger is 90-100% within experimental error. We are currently performing experiments in different fab settings and during different weather seasons to gauge the presence of urea in fab air.

References

1. *Urea and TOC Detection - Are Your Current Systems Able to Meet Ever-Decreasing Detection Limits?*, S. Schoen, S. Anderson, and M. Haddix, Air Liquide Technoday 2006.