In-Line Detection and Measurement of Molecular Contamination in Semiconductor Processing Solutions

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Outline

- Introduction
  - Why the analysis of molecular contamination is important?

- Discussion
  - Use of the Metara Trace Contamination Analyzer (TCA) for molecular contamination measurement
  - Problem solving examples
    1. A nitrogen-containing compound in H_2O_2
    2. Organic additives in SC-1
    3. Urea in UPW
    4. Molecular contamination in UPW
    5. Plasticizers in IPA
    6. Sulfur-containing compounds in IPA

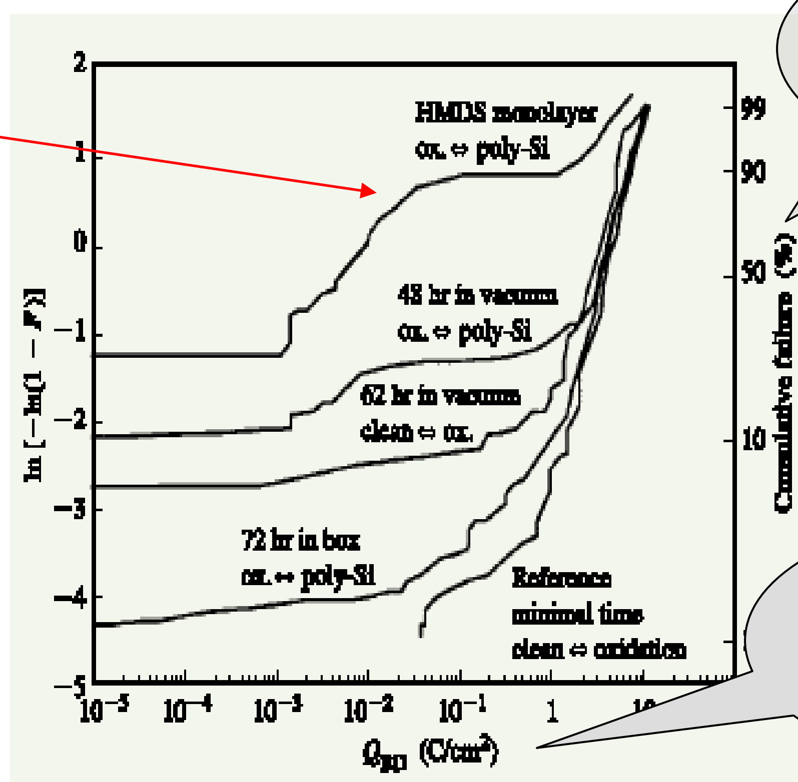
- Conclusion

Molecular Contamination Sources

- Process equipment
- Impurities in incoming process chemicals
- Transfer from earlier process steps
- Airborne molecular contamination
- Deliberate addition of organics to process chemicals
  - Surfactants and chelating agents
  - “Proprietary” additives

Gate Oxide Degradation Due To Organic Contamination

*** HMDS Monolayer on Oxide**



Cumulative Failure (%)

Q_{BD} = Charge-to-Breakdown measurement

* HMDS =

Hexa-methyl-di-silazane

“Cost Effective Cleaning and High-quality Thin Gate Oxides”,

IBM J. Res. Develop. Vol. 43, No. 3, May 1999, M. Heyns and et. al.

International Technology Roadmap for Semiconductor (ITRS)

(2003 Edition) *Table 70a Surface Preparation Technology Requirements—Near-term*

Year of Production	*2003*	*2004*	*2005*	*2006*	*2007*	*2008*	*2009*	*Driver*
Critical GOI surface metals (10^{10} atoms/cm^2) [F]	0.5	0.5	0.5	0.5	0.5	0.5	0.5	*M*
Critical other surface metals (10^{10} atoms/cm^2) [F]	1	1	1	1	1	1	1	*M*
Mobile ions (10^{10} atoms/cm^2) [G]	1.8	1.9	1.9	2	2.2	2.4	2.5	*M*
Surface carbon (10^{13} atoms/cm^2) [H]	1.8	1.6	1.4	1.3	1.2	1	0.9	*D ¼, M*

Surface Carbon

ITRS 2004 Updated, Table 114a Technology Requirements for wafer environmental contamination control

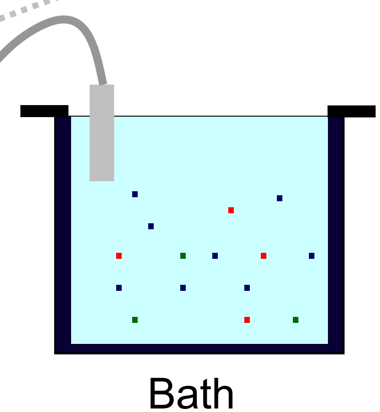
	30% H_2O_2 total oxidizable carbon (ppb)	**-**	**TBD**	**TBD**	**TBD**	**TBD**	**TBD**	**TBD**
ADD	**IPA: High molecular weight organics (ppb)**	**-**	**TBD**	**TBD**	**TBD**	**TBD**	**TBD**	**TBD**
ADD	**30% H_2O_2: Resin byproducts (ppb)**	**-**	**TBD**	**TBD**	**TBD**	**TBD**	**TBD**	**TBD**

TCA (Trace Contamination Analyzer)

for Metallic, Organic and Molecular Contaminants

Trace Contaminant Analysis (TCA) Platform			
		Mass-Spectrometer	
Sample Extraction Unit	Sample Preparation Module	Electrospray Ionization Interface	Mass-Analyzer Ion-Trap & TOF (Time of Flight)

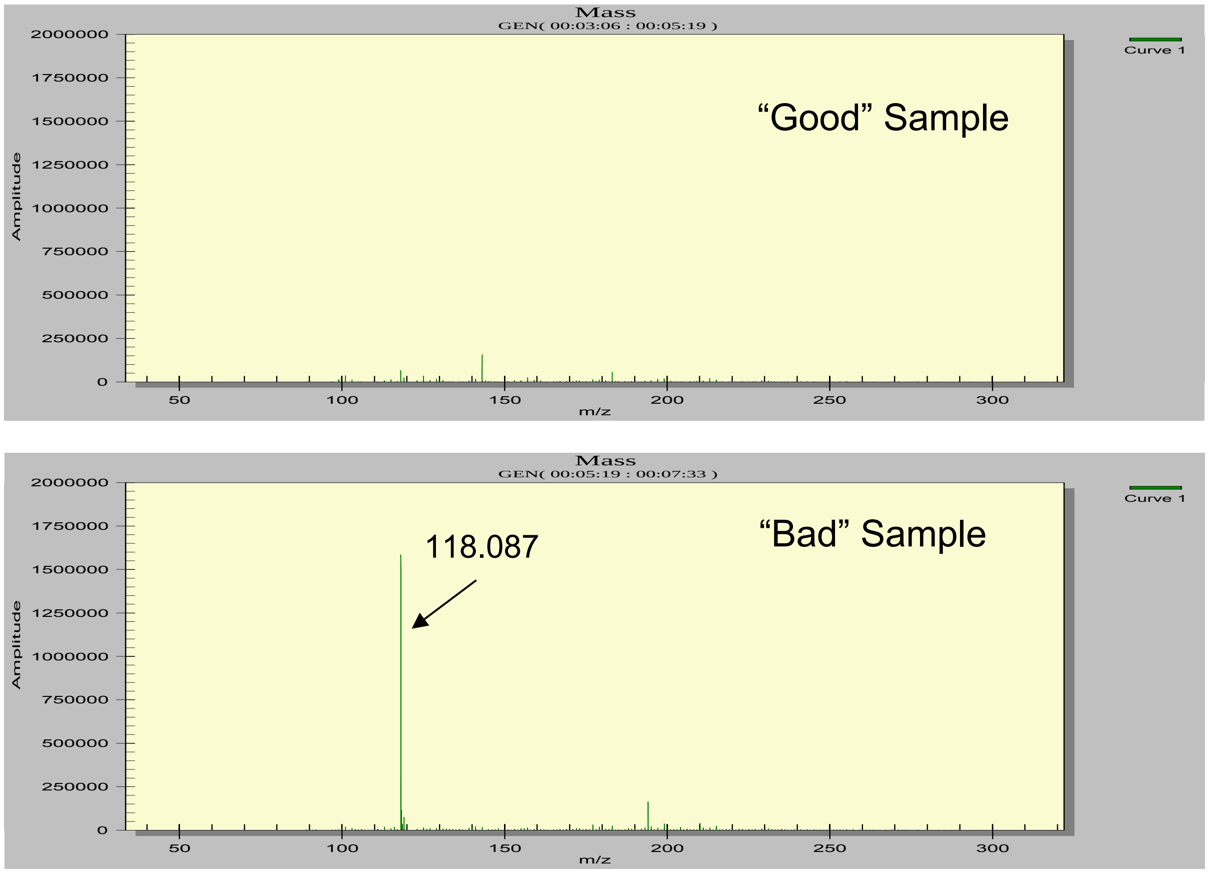
- **Cations**
- **Anions**
- **Metallics**
- **Organics**
- **24/7**



Example 1: H_2O_2 Excursion at a Production Fab

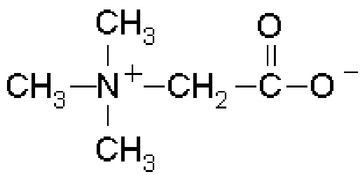
- Contaminated H_2O_2 suspected to cause yield crash at a fab
- Analyses of traditional lab methods show inconclusive results between the “Good” & the “Bad” H_2O_2 samples
  - ICP-MS (Inductively Coupled Plasma Mass Spectrometry),
  - IC (Ion Chromatography),
  - TOC (Total Oxidizable Carbon)
  - Assay
- Results of TCA showed Intensity of peak at m/z 118 was ~ 20x higher in “bad” sample than in “good” sample

Contaminant found from H_2O_2 Sample by TCA

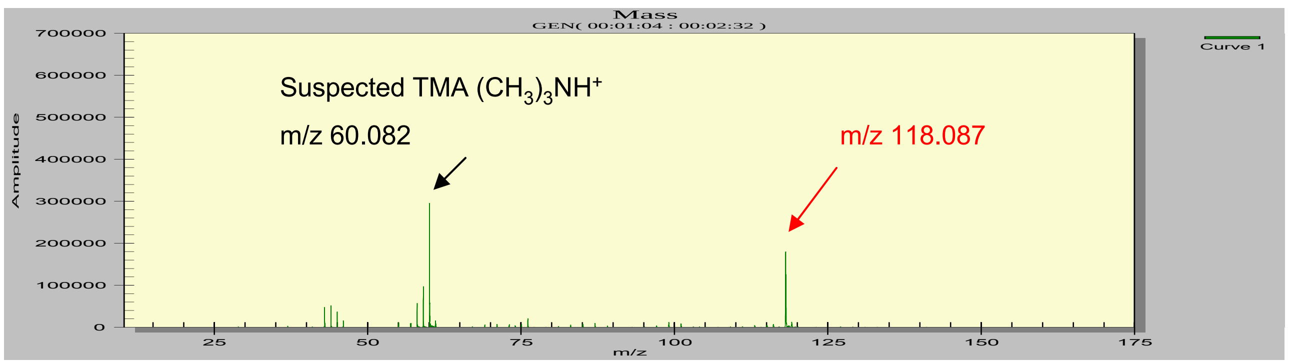


Intensity of 118 peak was found to be ~ 20x higher in “Bad” sample

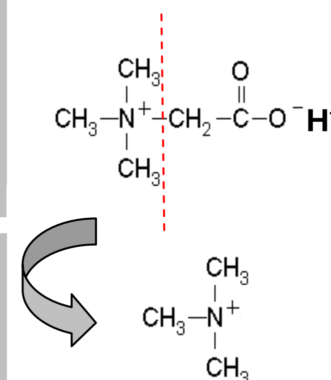
Identification of Contaminant in “Bad” H_2O_2 Sample

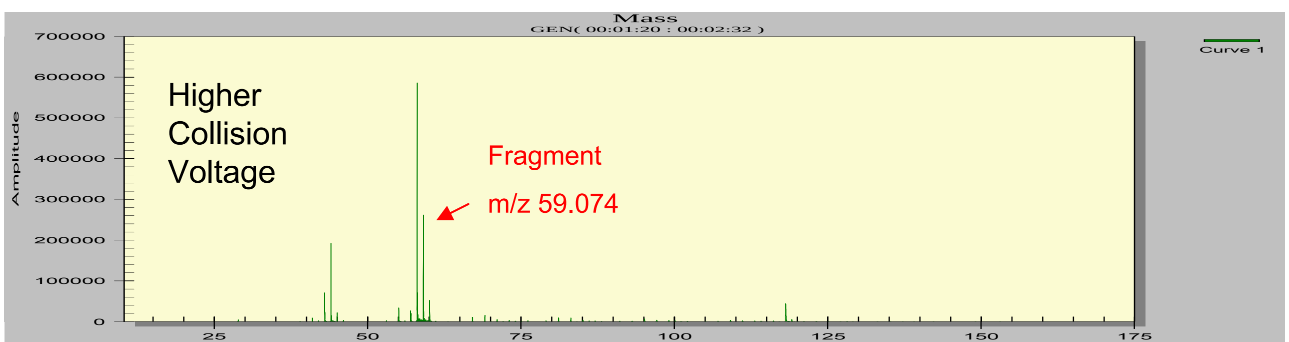


Possible compound: Tri-methyl-glycine



m/z = 118.087

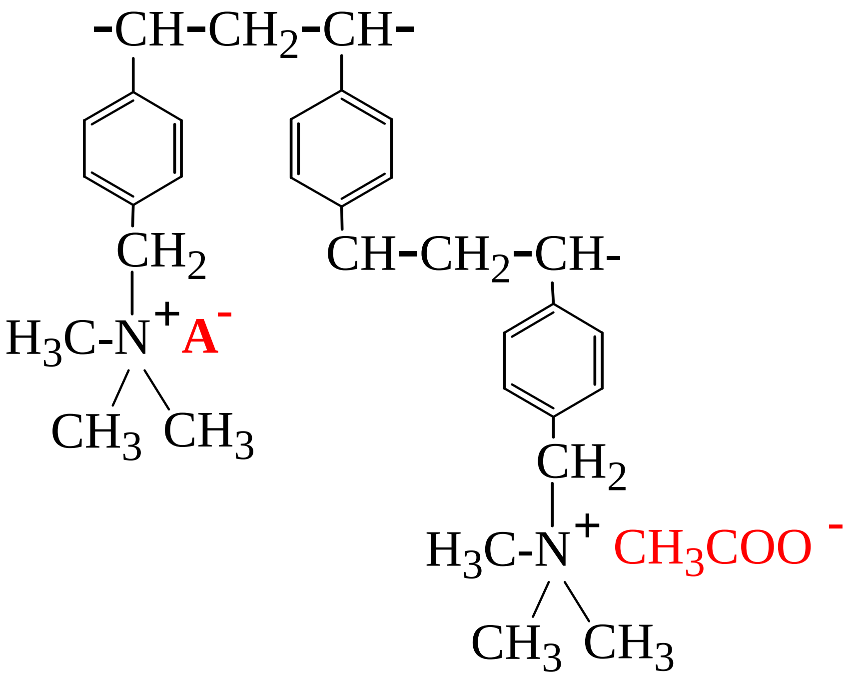


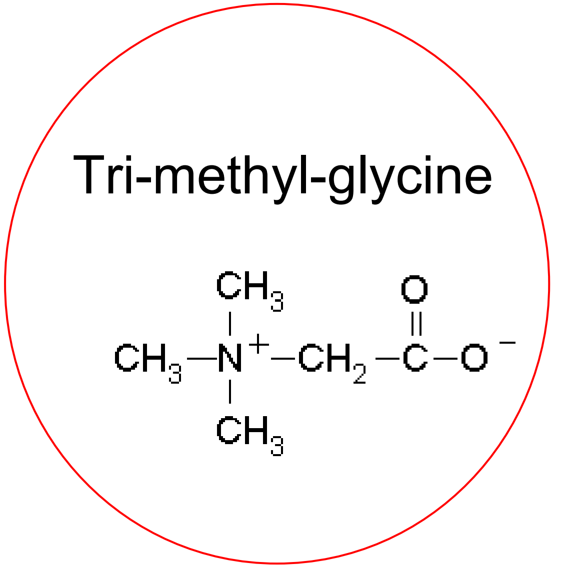


m/z = 59.074

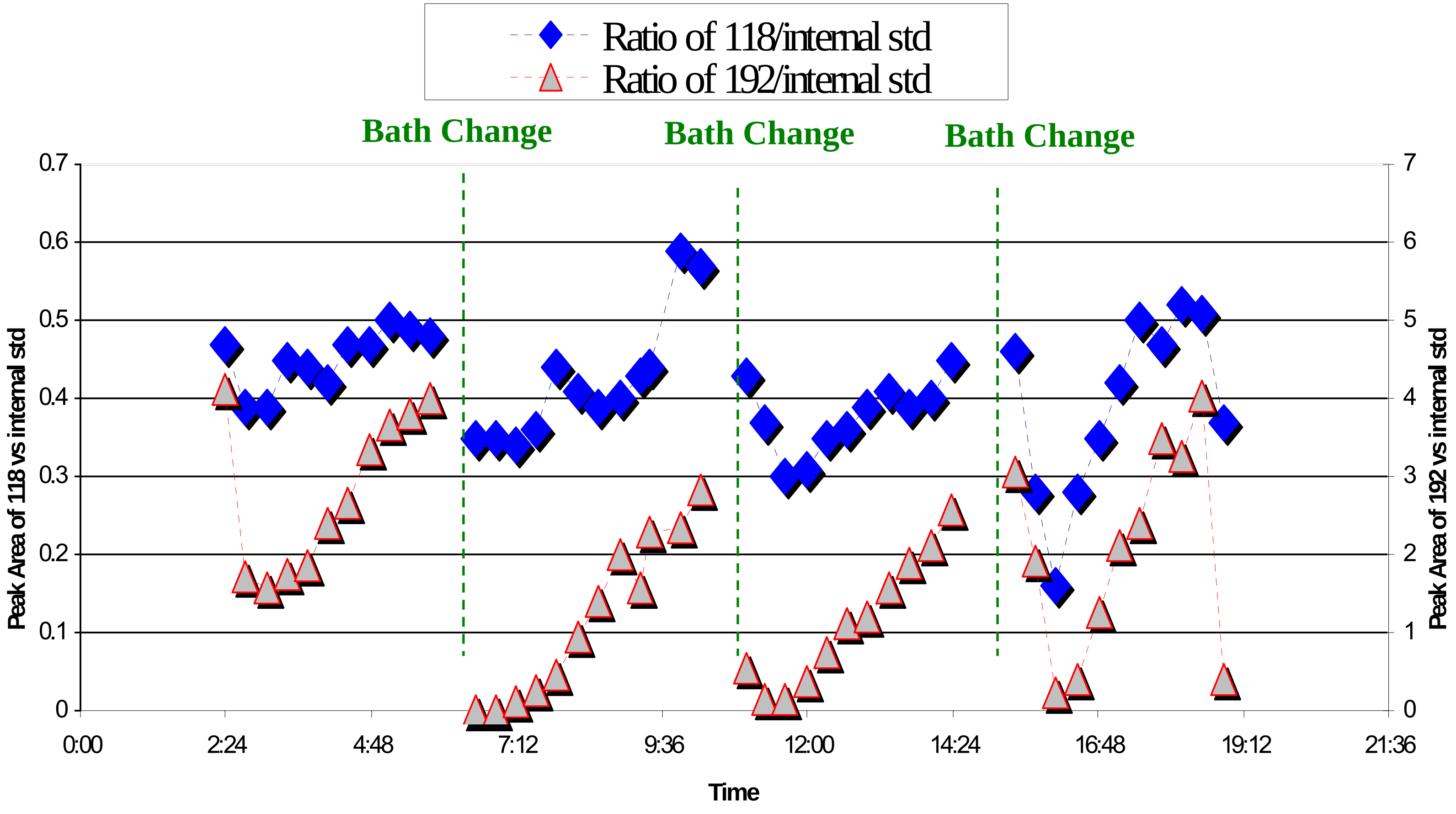
Contaminant from Ion Exchange Resin

Structure of Ion Exchange Resin





TCA In-Line Monitoring Molecular Contamination in SC-1 ($NH_4OH:H_2O_2:H_2O$) Bath at a Fab



High Organic Content in High Purity H_2O_2

Total Organic Carbon (TOC)

	Specification
Assay (H_2O_2) % by weight	31.0 - 31.8
Stability, 24 hours @ 100° C	90.0% min
Color (APHA)	6 max
Chloride (Cl)	10 ppb max
Nitrate (NO_3)	20 ppb max
Phosphate (PO_4)	20 ppb max
Sulfate (SO_4)	20 ppb max
Total Organic Carbon (TOC)	5000 ppb max
Free Acid	0.6 μeq/g max
Aluminum (Al)	10 ppt max
Antimony (Sb)	10 ppt max
Arsenic (As)	10 ppt max
Boron (B)	20 ppt max
Calcium (Ca)	10 ppt max
Chromium (Cr)	10 ppt max
Copper (Cu)	10 ppt max
Gold (Au)	10 ppt max
Iron (Fe)	10 ppt max
Lead (Pb)	10 ppt max
Lithium (Li)	10 ppt max
Magnesium (Mg)	10 ppt max
Manganese (Mn)	10 ppt max
Nickel (Ni)	10 ppt max
Potassium (K)	10 ppt max
Sodium (Na)	10 ppt max
Strontium (Sr)	10 ppt max
Tin (Sn)	10 ppt max
Titanium (Ti)	10 ppt max
Zinc (Zn)	10 ppt max

5000 ppb max

High Organic Content

Problems

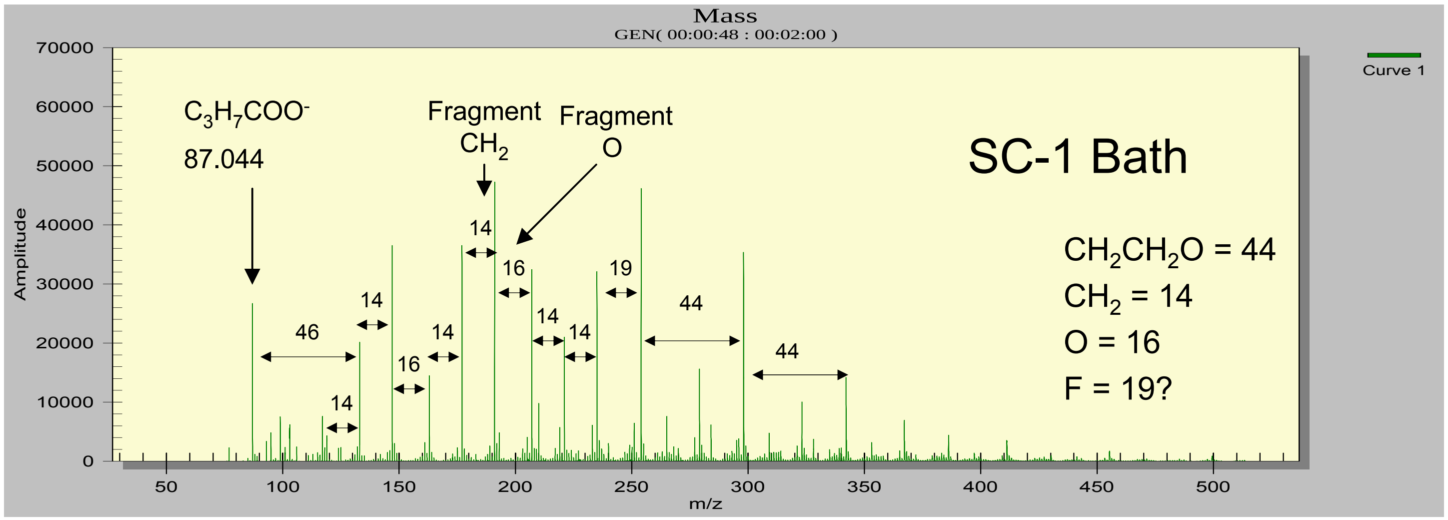
10 ppt max

Low Metallic Content

Example 2: Deliberate Addition of Surfactant or Chelating Agents in Baths

- Industrial Trend for Using Diluted Chemistry
  - SC-1 NH4OH:H_2O_2:UPW from x:1:5 (x = 0.05-3), up to 1:1:500
  - SC2 HCl:H_2O_2:UPW up to 1:1:1000
- Addition of Surfactant or Chelating Agents in Baths
  - Improve Particle & Metal Removal Efficiency
  - Improve Surface Wetability for Uniform Wafer Surface Preparation

Chelating Agent found from a SC-1 ($NH_4OH:H_2O_2:H_2O$) by TCA



Possible Formulation:

A Mixture of Compounds with Functioning Groups R-COO^- and -$(CH_2CH_2)_n$-O

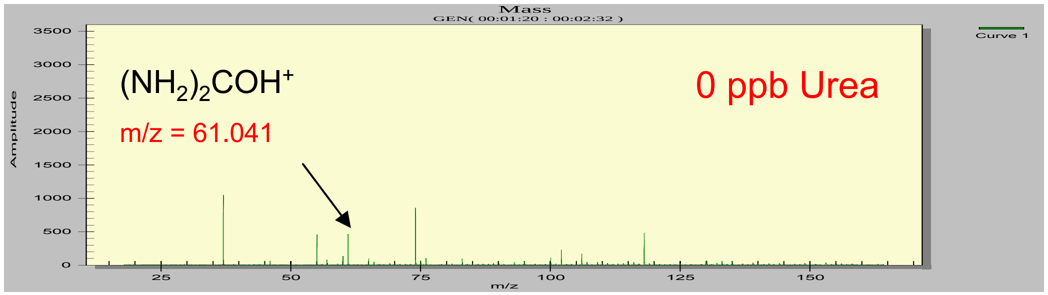
Chelating agents/surfactants Need to be completely rinsed off from wafer surface

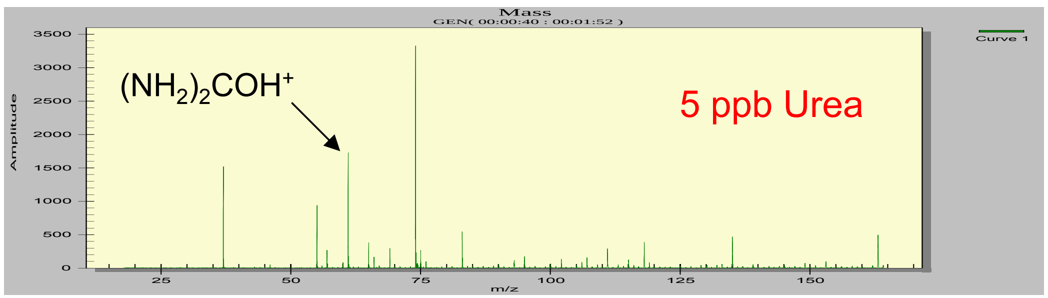
Example 3: TOC (Total Oxidizable Carbon) Excursions at a Fab

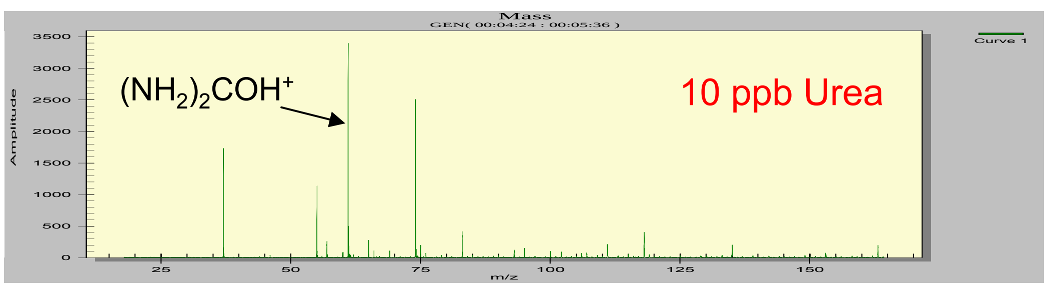
- Seasonal TOC excursions at a fab
  - Urea (fertilizer) in UPW (Ultrapure Water) was suspected
  - "No way to confirm suspicions" because "no laboratory methods available to accurately measure low ppb concentrations of urea contamination in water"*

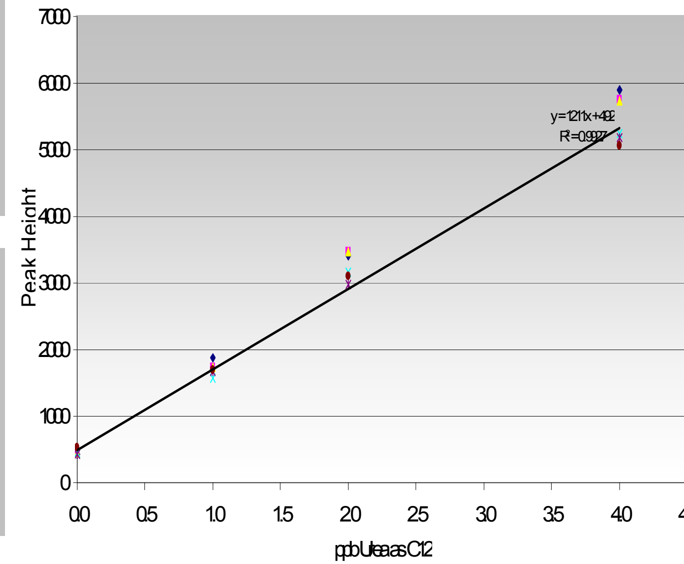
*Ref. "Undetectable TOC in UPW can influence DUV photolithography processes", J. Rydzewski & R. Godec, proceedings of SPWCC 2002 (Semiconductor Processing with Wet Chemicals Conference)

TCA Quantitative Analysis of Urea in UPW





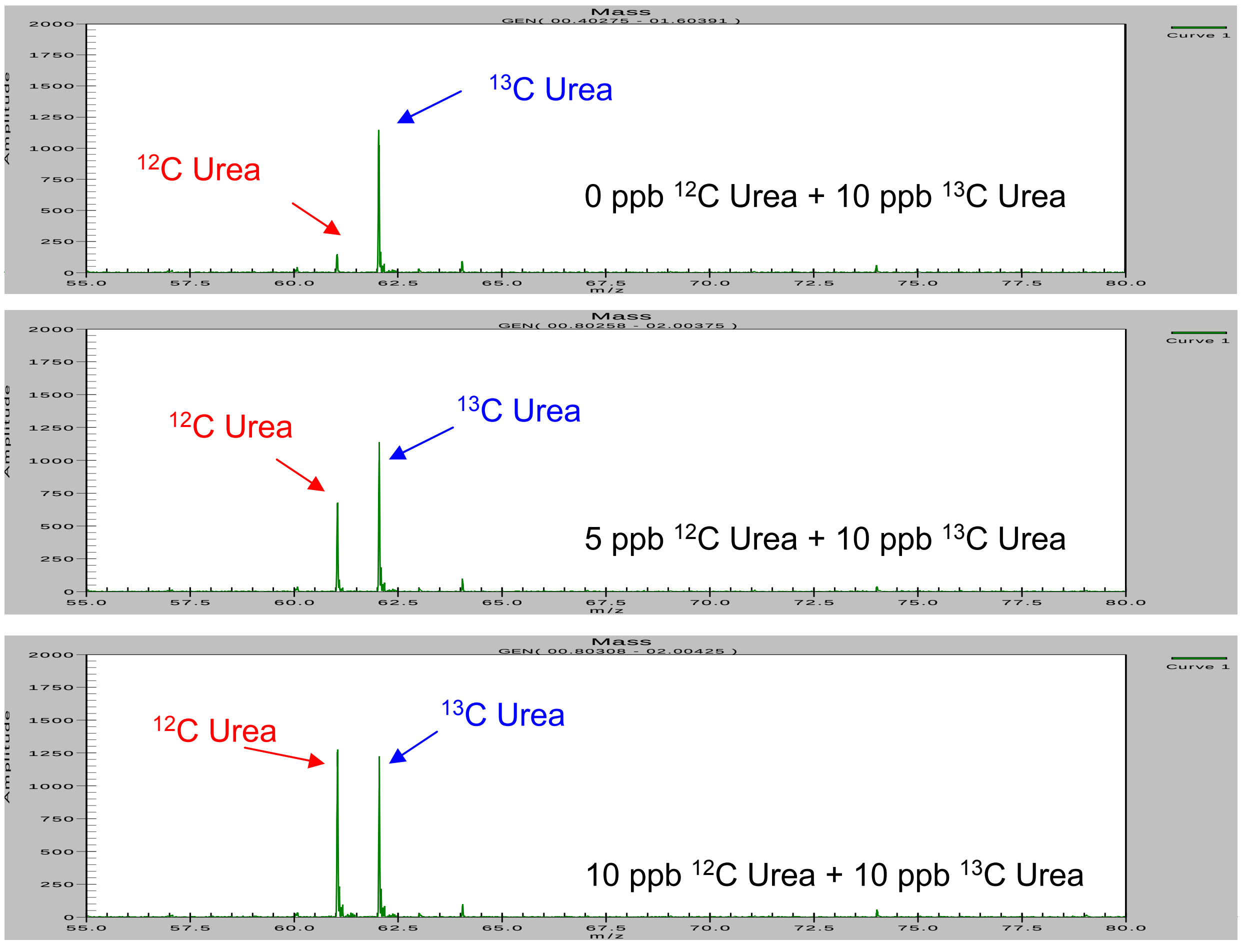




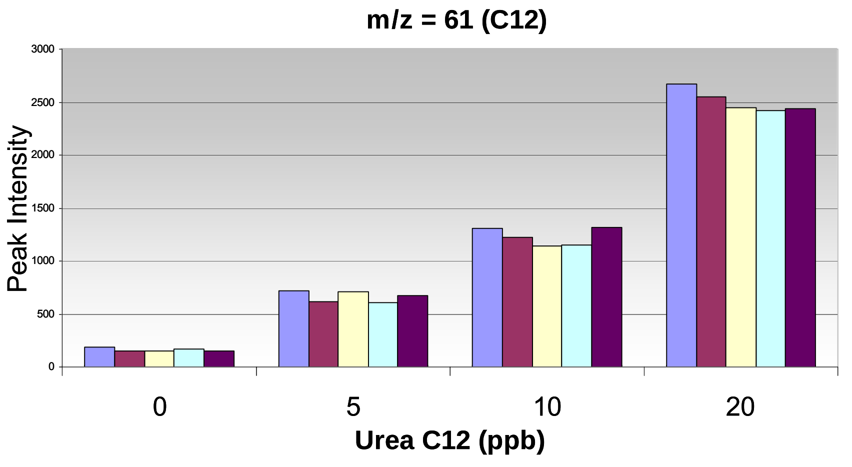
DL = 3σ/m = 0.084 ppb

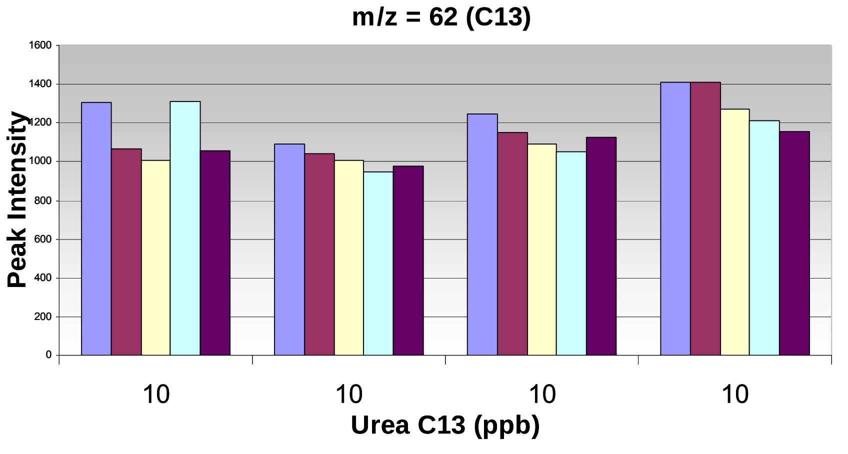
C = 84 ppt C, n = 6

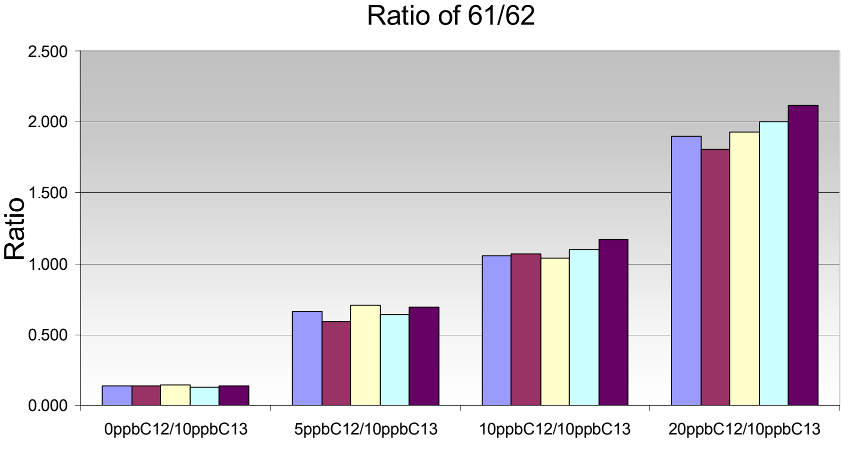
TCA Analysis of Urea by Ratio Technique



Ratio Measurement of ^{12}C Urea/^{13}C Urea



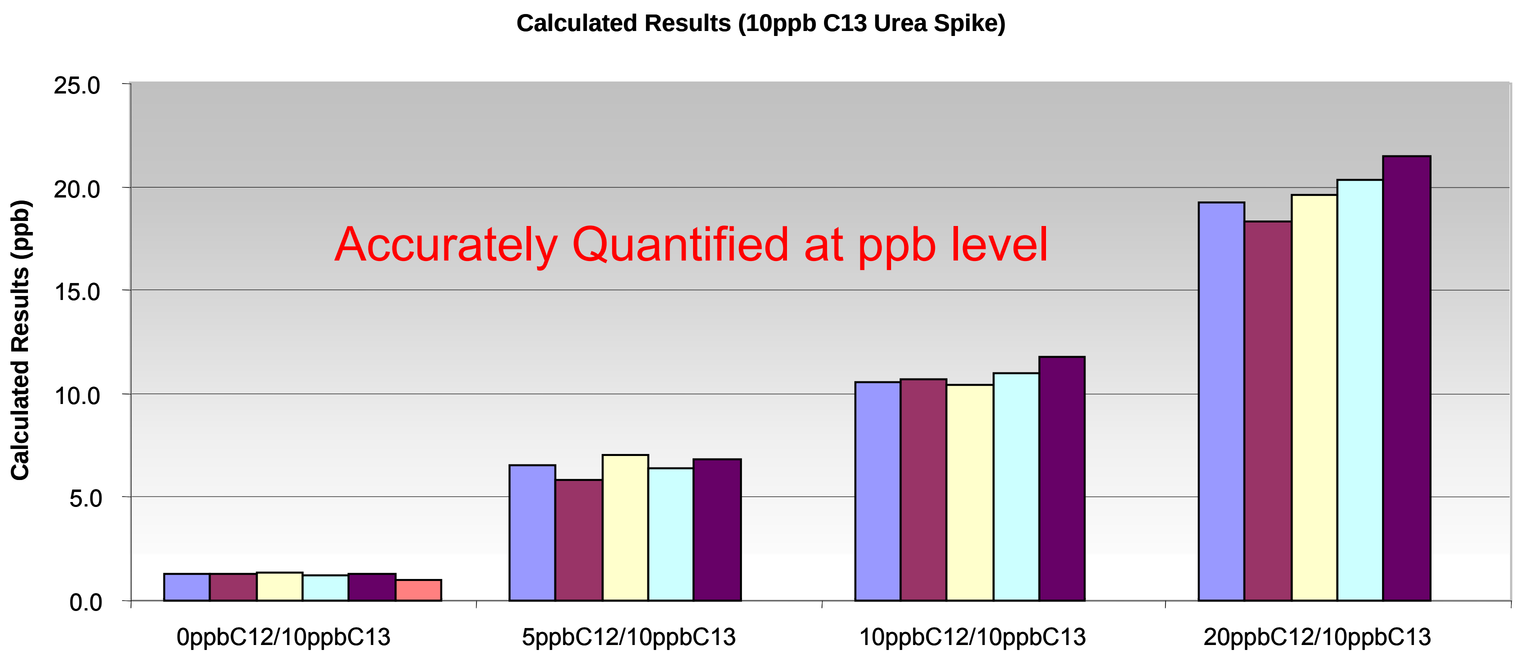




TCA Analytical Results of Urea

$$C_s = C_{sp}\left(\frac{V_{sp}}{V_s}\right)\frac{(A_{sp} - \mathbf{Ratio} \times B_{sp})}{(\mathbf{Ratio} \times B_s - A_s)}$$

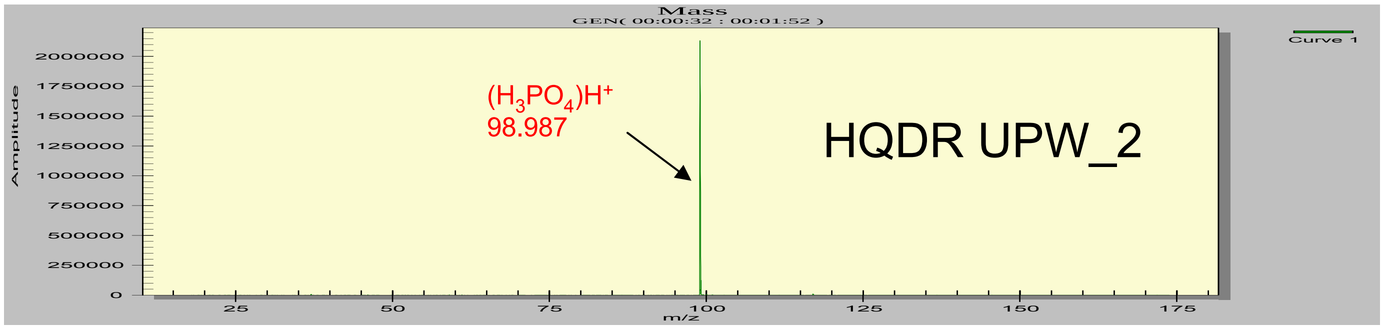
TCA Automatic Quantification

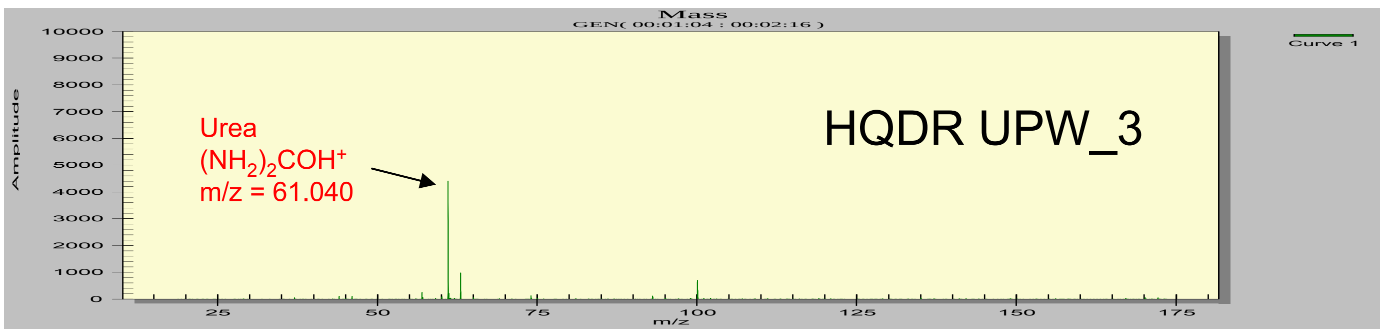


Example 4: Molecular Contamination in Pre-Gate Cleaning Processes at a Fab

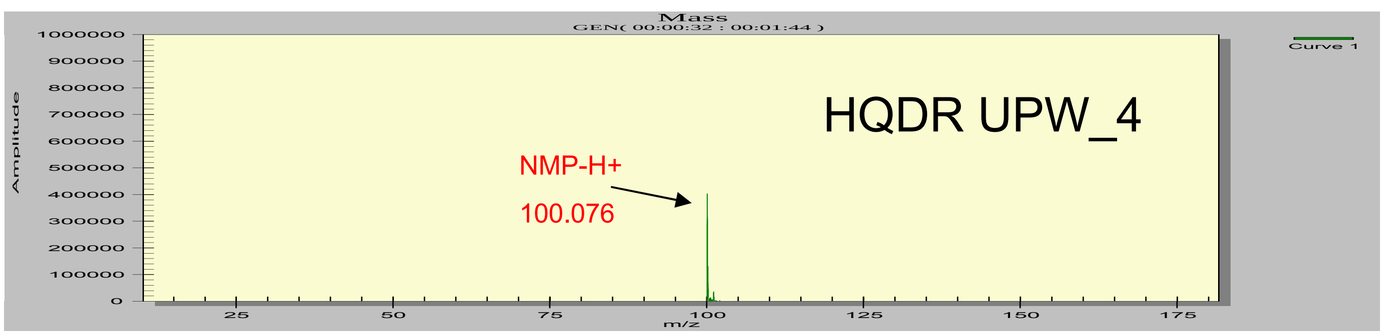
- Yield problems at a Fab
  - Gate oxide breakdown voltage reduction
- Results of TXRF and VPD-ICP/MS
  - No metallic contamination
- Organic or molecular contamination was proposed
  - No significant suspect by routine lab methods

Contaminants Found from HQDR (Hot Quick Dump Rinse) UPW by TCA



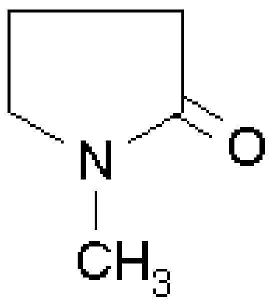


Scale
Different



Metara

Possible Contamination Sources in Fab



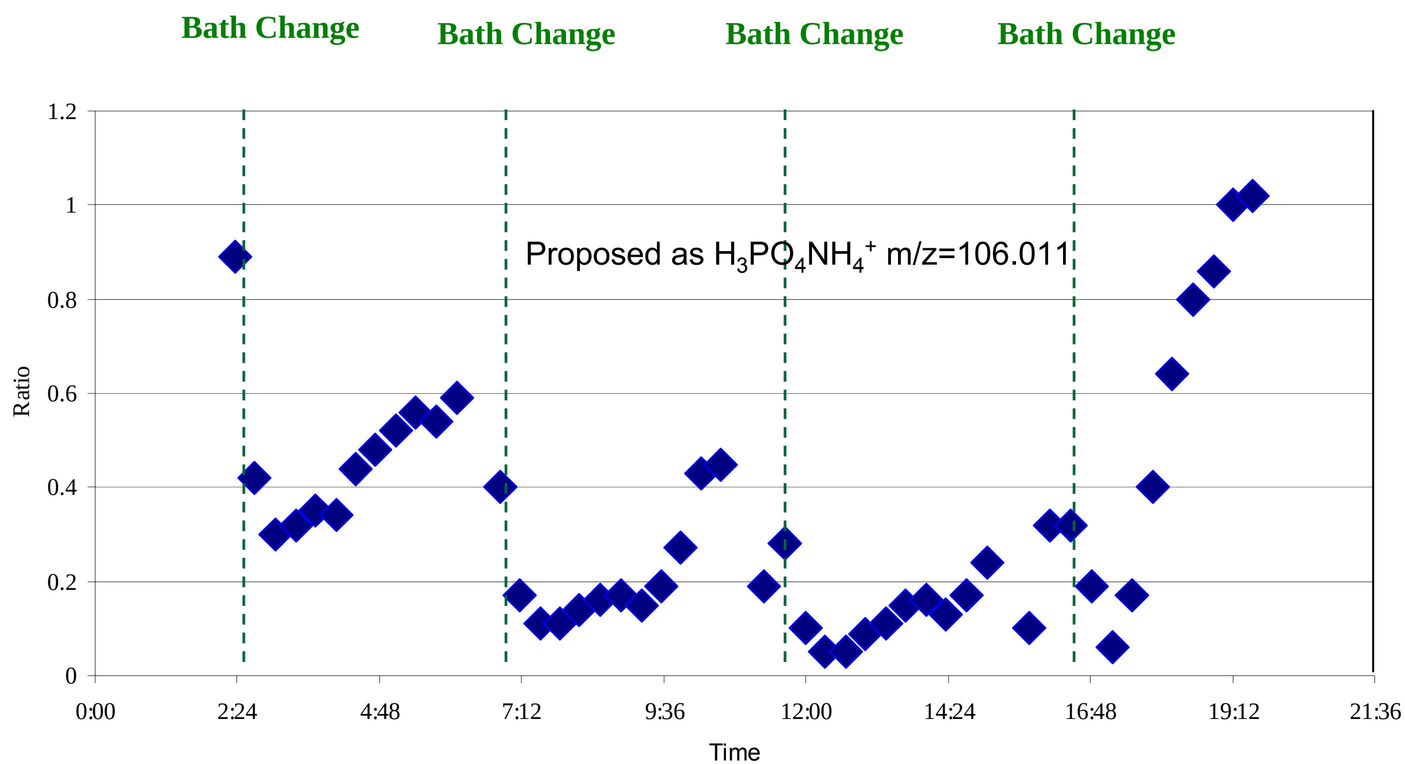
NMP = N-Methyl-2-pyrrolidone (C_5H_9NO m/z = 99.068)

- Photoresist stripper
- Wafer cleaning
- Semi-aqueous defluxing
- Degreasing
- Coatings (polyamide, epoxy, & polyurethane)

H_3PO_4 Incomplete rinse from nitride etching?

Urea Source water, re-cycling or reclaimed water?

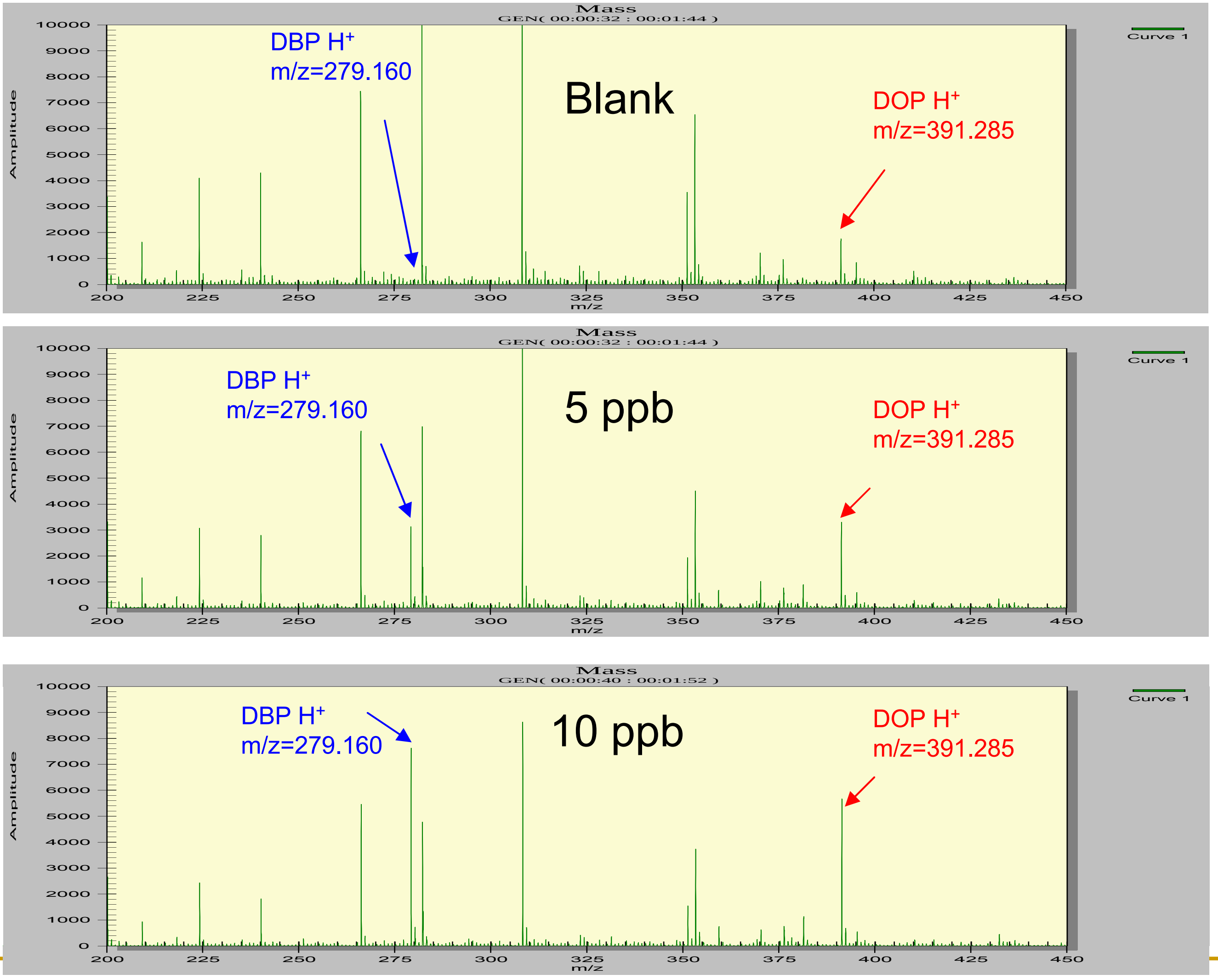
TCA In-Line Monitoring Phosphorus Species in SC-1 Bath at a Production Fab



Example 5: Phthalate (Plasticizer) Contamination in IPA (Isopropyl Alcohol)

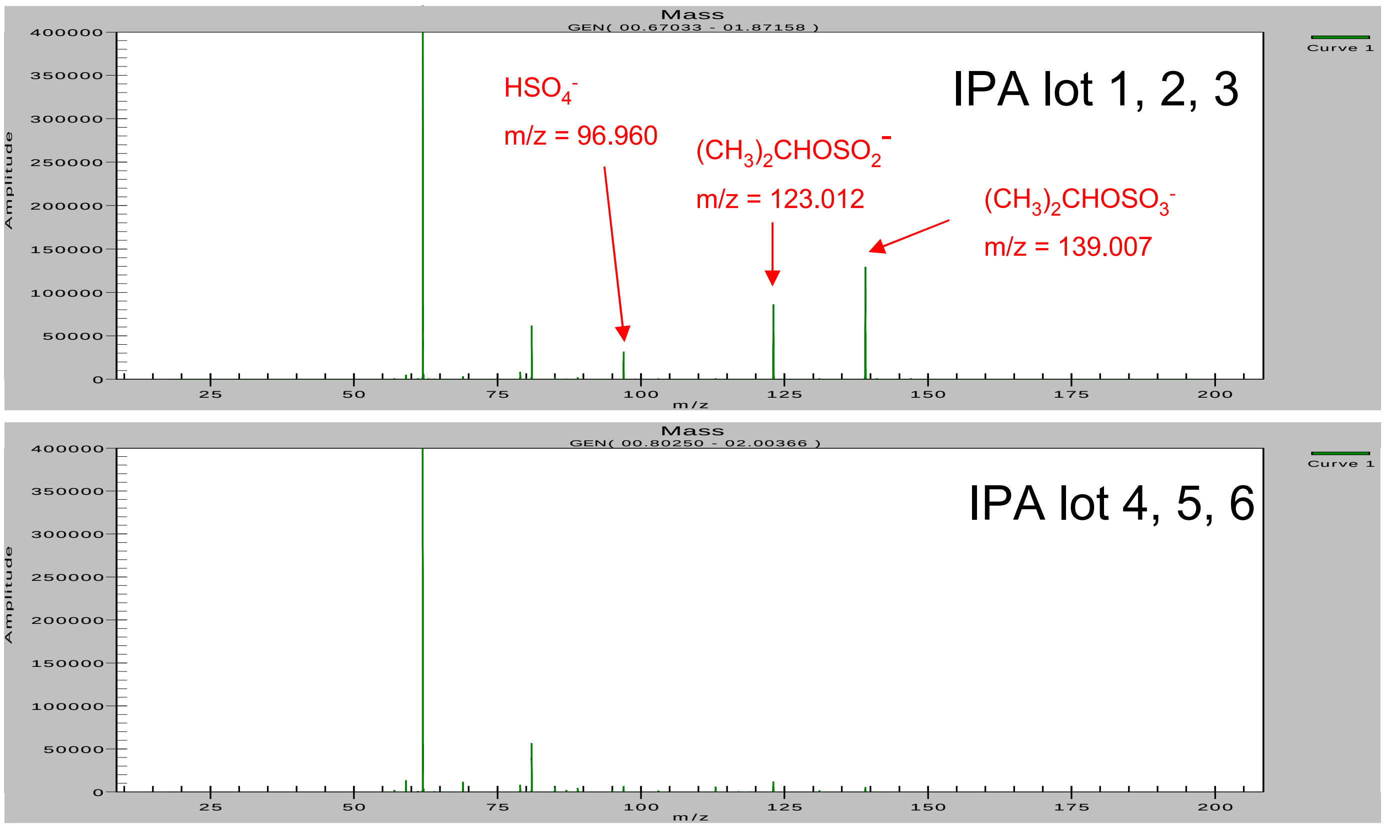
- It has been reported:
  - Dibutyl phthalate (DBP) in high density polyethylene (HDPE) containers leaching into IPA
  - Plasticizers deposit inside the gas nozzles and chamber in a dryer
- Phthalates have deleterious effects on wafers

TCA Analysis of Dioctyl Phthalate (DOP) and Dibutyl Phthalate (DBP) in IPA

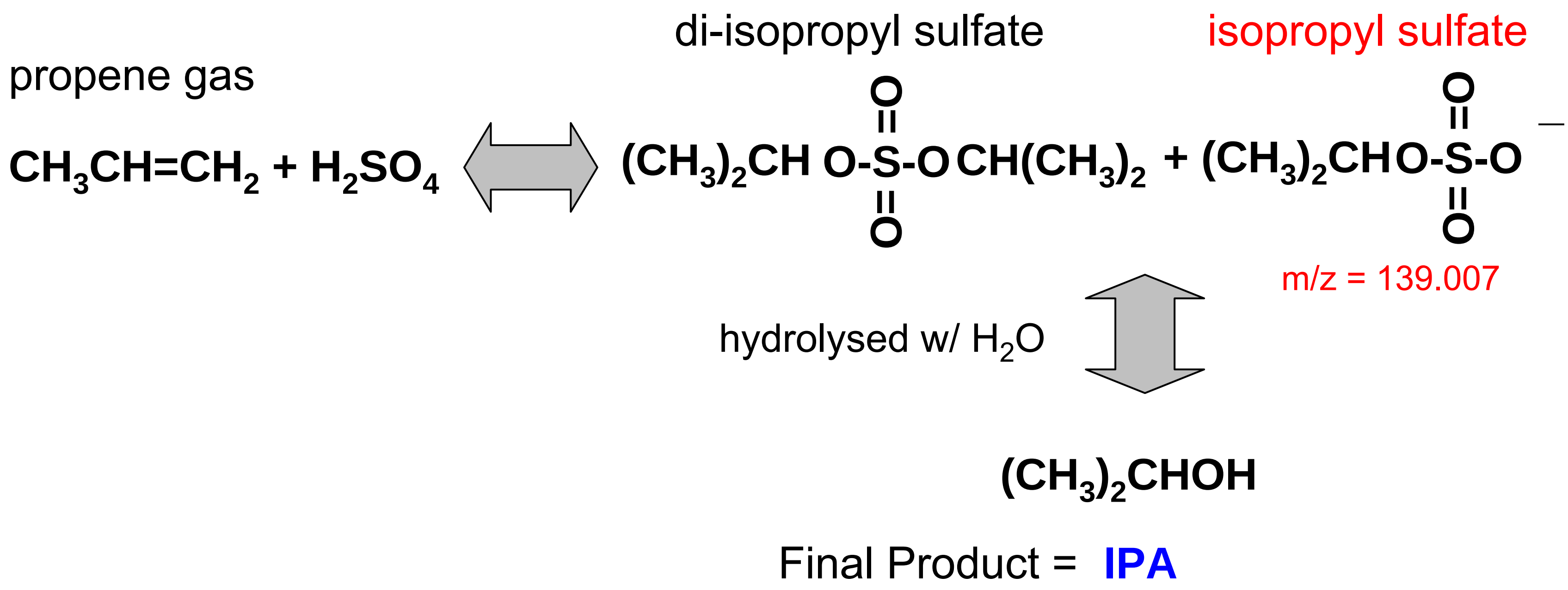


Example 6: Molecular Contamination in IPA (Isopropyl Alcohol) at a Fab

- IPA from lot 1,2 3 suspected causing multiple excursions
- No significant difference between lot 1,2,3 and lot 4,5,6 by routine lab methods



Contamination Sources from IPA Manufacturing Processes



Isopropyl sulfate is a highly suspect in IPA lot 1, 2, 3

Summary

- Using the TCA we have demonstrated the ability to:
  - Analyze molecular contamination in a variety of process solutions including UPW, SC-1 and IPA
  - Identify specific molecular contaminants
  - Provide quantitative concentration measurement
  - Make measurements in-line and in near real-time
  - Provide process chemistry trends that correlate to Wafer Fab yield problems

Conclusion

- We believe this new measurement capability will:
  - Enable statistically valid real-time process chemistry control decisions
  - Provide advanced warning of excursions
  - Enable chemical specifications and bath life decisions based on process data and yield correlation