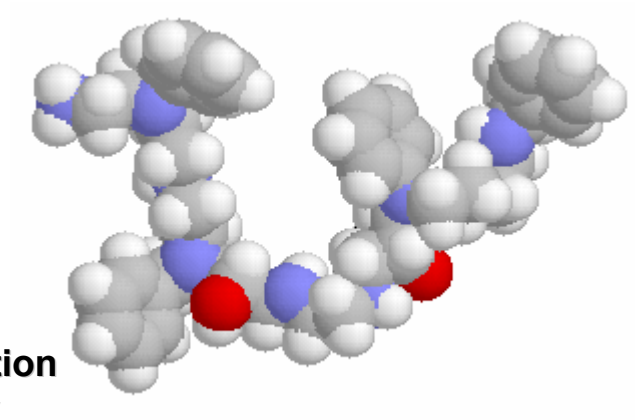
Automated and Near Real-time, Trace Contamination and Chemical Species Analysis for the Semiconductor Industry

H.M. 'Skip' Kingston

March 27, 2003



Duquesne University,
Professor of Analytical Chemistry
Departments of Chemistry and Biochemistry,
Center for Environmental Research and Education
Center for Microwave and Analytical Chemistry
Pittsburgh, PA 15282

Metara Incorporated,
Chief Technical Officer
2567 East Arques Ave
Sunnyvale, CA 94085

Overview

- **The "problems" as seen by a metrologist**
- **Metrology for contamination analysis in Semiconductor Fabrication**
- **New enabling technology needed**
- **Inventions required to impact the problem**
- **Analytical chemistry metrology tools**
  - Standard methods and new methods
  - IDMS, IPMS, SIDMS
- **Speciation and why it is important**
  - "Chemically Significant Data"
    - Bob Helms, SEMATECH – ULSI 3/25/02
    - Thomas Theis, IBM-ULSI 3/25/02
- **Time relevant inclusive data – initial tests**

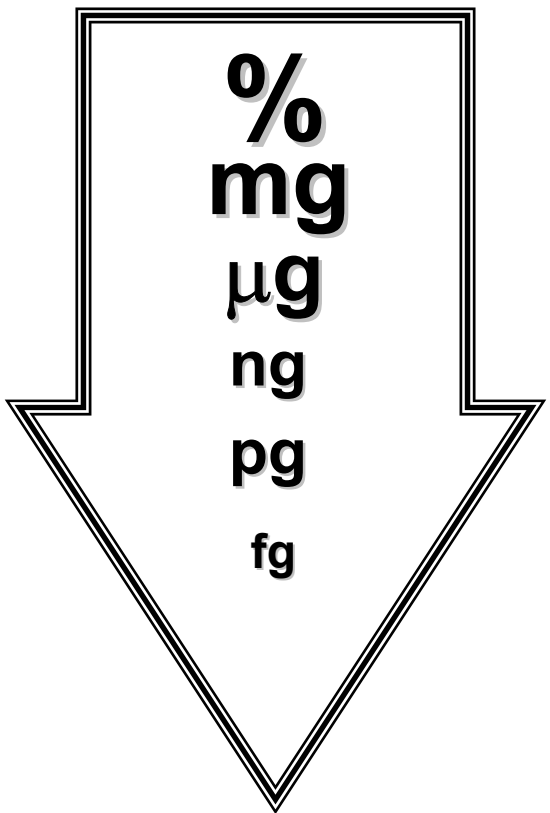
The Problem:

At these dimensions Contamination is a critical parameter in the function and assembly of Semiconductors and Nanotechnology devices

- ***Nanotechnology*** **- As devices become 3 to 20 atoms in size, nanotechnology and micromachines predict contamination determines the viability of the device**
- ***Semiconductor*** **- As semiconductor line widths go to <0.13 micrometers contamination become a critical limitation of the performance of these devices**

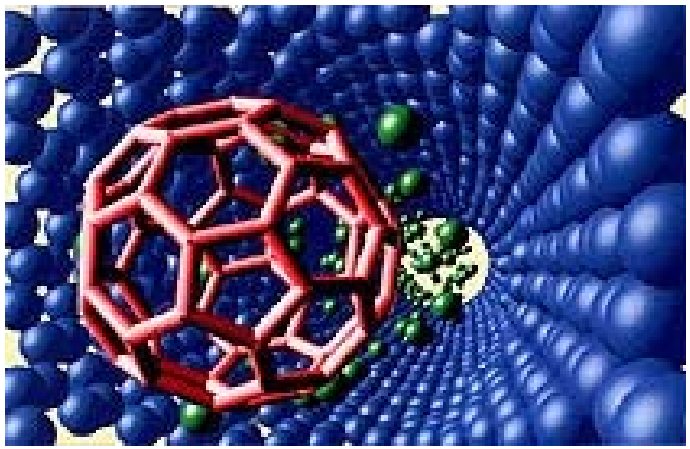
The Relationship: As trend in ultra-trace element analysis go lower, previous techniques become inadequate and new methods are required to maintain or achieve accuracy & precision

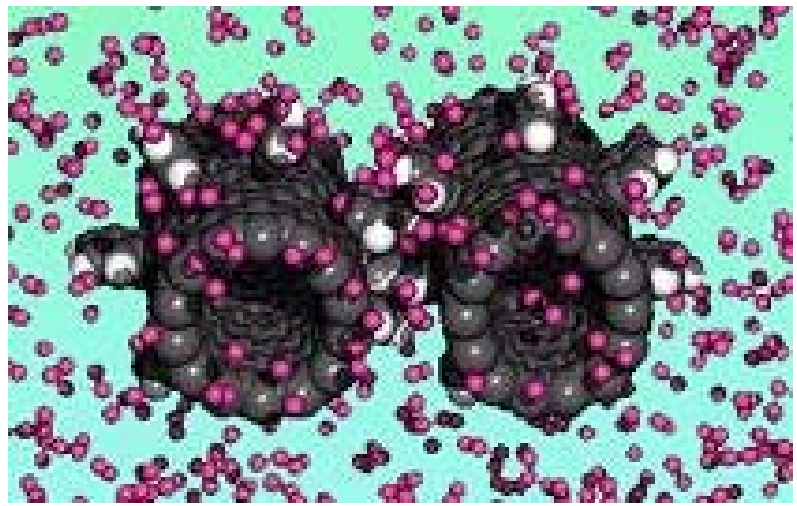
"New Thresholds Require New Methods"

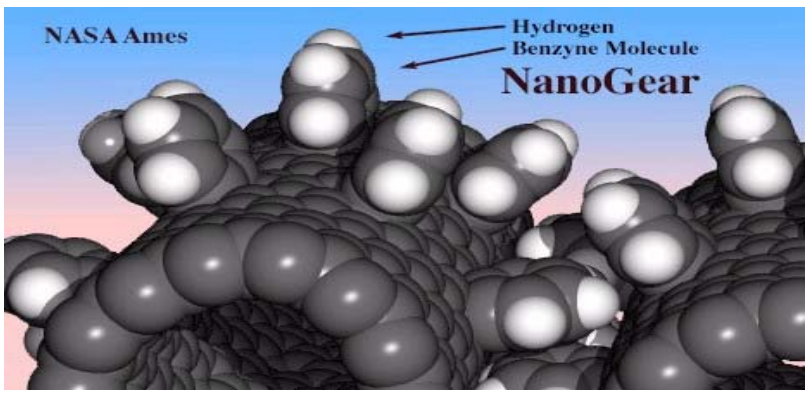


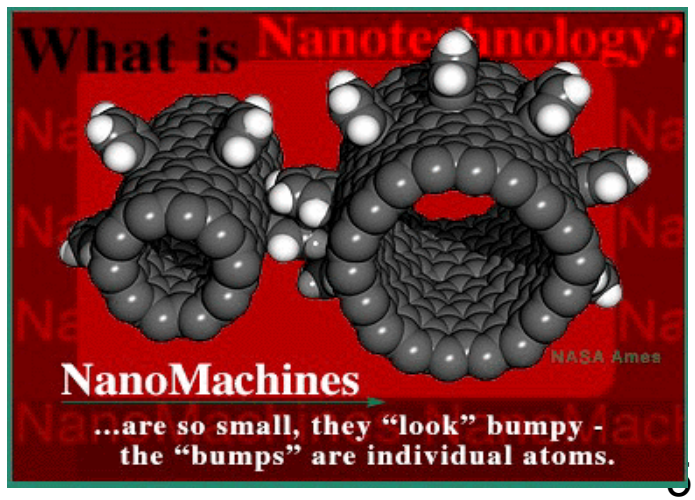
Nanotechnology

How much contamination does it take to act as a monkey wrench in the gears at the molecular level?









ITRS Challenge #1

Semiconductor Road Map for Development Important Industry Directions!

"Key Area of the 2001 edition of the ITRS focus on the yield model and defect budget, defect detection and characterization, yield learning, and wafer environment contamination control."

Reference: "Examining upcoming yield enhancement challenges in the 2001 roadmap" Micro, February 2002

The Challenge?

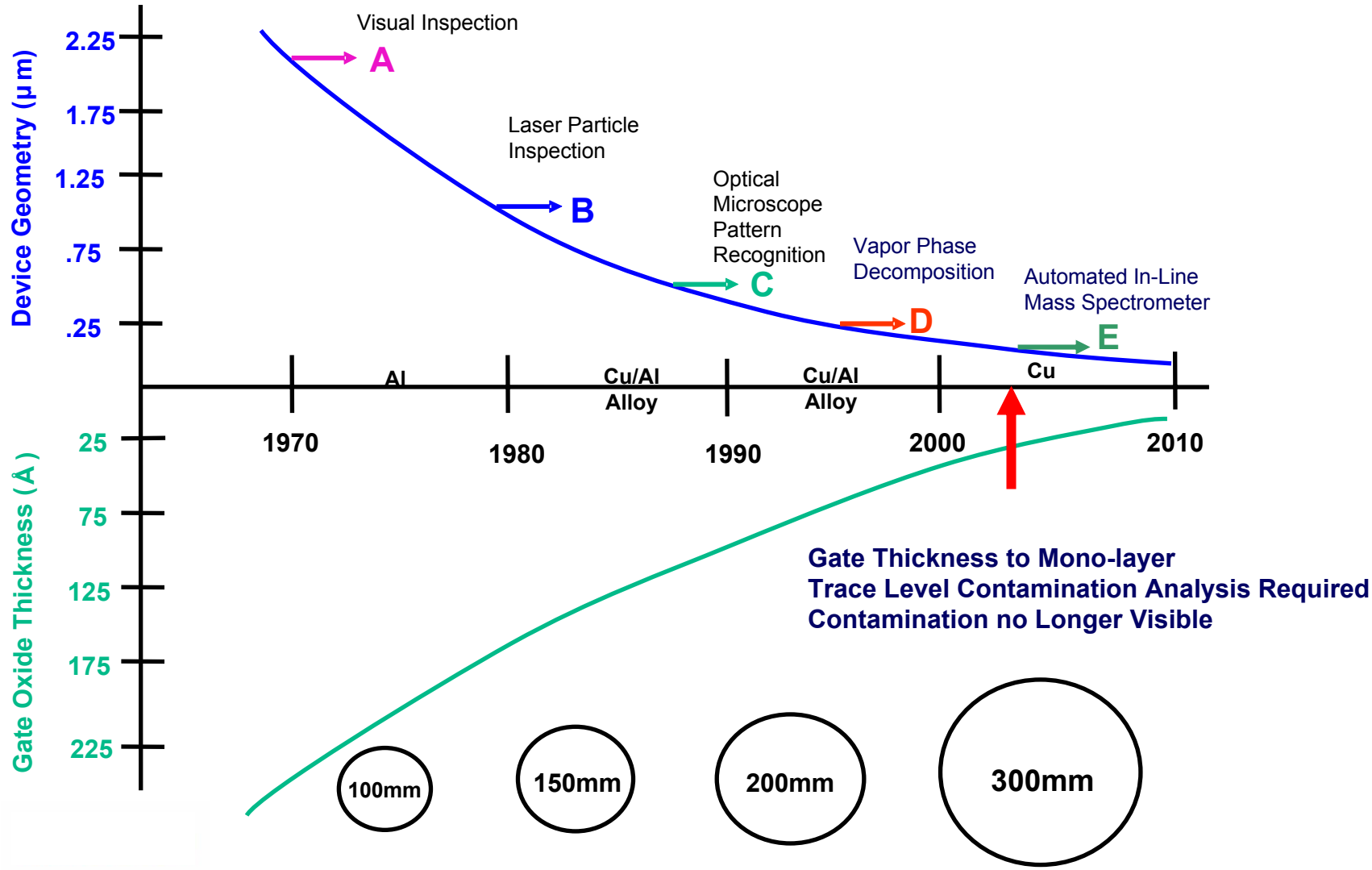
"The most critical challenge is to find ways to determine the effects of trace impurities on device performance and yield."

Reference: "Examining upcoming yield enhancement challenges in the 2001 roadmap"
- ***Micro***, February 2002

Authors: Christopher Long, IBM;
Milton Godwin, Applied Materials;
Manuela Huber, Sematech/Infineon;
Richard Jarvis, Sematech/AMD
Fred Lakhani, Sematech

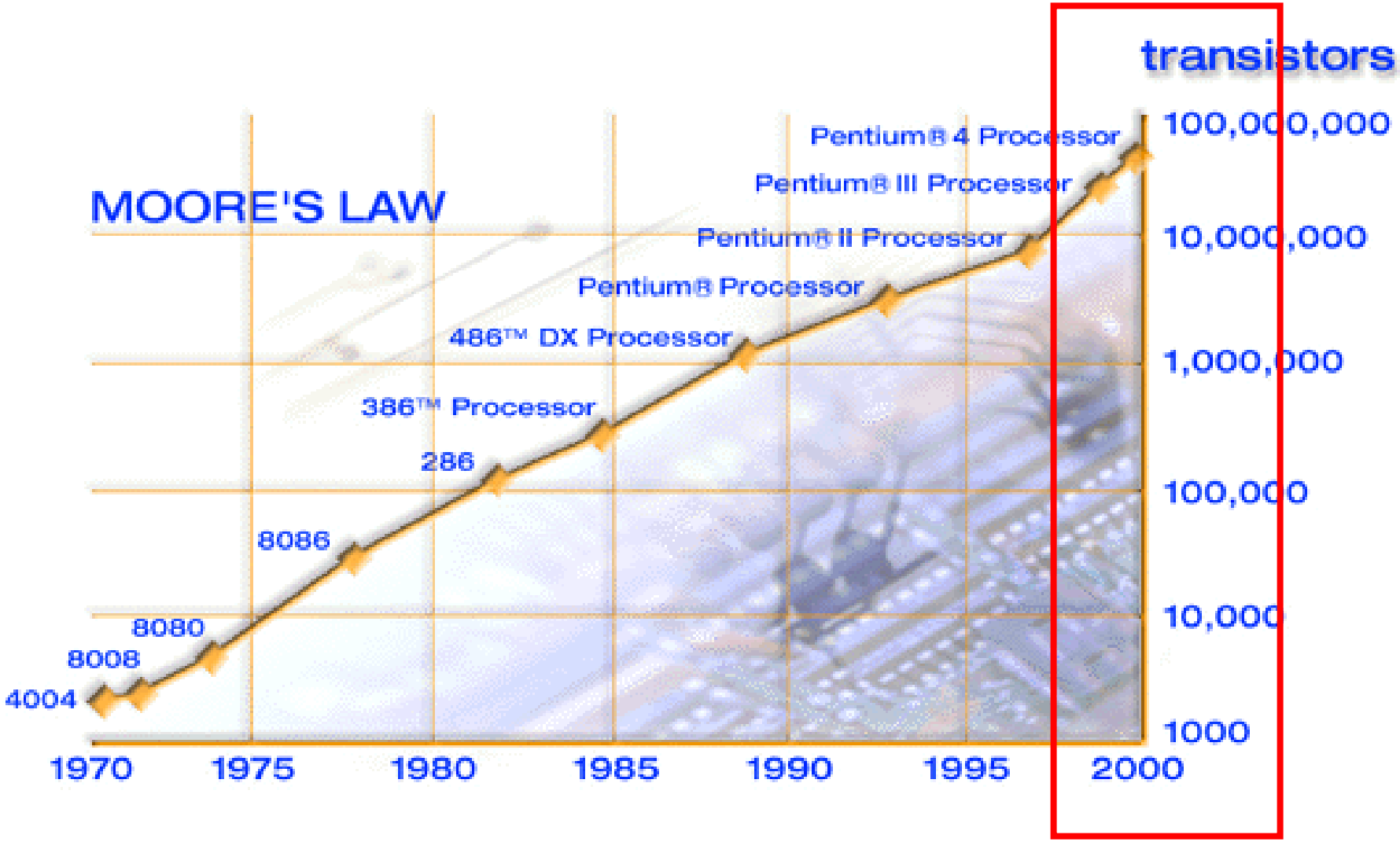
Moore's Law & Drives Contaminate Analysis

Device dimensions increase importance and implementation of contamination measurement metrology



Moore's Law

Analytically Significant Threshold



History of Contaminate Analysis for Semiconductors

Visual Inspection

Laser Particle Counters

Automated Microscopes
With Pattern Recognition

Vapor Phase Decomposition

TXRF Analysis, VPD/TXRF

Laboratory Metal Analysis by
ICP-MS

Need for Automated
On-Line
Mass Spectrometry
"Chemically Relevant"

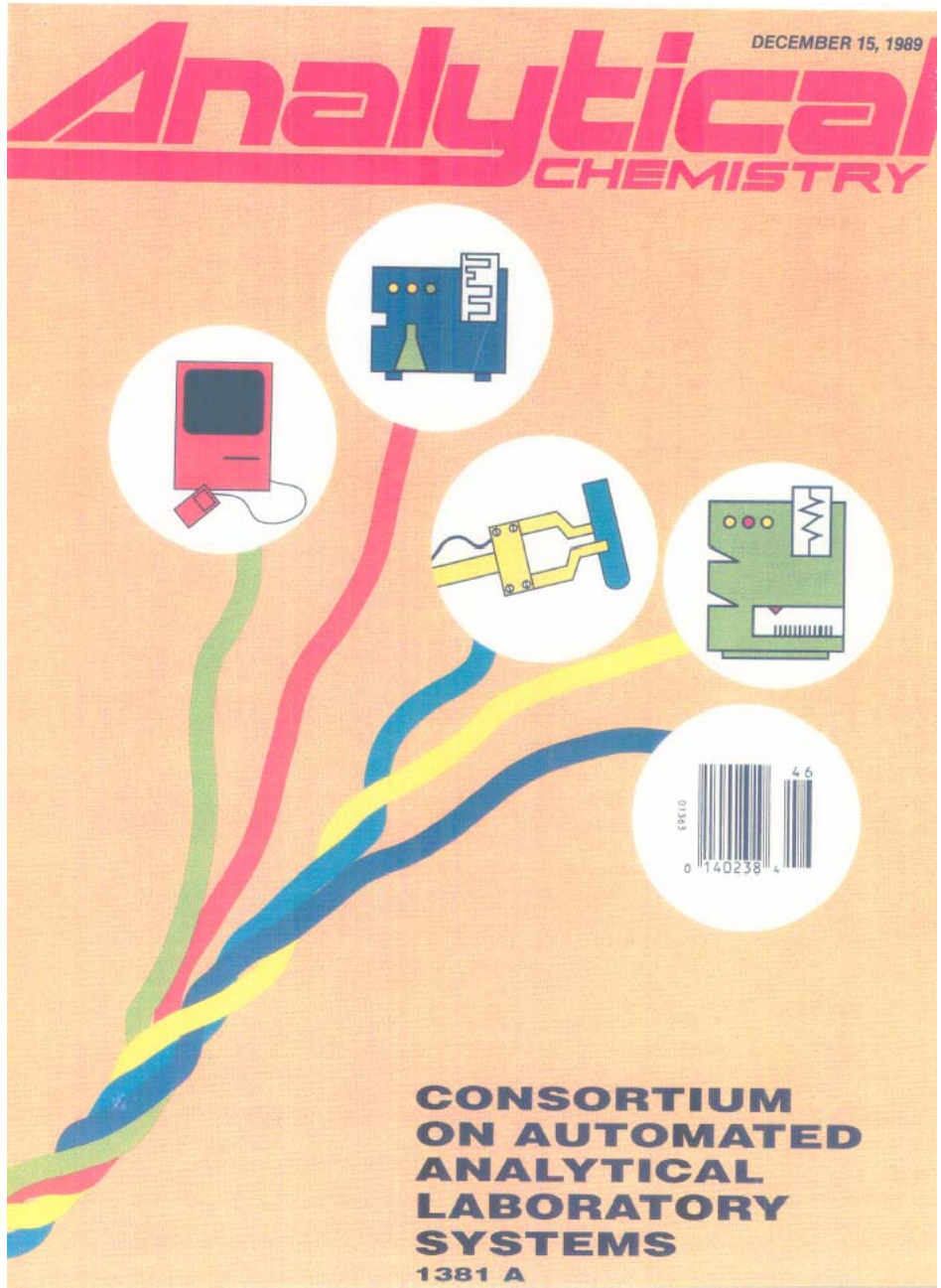
critical nature of contamination metrology

State-of-the-art: mid 2000 Project Begins

- **Elemental metal analysis primarily**
  - Few anion, organic and no species information
- **Species evaluation not considered feasible**
- **6-12-24-48 hour sample to data turnaround is usual for metal analysis in semiconductor fabs**
- **Lack of on-line metrology for liquids**
- **Up to 60 liquid cleaning steps required in some advanced wafer processing**
- **Constituent analysis needs emerging eg. Cu ECD**

U.S. Industries had before addressed a selected set of these critical metrology issues in an industry government consortium known as CAALS:

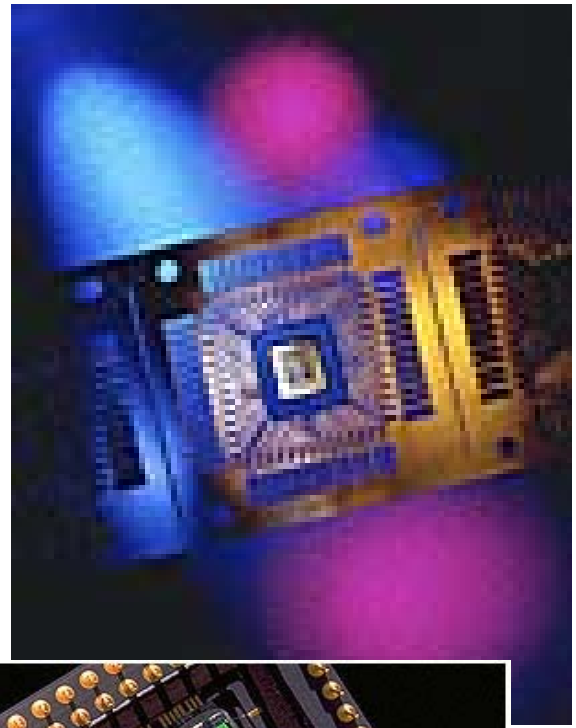
- NIST
- Hewlett-Packard
- Perkin-Elmer
- Dupont
- Union Carbide
- Kodak
- Department of Energy
- Zymark
- et. al.

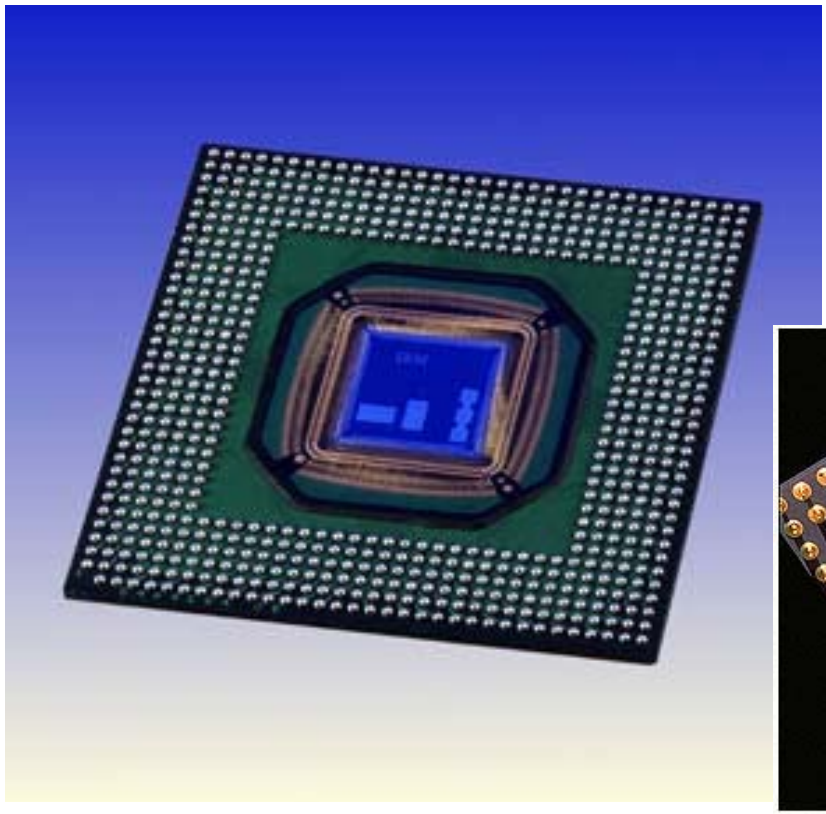


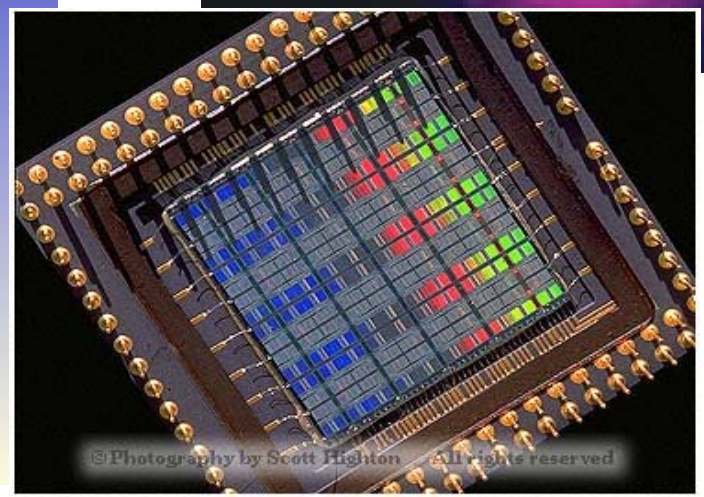
State-of-the-art ICP-MS Desired Technology "Wish List"

Item	ICP-MS	Desired Technology
Target Application	Lab applications	Real-time, In-line, In-fab: Trace contamination monitoring of standard aqueous semiconductor solutions
Sample Matrix	UPW, SC1, SC2, IPA, DHF, $HN0_3$, H_2O_2	UPW, SC1, SC2, IPA, DHF, $HN0_3$, H_2O_2
Monitors	Depends Upon Available Standards Cations (+) Elements Inorganics	20 - 28 Trace Contaminants Cations (+) and anions (-) Elements and species Inorganics and Organics
Sample Preparation	Manual	Automated
Limit of Detection	< 20 ppt	< 20 ppt
Calibration and Quantitation Standards	Calibration Curves	Direct Analysis, Automated Calibration NIST tracible
Sample Volume	5 mL	<5 mL
Technology	ICP-MS	Based on Mass Spectrometer
Throughput	24 to 72 hours	5-10 sample/hr (5 min/sample)
Accuracy	± 25% at the quantitation limit	<± 25% at the quantitation limit

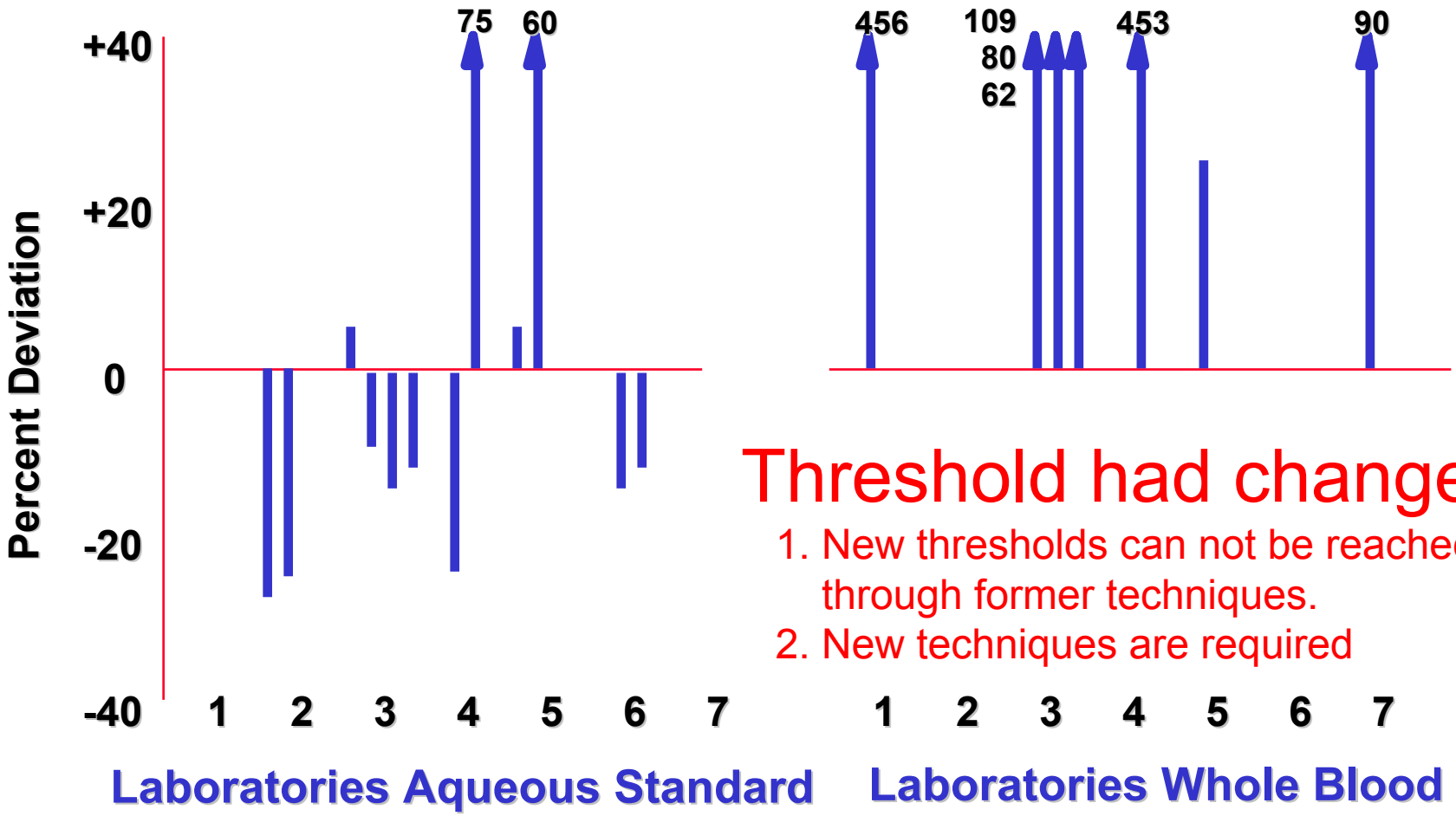
Demanding Technology Requires Demanding Metrology







Example: Comparison of Interlaboratory results of an Aqueous Standard and Whole Blood



Threshold had changed!

1. New thresholds can not be reached through former techniques.
2. New techniques are required

Reproduced from "The Role of the Analytical Blank in Accurate Trace Analysis" by T. J. Murphy, National Bureau of Standards Special Publication 422, Accuracy in Trace Analysis: Sampling, Sample Handling, and Analysis, Proceedings of the 7th IMR Symposium, Oct. 7-11, 1974, Pub. 1976.

New Technology Required

An Unconventional Instrument:

An Automated real-time integrated sample preparation and analysis system for inorganics, organics, and species, for the majority of cleaning and process solutions

What to do?

Invent and Engineer a New Technology

Recall – ITRS Challenge #2

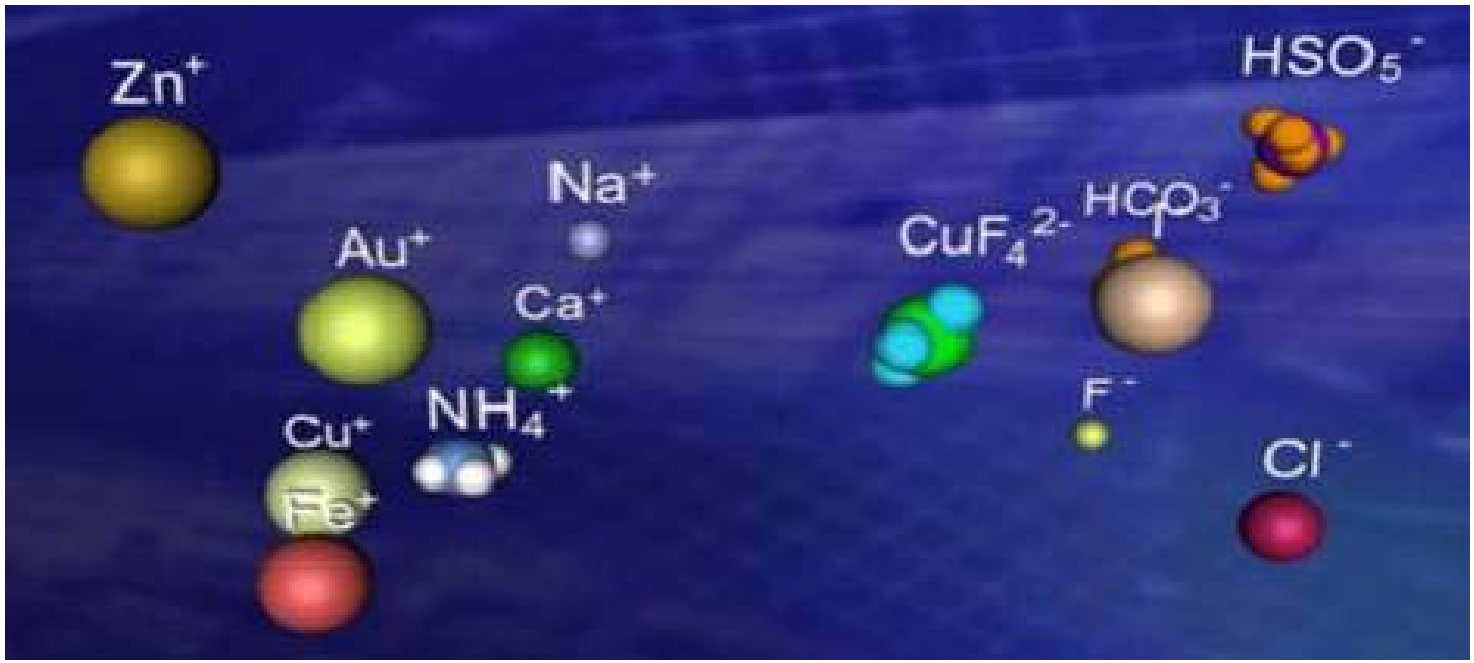
"The most critical challenge is to find ways to determine the effects of trace impurities on device performance and yield."

i.e. Statistically valid correlation and modeling
i.e. "Chemically" significant determinations

Reference: "Examining upcoming yield enhancement challenges in the 2001 roadmap"
- ***Micro***, February 2002

Authors: Christopher Long, IBM;
Milton Godwin, Applied Materials;
Manuela Huber, Sematech/Infineon;
Richard Jarvis, Sematech/AMD
Fred Lakhani, Sematech

Cations(+) & Anions(-)

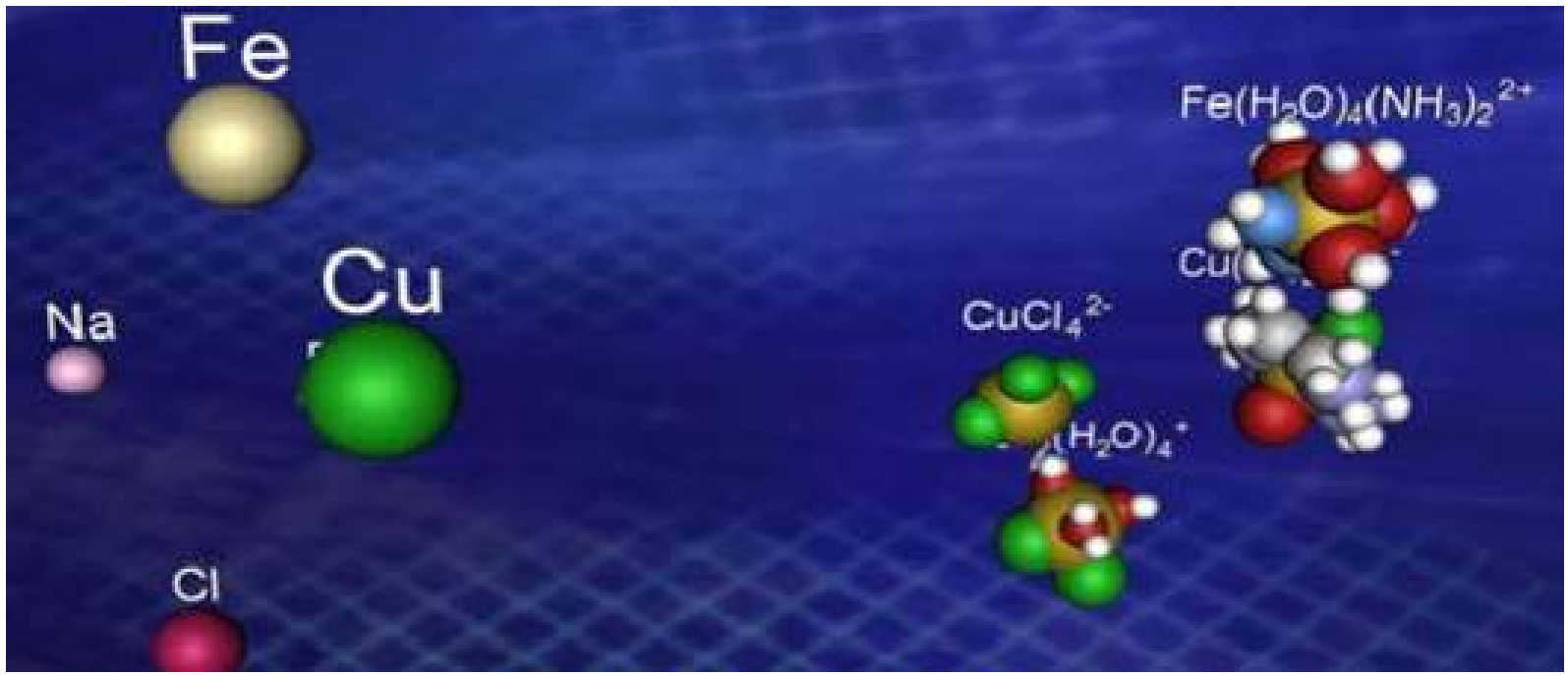


Cations

Anions

Elements & Species:

Elemental Species
Organic Molecules
Inorganic Complex Species
Organic Complex Species



Elements Species

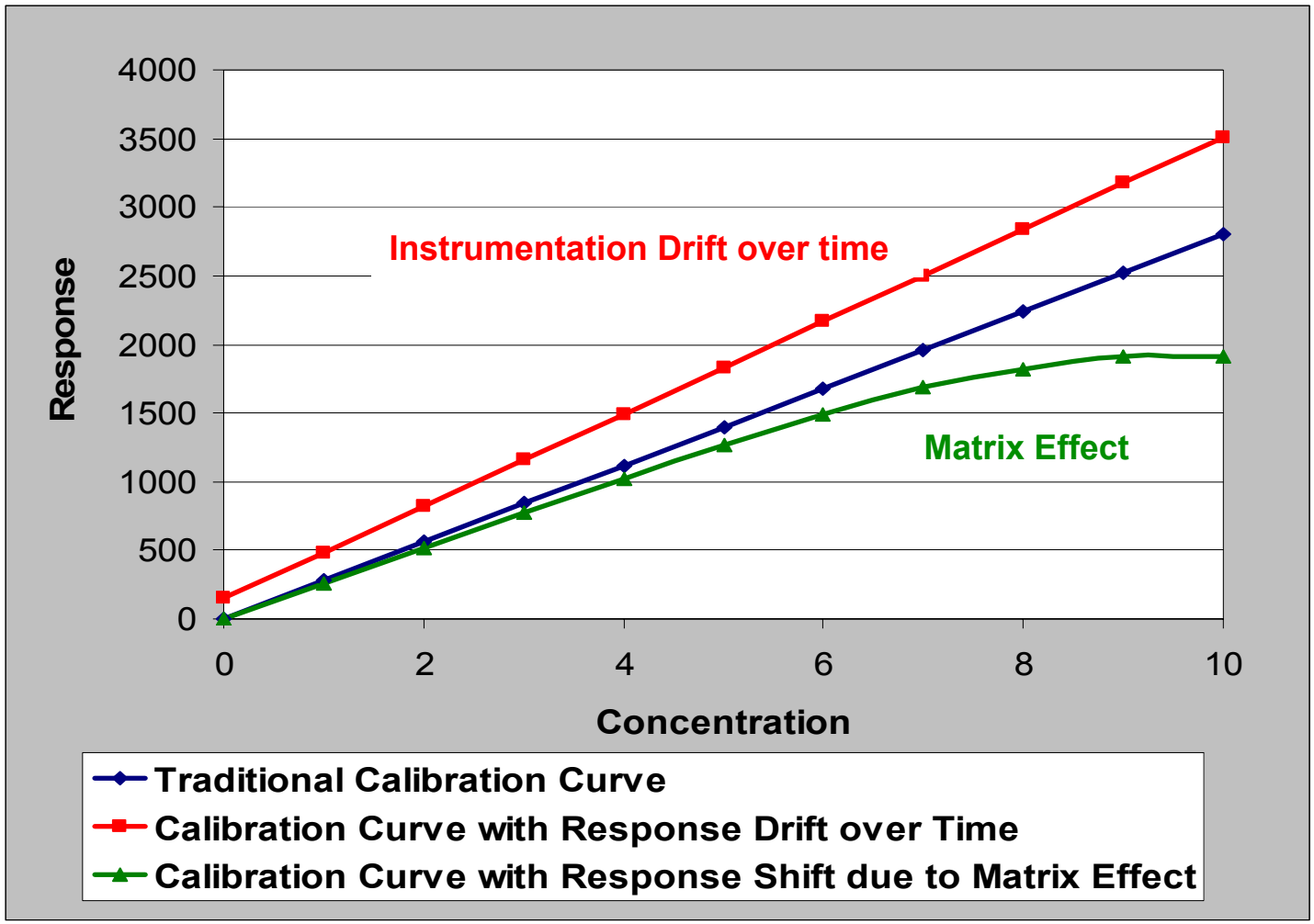
Why Have Mass Spectrometers Not Been Used in On-Line, Real Time, Multi-matrix Rapid Sequential Analysis?

- Manual calibration requirement
- Lack of long term stability
- Matrix interferences
- Lack of instrument sensitivity in some matrices
- Inappropriate and unstable MS ionization sources
- Unavailability of fully automated systems
- Lack of applicable sample preparation integrated and automation with the mass spectrometer

Mass Spectrometer Calibration

- Mass Spectrometer Drift
- Requires Continual Calibration
- Method of Calibration Must be Reliable
- Method Desired to be Matrix Independent
- Calibration Solutions Should Inexpensive
- Method must be very fast

Quantitation: Traditional Calibration Curve



Example, Examination of One Approach: On-Line, Real-Time, Automated, Direct Quantization for Elements, Species and Complex Molecular Species

- **Direct Quantization through On-Line IDMS and SIDMS as a new capability:**
  - In Process Mass Spectrometry or "IPMS"
- **Fundamental enabling technology**
- **Alternative and simultaneous measurement of elements, molecules, and molecular species**

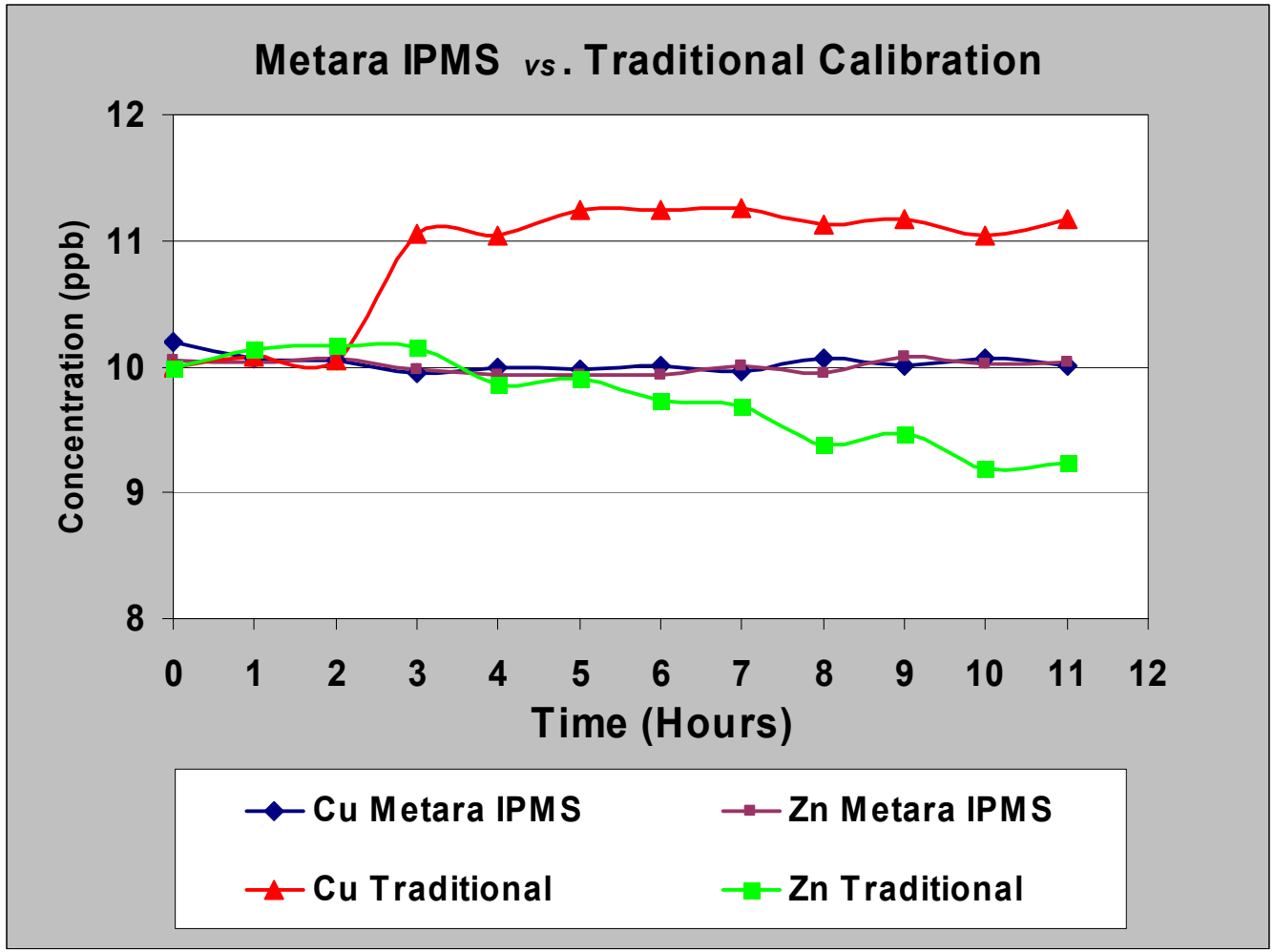
Questions to consider:

1. What new technology do you see that you do not expect?

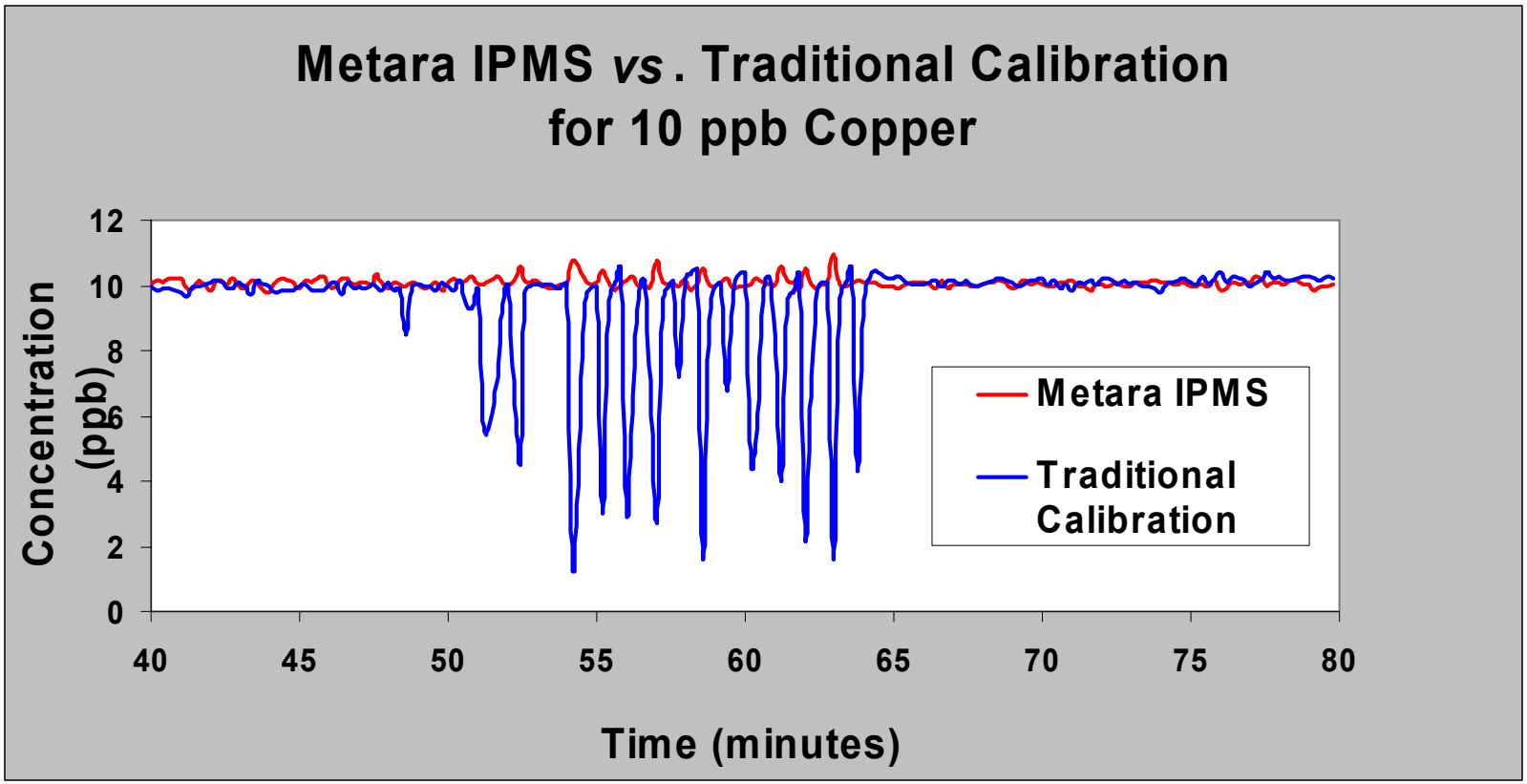
2. Does technology Changes the way we do things?
3. Does it change what we call “normal”?

4. Do you think his son will use a drum?

Mass Spectrometer Drift
Example: IPMS *vs.* Traditional -
IPMS reduces or eliminates effects of mass spectrometer drift, enabling automation (patent pending)



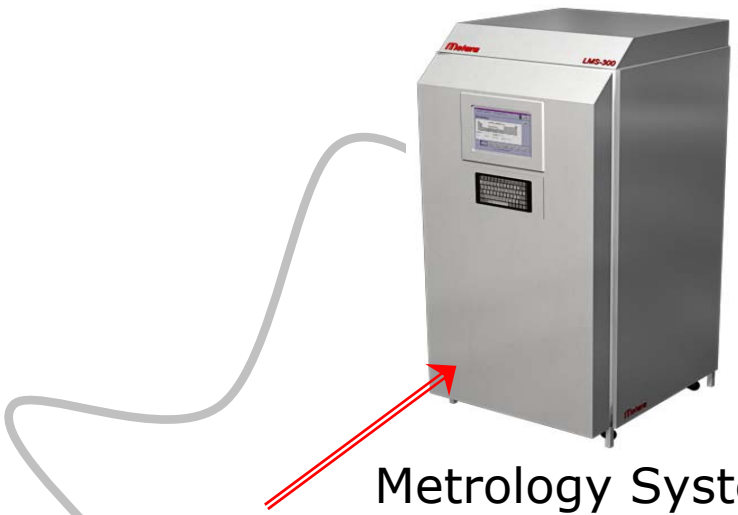
Mass Spectrometer Signal Stability
Example: IPMS compensating for MS stability, retaining accuracy, and enabling automation (patent pending)



With a typical analytical instrument, air bubbles in the sample introduction system may cause a dramatic instability and/or decrease in signal.

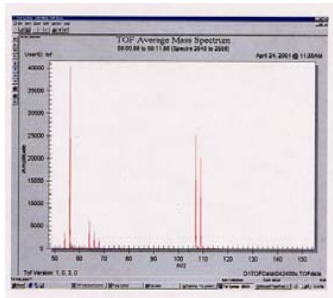
However, ^{63}Cu: ^{65}Cu isotope ratio measured by the IPMS Method remain constant.

Technology Overview



Metrology System

Sample



Data

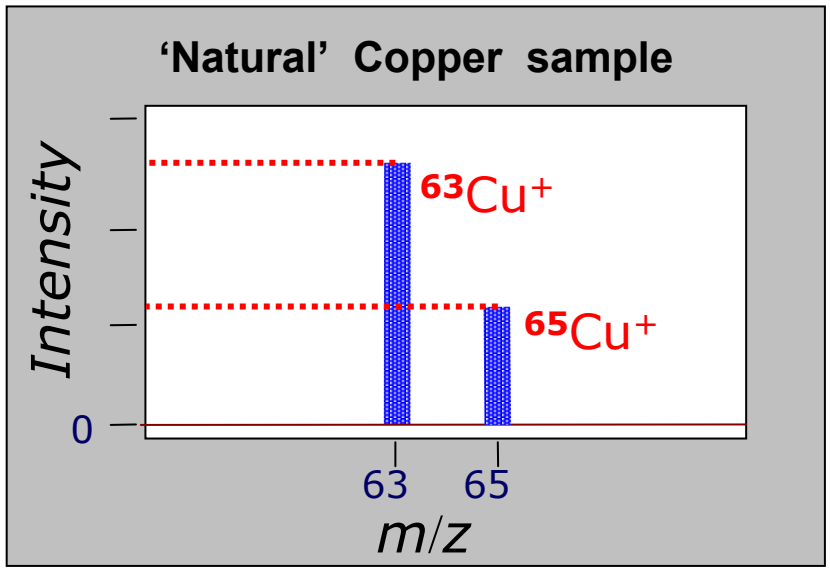
Information

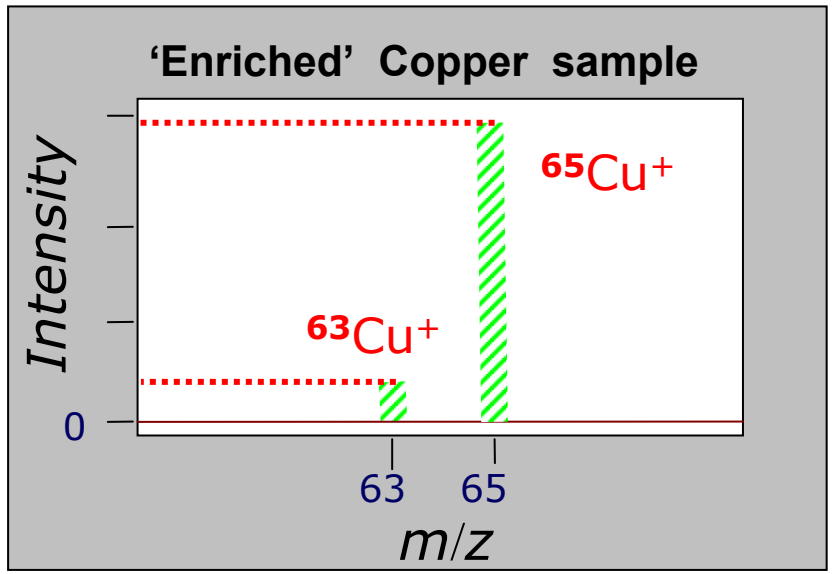
Element	Conc.
Ionic & Metalic	1.23 ppb
Organic Molecules	190 ppt
Species	640 ppt

Quantification Method

Metara In-Process Mass Spectrometry (IPMS)

e.g. Mass-Spectra of Copper Samples





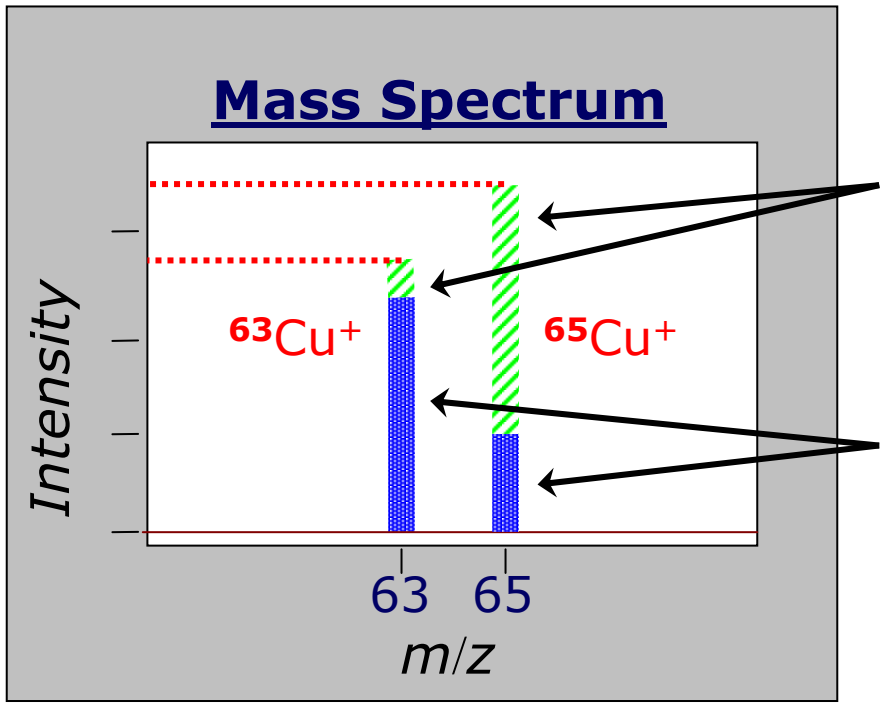
^{63}Cu & ^{65}Cu occur naturally in a 69:31 abundance ratio.

Isotopically-enriched solutions are commercially available (*e.g.* 5:95).

Quantification Method

Metara IPMS

A sample of copper of unknown concentration is 'spiked' with a known amount of an isotopically-enriched standard, and introduced into the LMS-300 TCA.

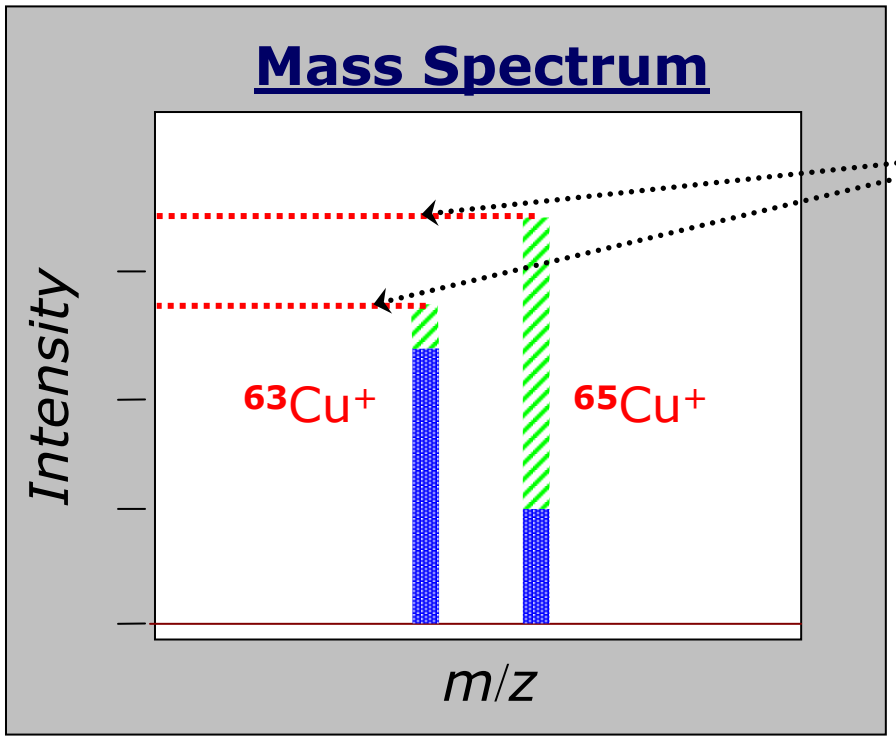


Contributions to signals from the spike.

Contributions to signals from the sample.

Quantification Method

Metara IPMS



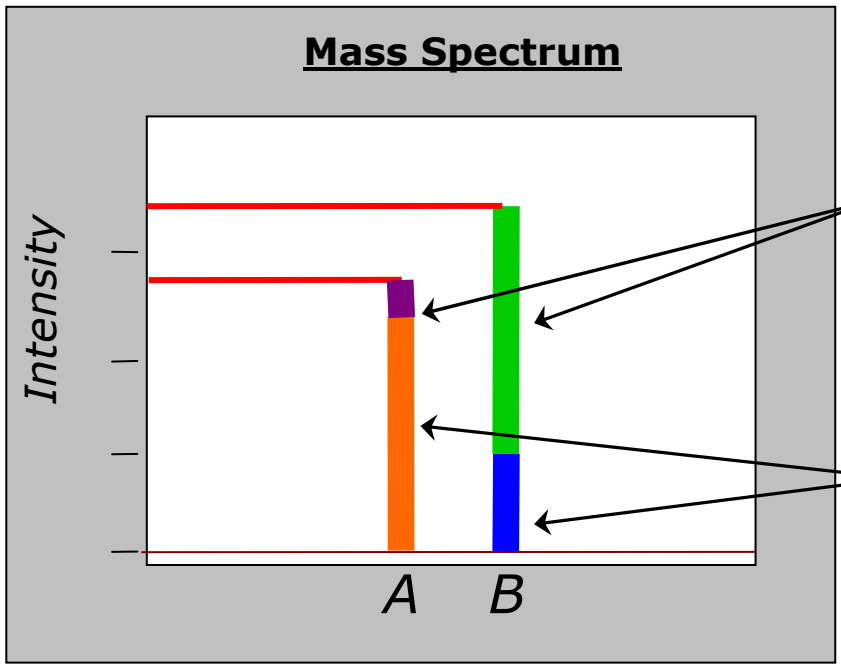
*The concentration of copper in the sample is deduced from the **RATIO** of the isotope signals…*

This calculation is exemplified in a later example.

Element	Conc.
Fe	1.23 ppb
Cu	190 ppt
Ni	640 ppt

Metara IPMS Calculation

$$\text{Ratio}\left(\frac{\text{Isotope } A}{\text{Isotope } B}\right) = \frac{(\text{Amount of } A \text{ from Sample} + \text{Amount of } A \text{ from Spike})}{(\text{Amount of } B \text{ from Sample} + \text{Amount of } B \text{ from Spike})}$$



Contributions to the signals from the *Spike*.

Contributions to the signals from the *Sample*.

... cntd

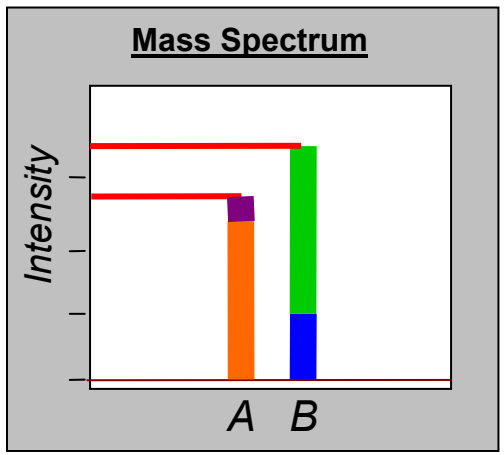
Calculation & Formula

… cntd

$$\text{Ratio}\left(\frac{\text{Isotope } A}{\text{Isotope } B}\right) = \frac{(\text{Amount of } A \text{ from Sample} + \text{Amount of } A \text{ from Spike})}{(\text{Amount of } B \text{ from Sample} + \text{Amount of } B \text{ from Spike})}$$

So …

$$\text{Ratio} = \frac{(A_s C_s V_s + A_{sp} C_{sp} V_{sp})}{(B_s C_s V_s + B_{sp} C_{sp} V_{sp})}$$

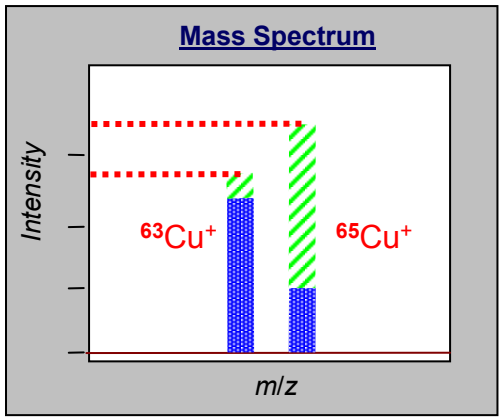


Where:

			Known?
A_s	=	Fraction of isotope A in sample (natural)	✓
B_s	=	Fraction of isotope B in sample (natural)	✓
A_{sp}	=	Fraction of isotope A in spike (altered)	✓
B_{sp}	=	Fraction of isotope B in spike (altered)	✓
C_s	=	**Concentration of element in sample**	✗
C_{sp}	=	Concentration of element in spike	✓
V_s	=	Volume of the sample	✓
V_{sp}	=	Volume of the spike	✓

Solve for C_s, (the concentration of the element in the sample) …

Quantitation of Cu



Known & Measured Values

1) The isotope ratio in the enriched spike standard,
   = 0.05 : 0.95 (^{63}Cu : ^{65}Cu) (***A_{sp} & B_{sp}***)
2) The concentration of the spike standard solution,
   = 0.88 ppb = 13.6 nmol/L (***C_{sp}***)
3) The relative volumes of the spike and sample.
   = 0.13 (spike / sample) (***V_{sp} / V_s***)
4) Measured Isotope Ratio
   = 0.82 (^{63}Cu / ^{65}Cu) (***Ratio***)
5) Natural Isotope Ratio
   = 0.692 : 0.308 (^{63}Cu : ^{65}Cu) (***A_s & B_s***)

… cntd

$$Ratio = \frac{(A_s C_s V_s + A_{sp} C_{sp} V_{sp})}{(B_s C_s V_s + B_{sp} C_{sp} V_{sp})}$$

Rearrange the equation to solve for C_s

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

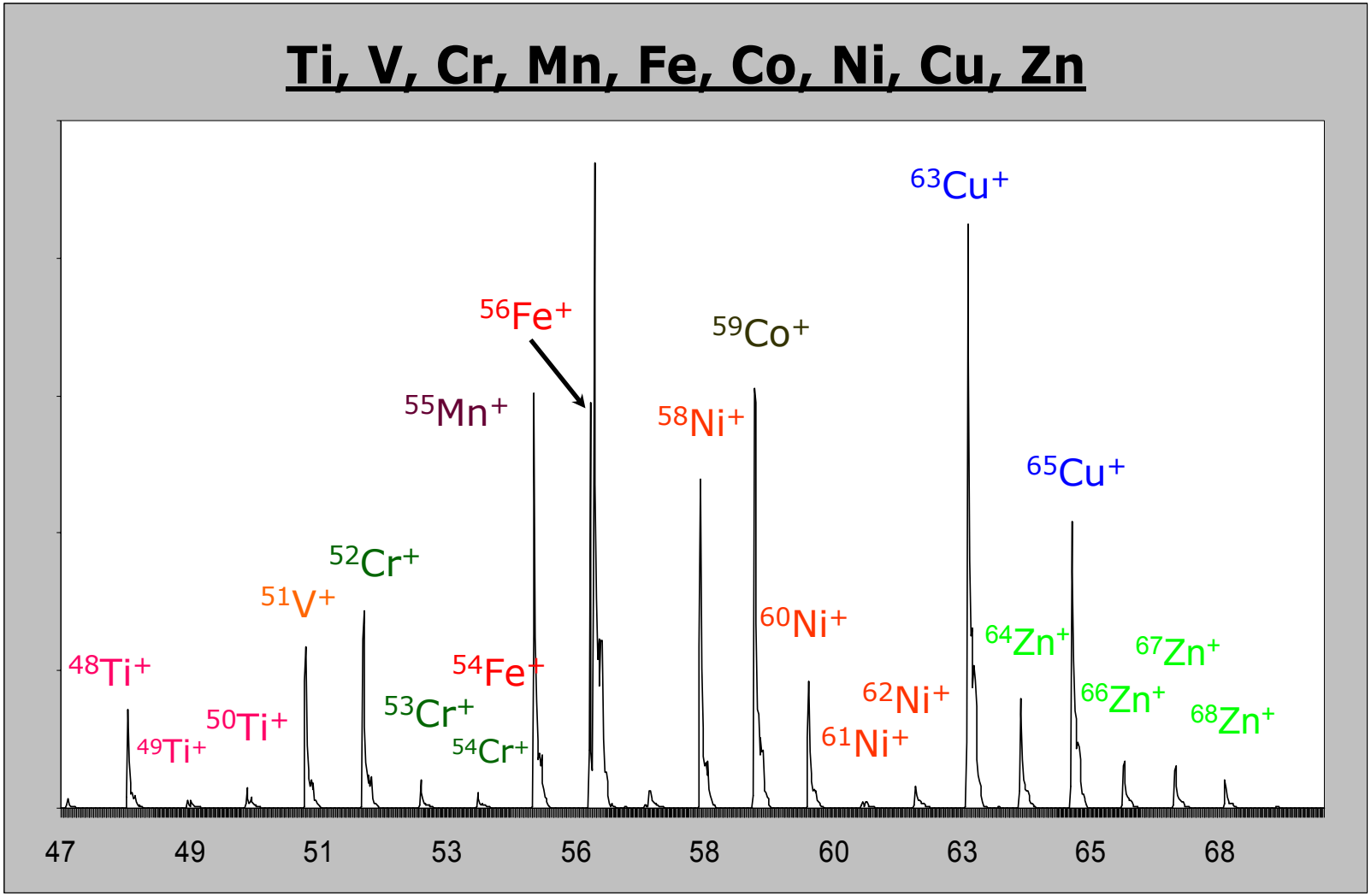
$$C_s = 13.6\ \text{nmol/L} \times 0.13 \times \frac{(0.05 - 0.82 \times 0.95)}{(0.82 \times 0.308 - 0.692)}$$

C_s = 2.93 nmol/L = **0.186 ppb**

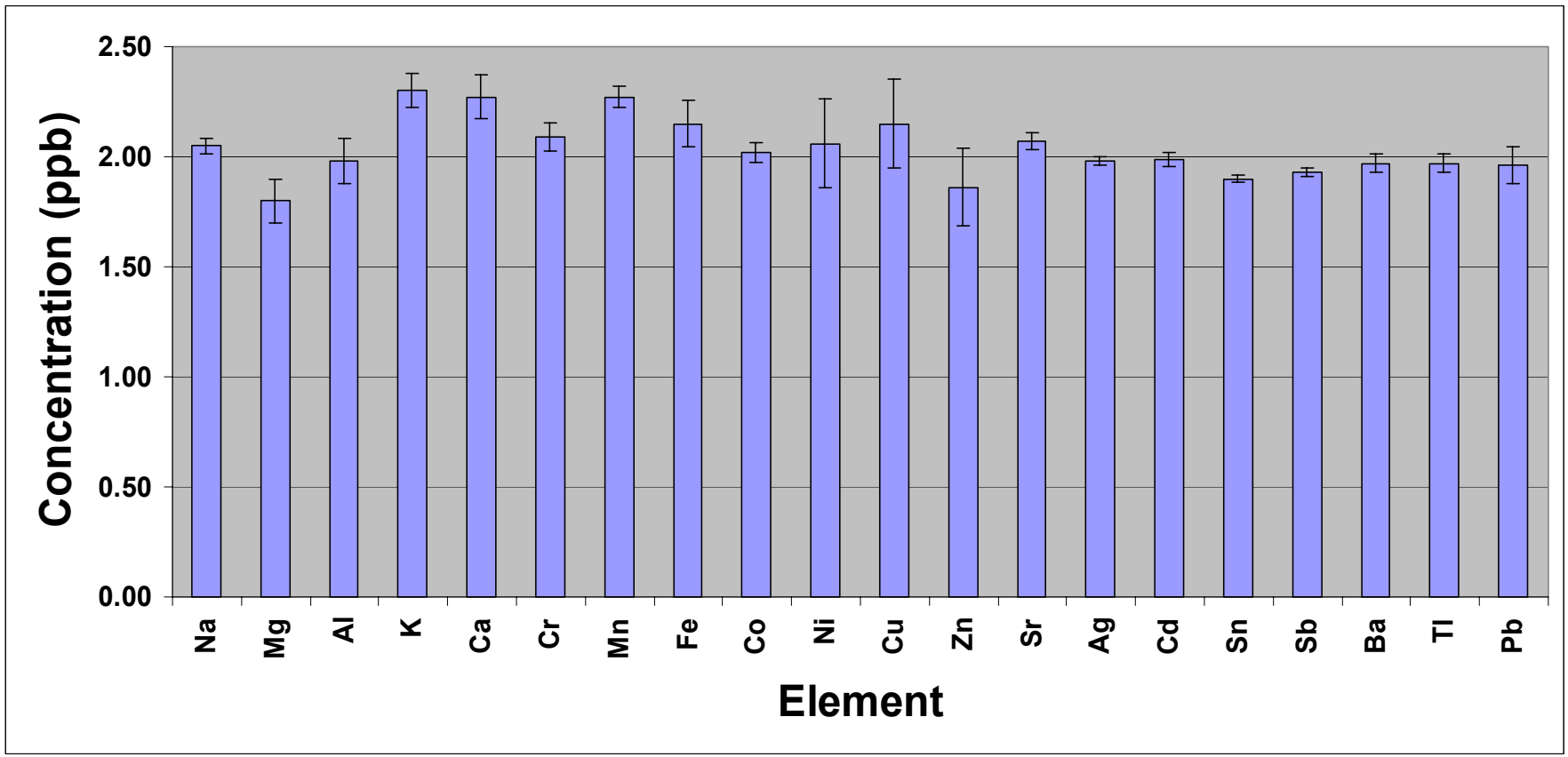
So …

Element	Conc.
Cu	**186 ppt**

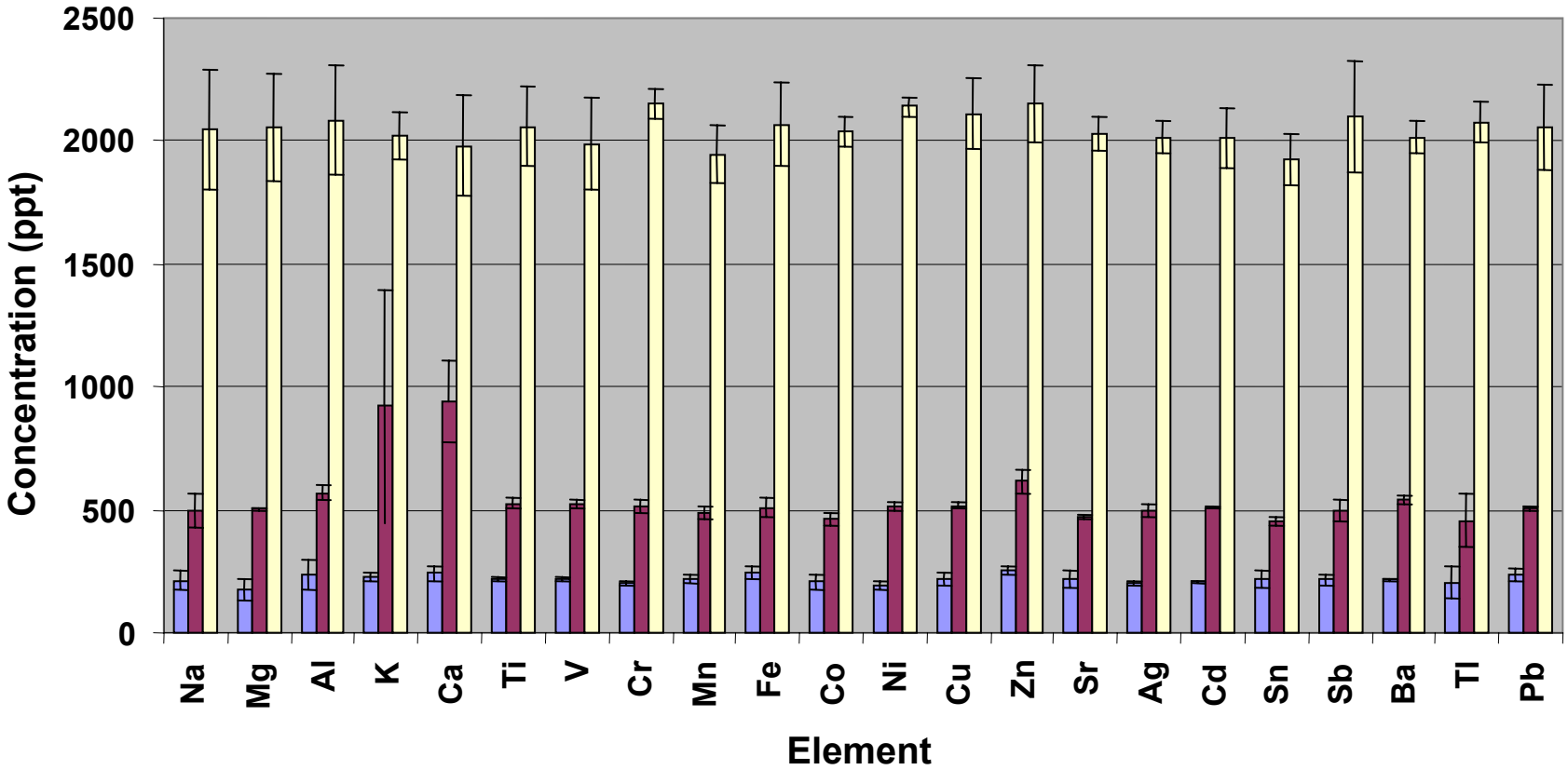
First Row Transition Metals In Hard Ionization Mode



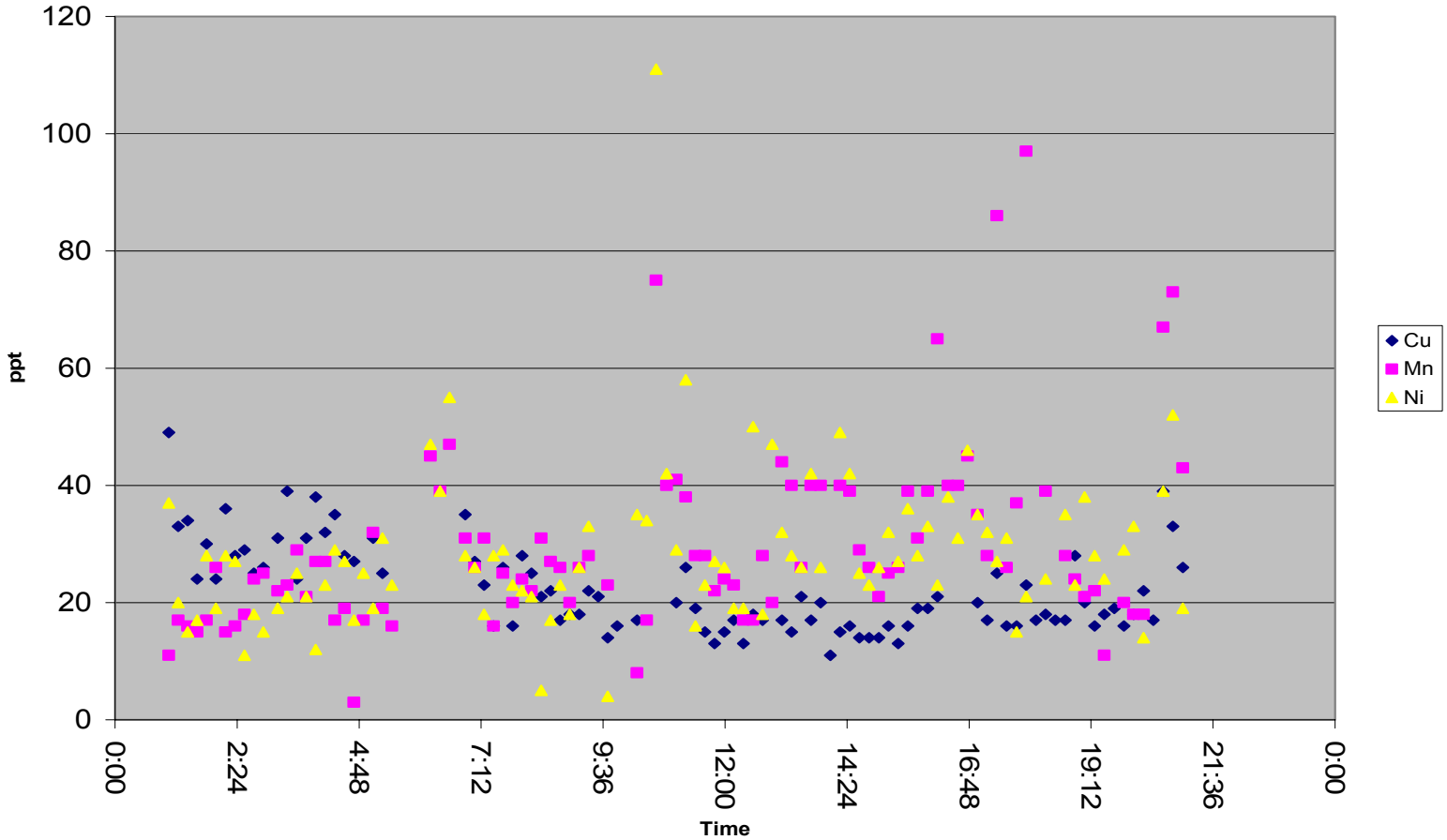
IP-MS Performance for SC1 at 2 ppb
90% Confidence Limits, n = 3



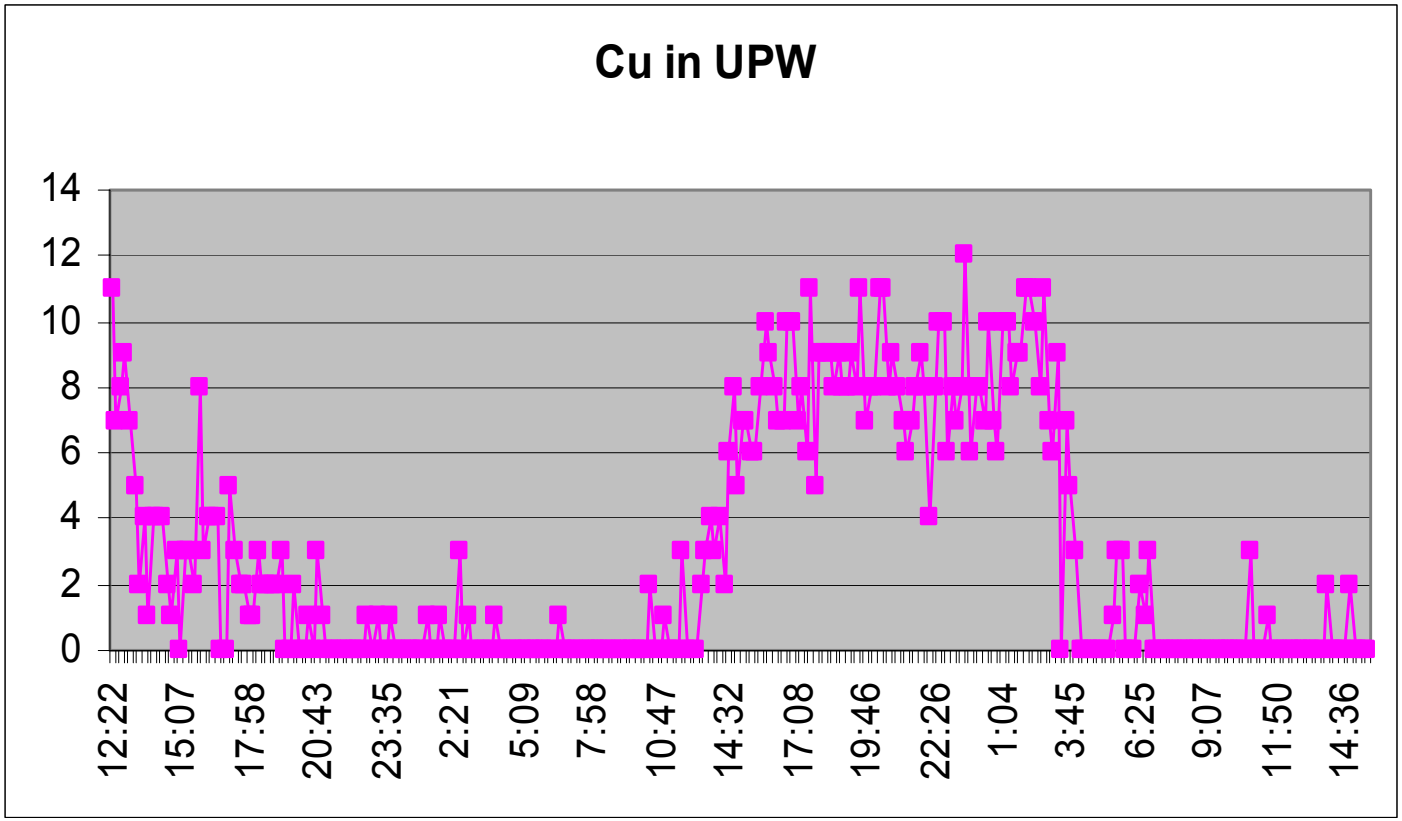
IPMS, TCA analysis of 200, 500, 2000 ppt Solutions UPW Matrix, n=3, 90% Confidence Limit



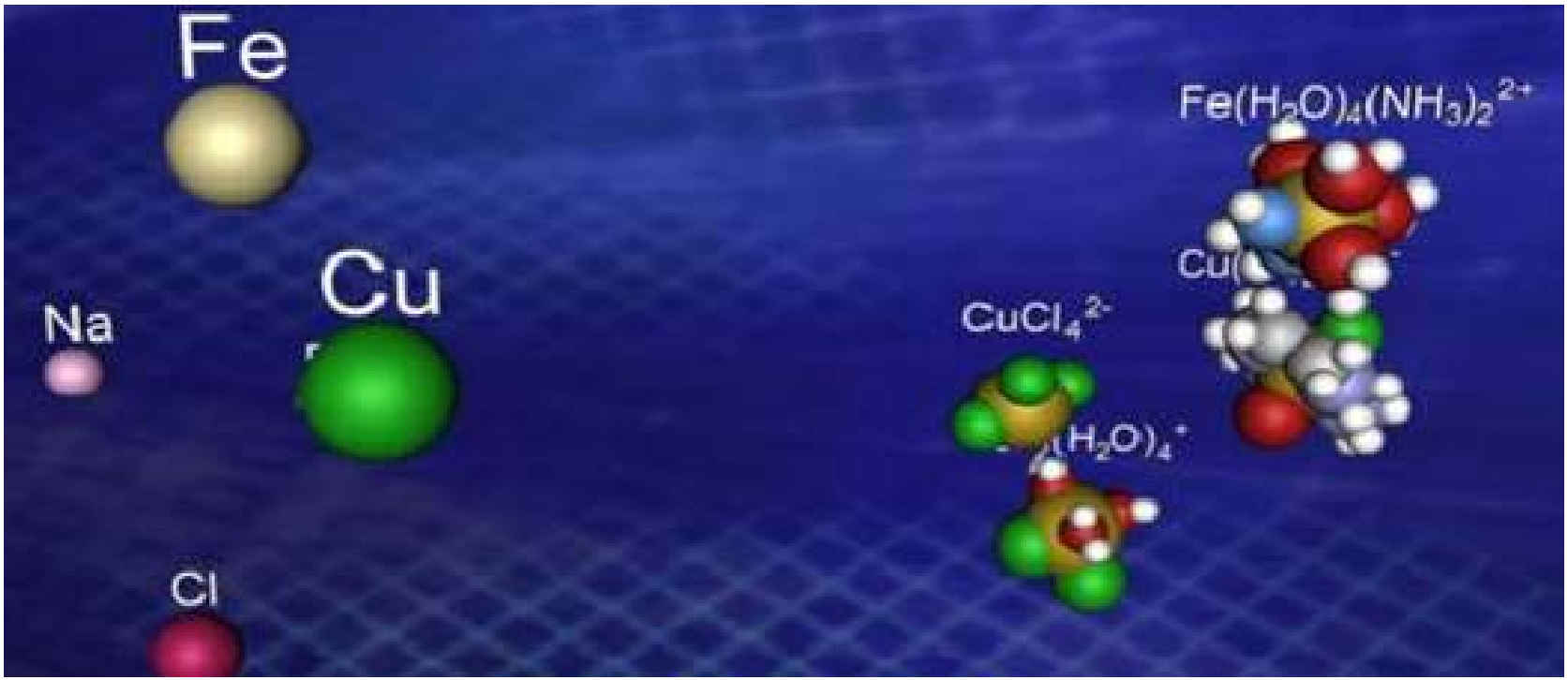
On-line Monitoring: Cu, Ni and Mn Concentrations vs. Time in a SC1 Cleaning Bath



Trend Data for Cu in UPW



Elements & Species

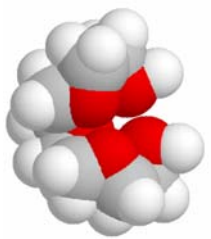


Elements Species

Ionization: Cations, Anions, Species

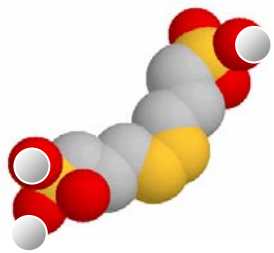
The instrument can detect *cations*, *anions, and molecular species* by reversing the polarity of appropriate voltages in the mass-spectrometer and using soft or hard ionization.

- ***Positive Mode***
- ***Negative Mode***



Suppressor

Copper

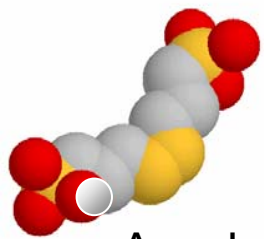


Sodium

Accelerator [*SPS*·3H]$^+$

Chloride

Sulfate

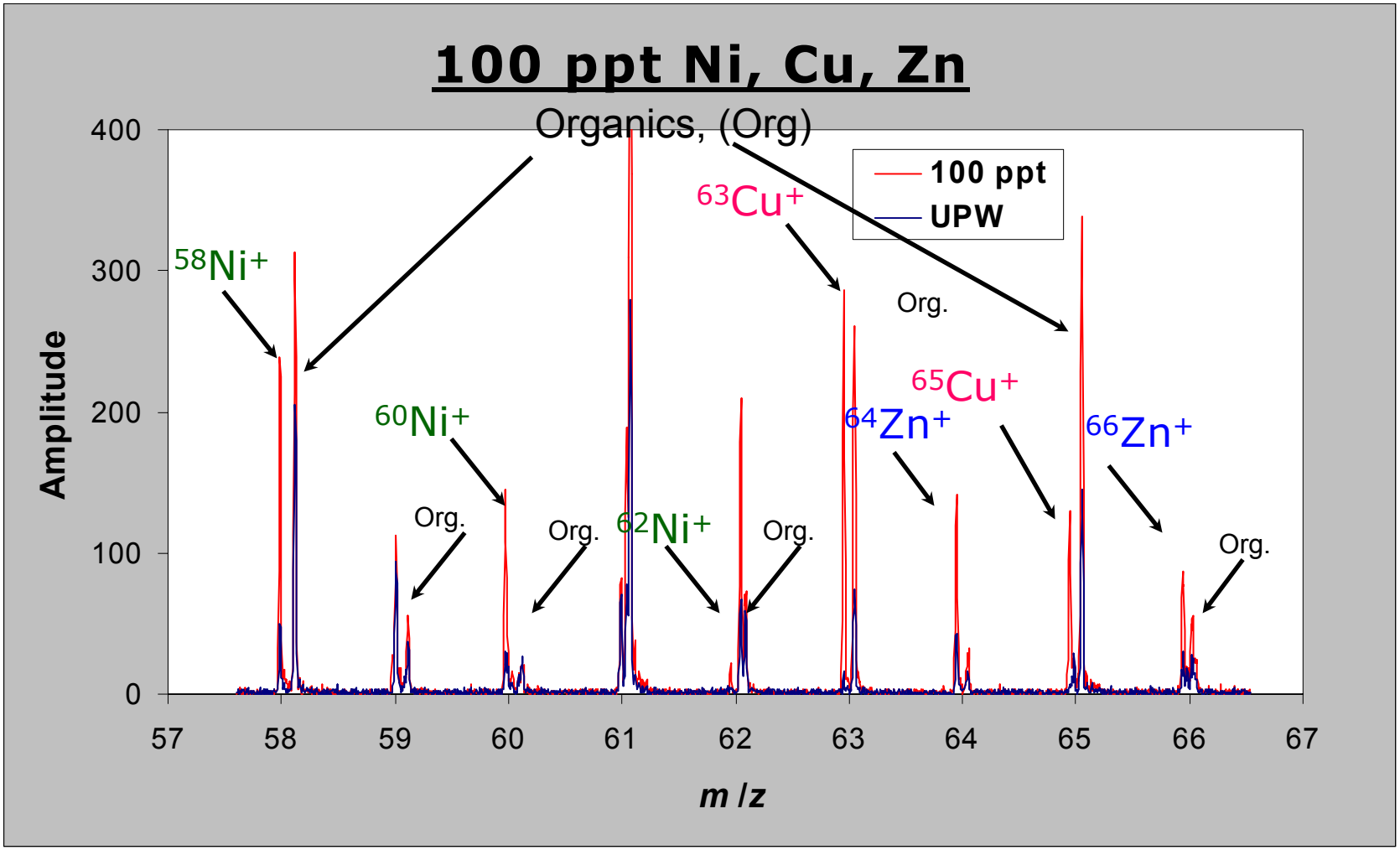


Accelerator [*SPS*·H]$^-$

Chemical Species Measurement Reveal Fundamental Molecular Structure and Chemical Mechanisms

- **Contamination control depends directly on molecular species and mechanisms causing the contamination or controlling the process**
- **Species reveal the chemical processes involved and contain information relating the**
  - Origin
  - Effect
  - Prevention
  - Remediation
  - System

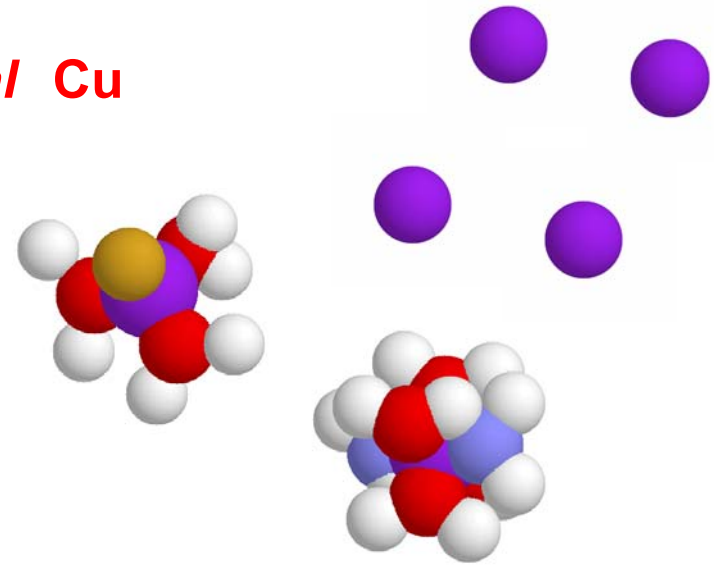
Ni, Cu, Zn In Soft Ionization Mode Include Organic Molecular Ions



Speciation Example: Cu Species Identification in Semiconductor Solutions

- Elemental quantitative mode: *total* Cu

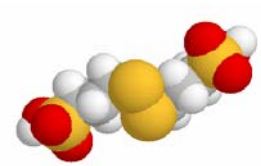
- Speciation mode – Process info
- Example
  - UPW bath: $[Cu(H_2O)_4]^{2+}$
  - HF bath: $[CuF(H_2O)_3]^{+}$
  - SC-1 bath: $[Cu(NH_3)_2(H_2O)_4]^{2+}$
  - SC-2 bath: $[Cu(OOH)Cl_2]^{-}$



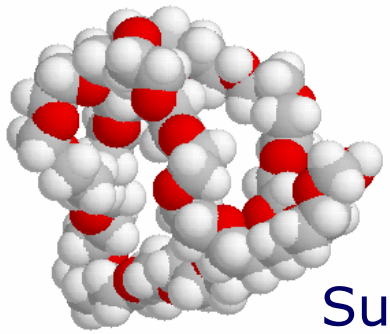
- Identifying Cu species in the monitored process, reveals sources, pathways and mechanisms of the Cu contamination.

Ionization: Elemental *vs.* Speciation

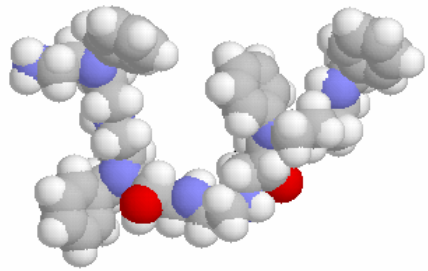
- ***Speciation Mode of Analysis for Organics & Inorganic Complexes***
  - 'Soft' mode – the molecular ions are imparted with a low kinetic energy in the gas-phase.
  - Gentle collisions minimize fragmentation and ligand loss.
  - The integrity of the solution-species is preserved:



Accelerator



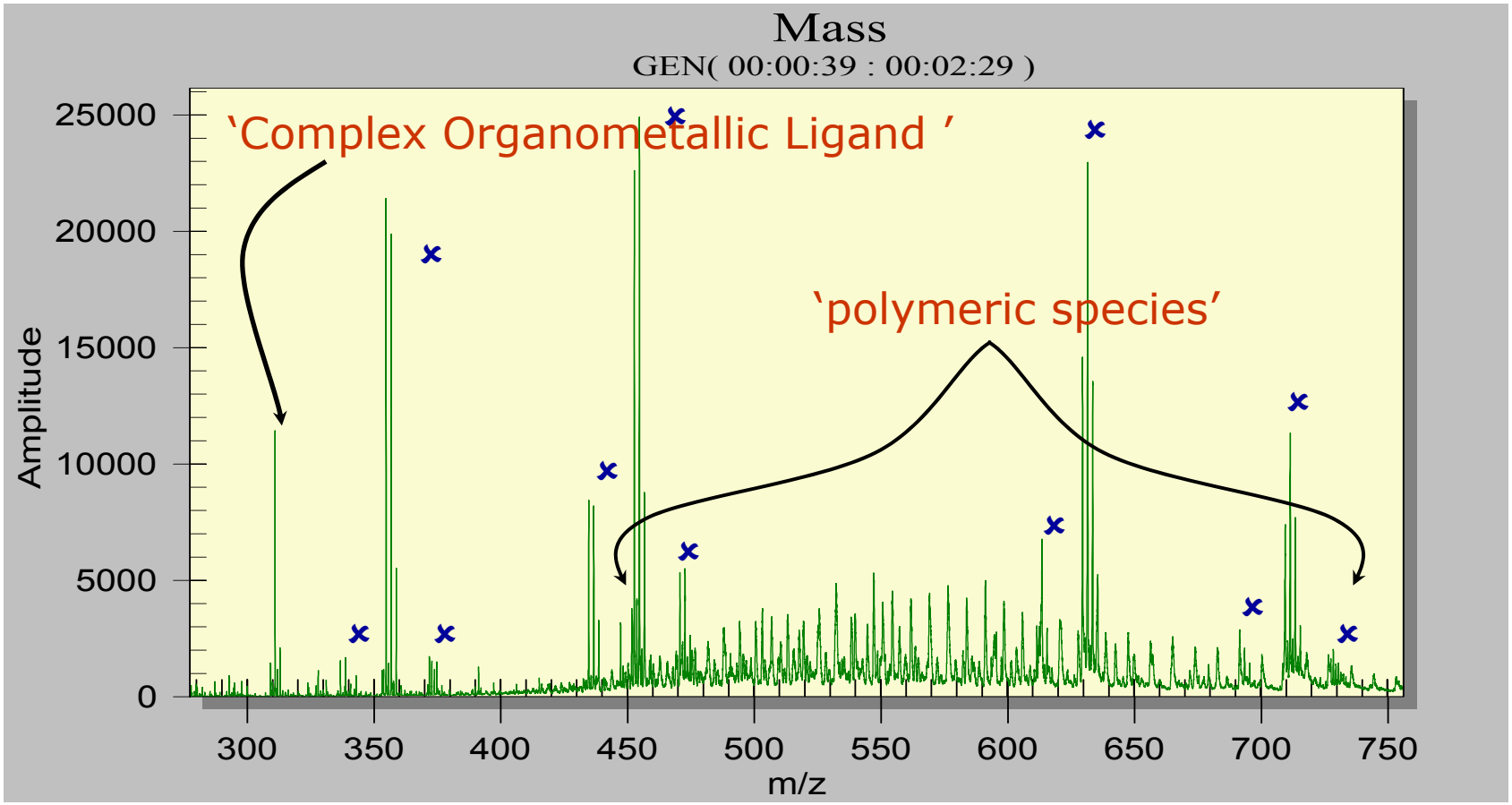
Suppressor



Leveler

  - Diagnostic tool for revealing the chemistry of the process
  - Provides rich information for yield enhancement tools

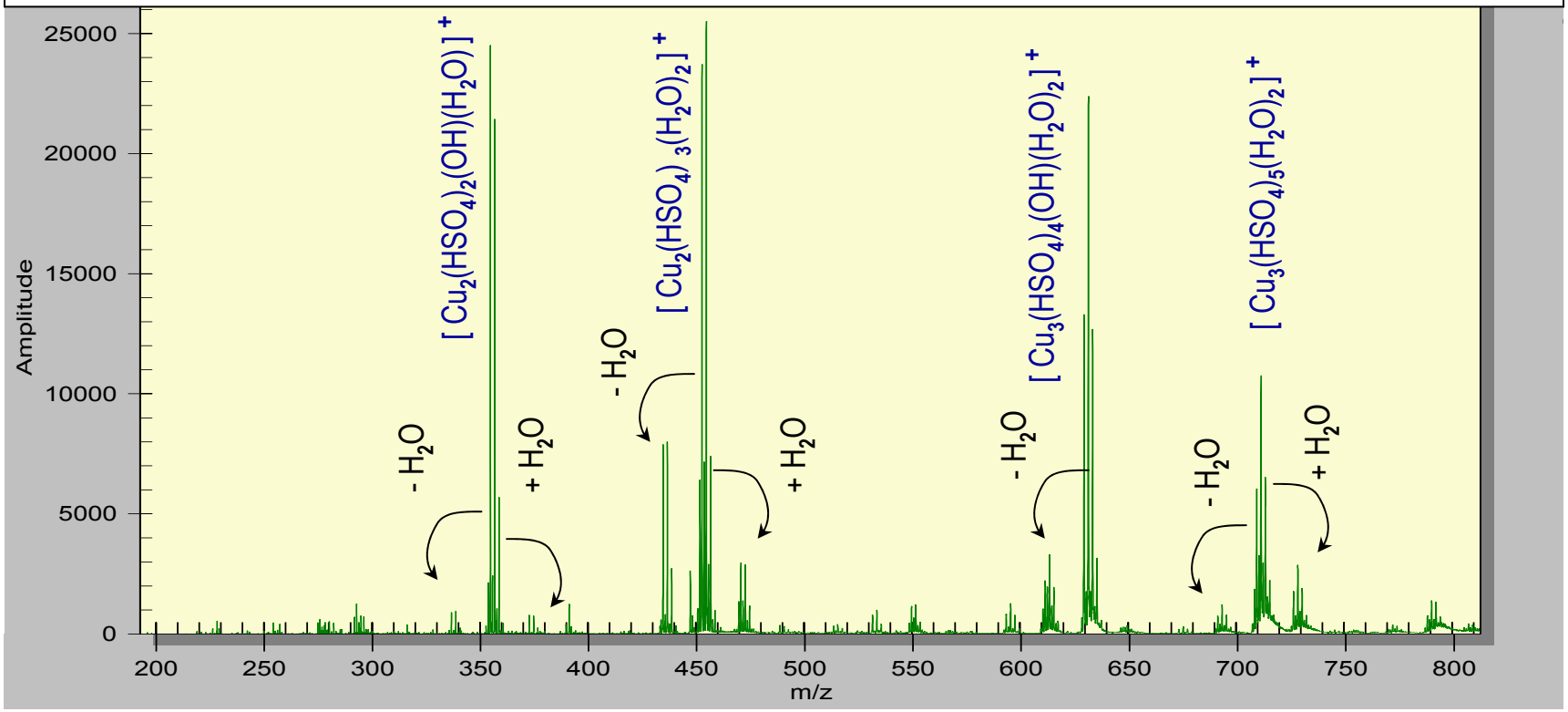
Mass Spectrum of Complex Sample: Cu plating bath solution



× = Organometallic cluster ions

Cu 'reagent': *Speciation Mode Qualitative and Quantitative*

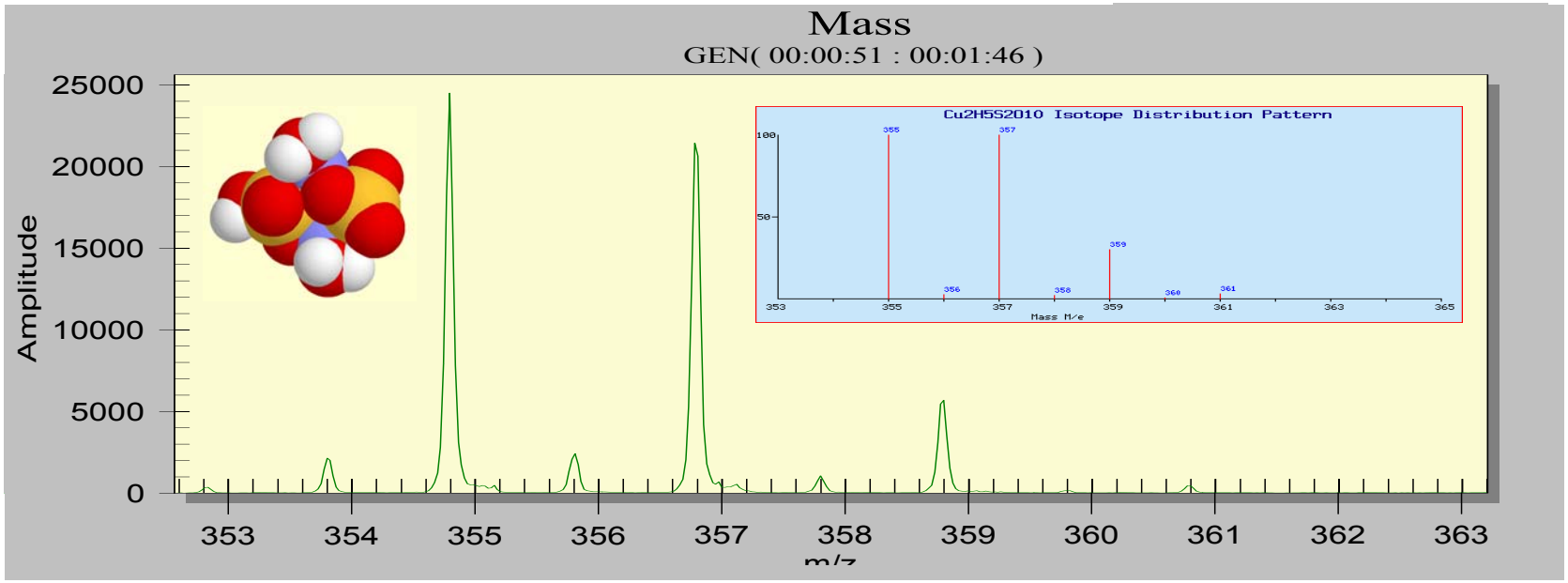
Ionic clusters of copper, sulfate & water ($CuSO_4 + H_2SO_4 + H_2O$)



- 'Soft Ionization' in Speciation Mode encourages detection of intact clusters of copper ions with sulfate and water, by minimizing their fragmentation in the mass-spectrometer.
- These parameters have selected for copper sulfate clusters containing 2 & 3 copper ions (at below and above $m/z \sim 500$ respectively) with a charge, z, of +1.
- The chemical formulae of the species are reliable, although the structural assignments are speculative.

Qualitative Identification and Quantitative Analysis of one Copper species:

$$[Cu_2S_2H_5O_{10}]^+$$

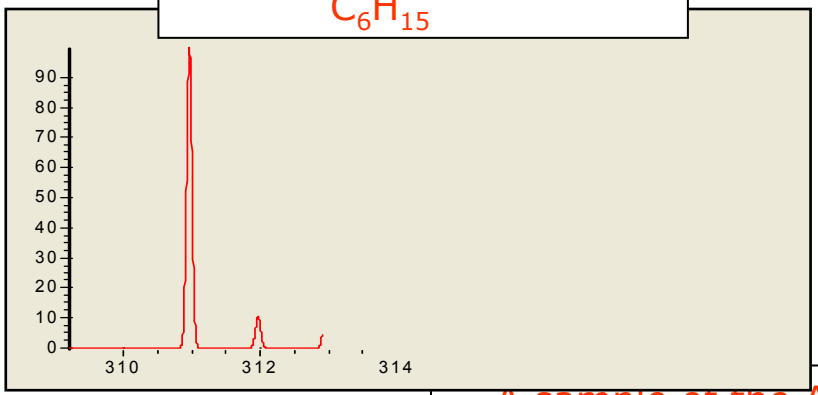


- The **isotope peak pattern** is consistent with the chemical formulation; the most abundant isotopes of both copper and sulfur differ by 2 a.m.u. (^{63}Cu & ^{65}Cu, and ^{32}S & ^{34}S).
- There is an excellent match between the **measured** & **calculated** masses for the major isotope peak (**354.7922** and **354.7916** a.m.u. respectively).
- The set of peaks of lower intensity offset by 1 a.m.u. is consistent with the formulation $[Cu_2S_2H_4O_{10}]^+$, perhaps formed by the collisional loss of a hydrogen atom in the mass-spectrometer.

Quantitation of the Accelerator Bis(3-sulfopropyl) disulfide (*SPS*) by Isotopically-Enriched Spike

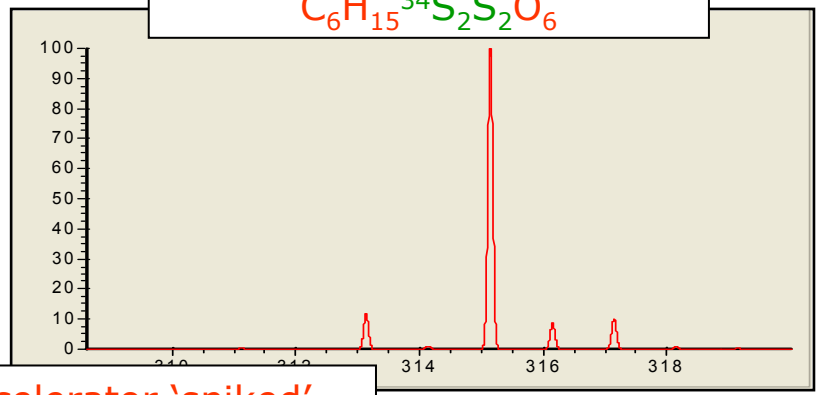
'Natural' Isotope Pattern,

C_6H_{15}

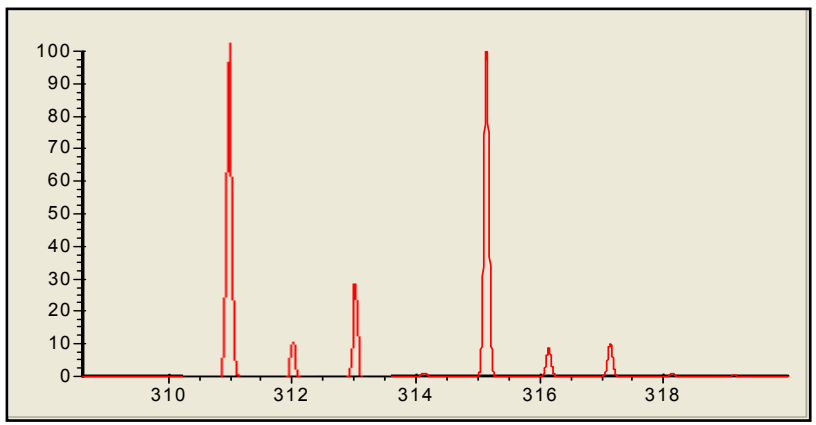


'Enriched' Isotope Pattern,

$C_6H_{15}{}^{34}S_2S_2O_6$

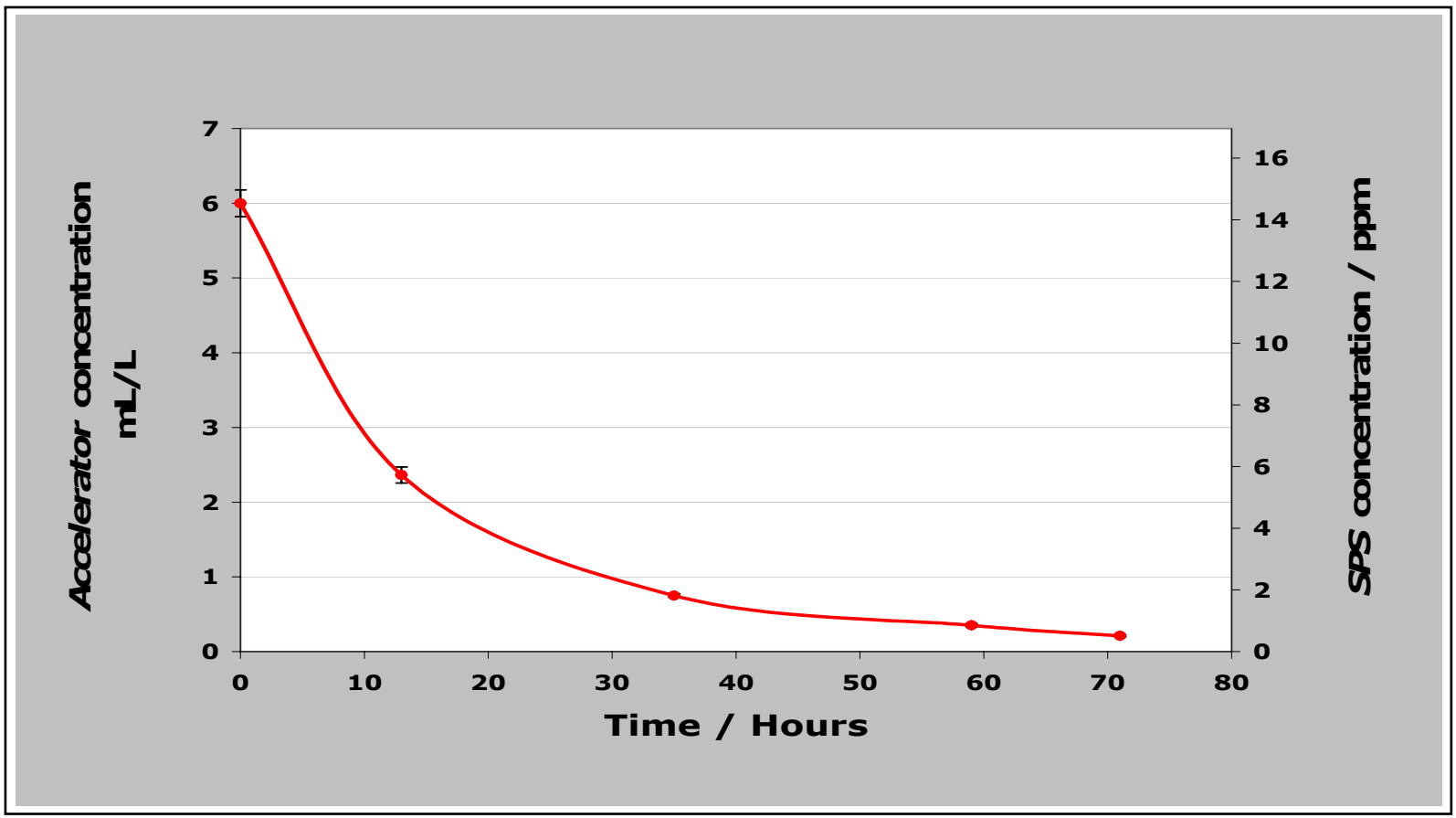


A sample of the Accelerator 'spiked' with an equal amount of the enriched-isotope standard



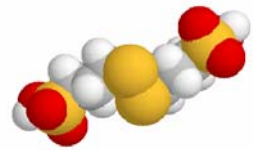
Trend Data

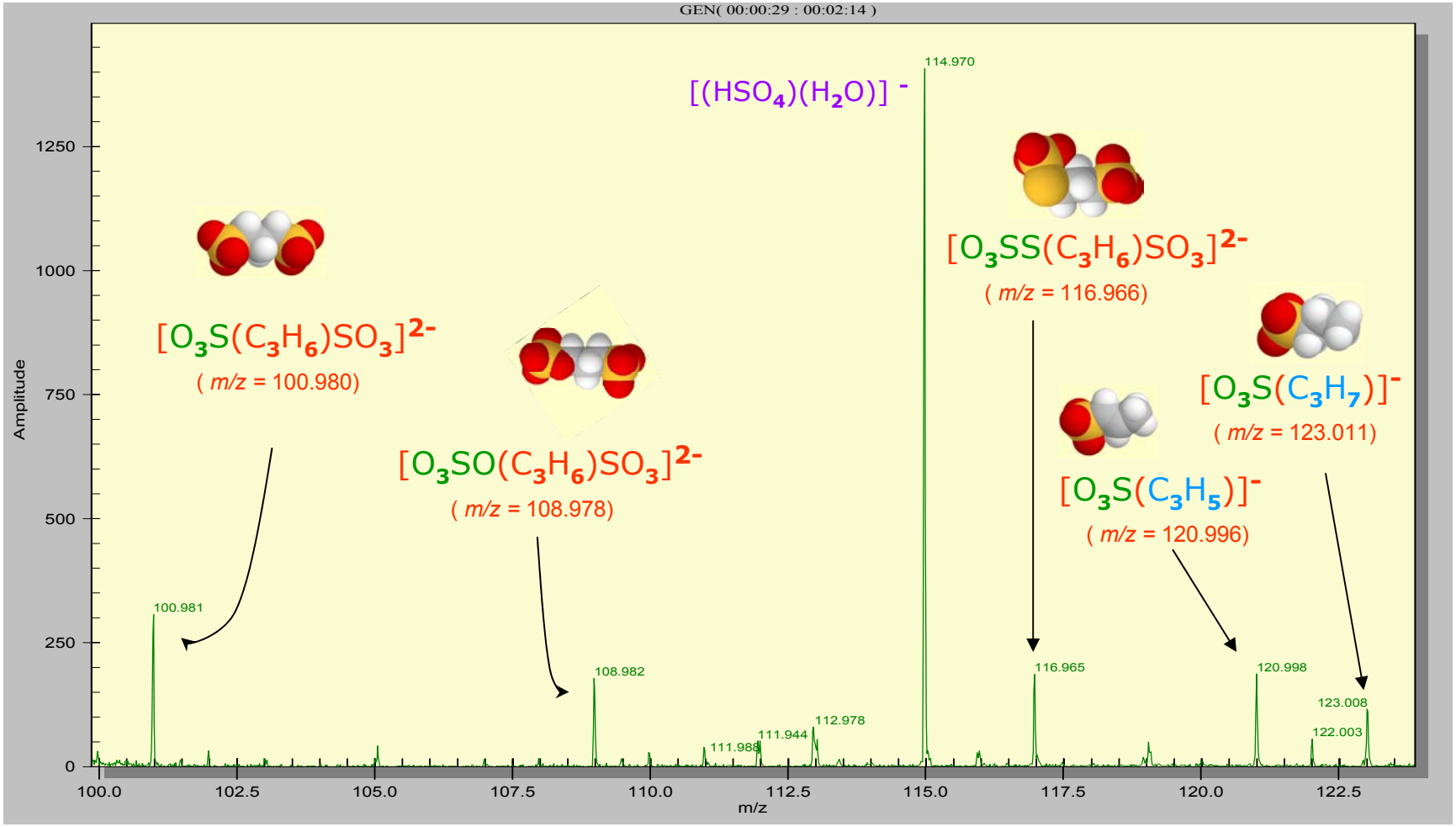
Rate of *Accelerator* (*SPS*) Change in a Cu-ECD Test Facility



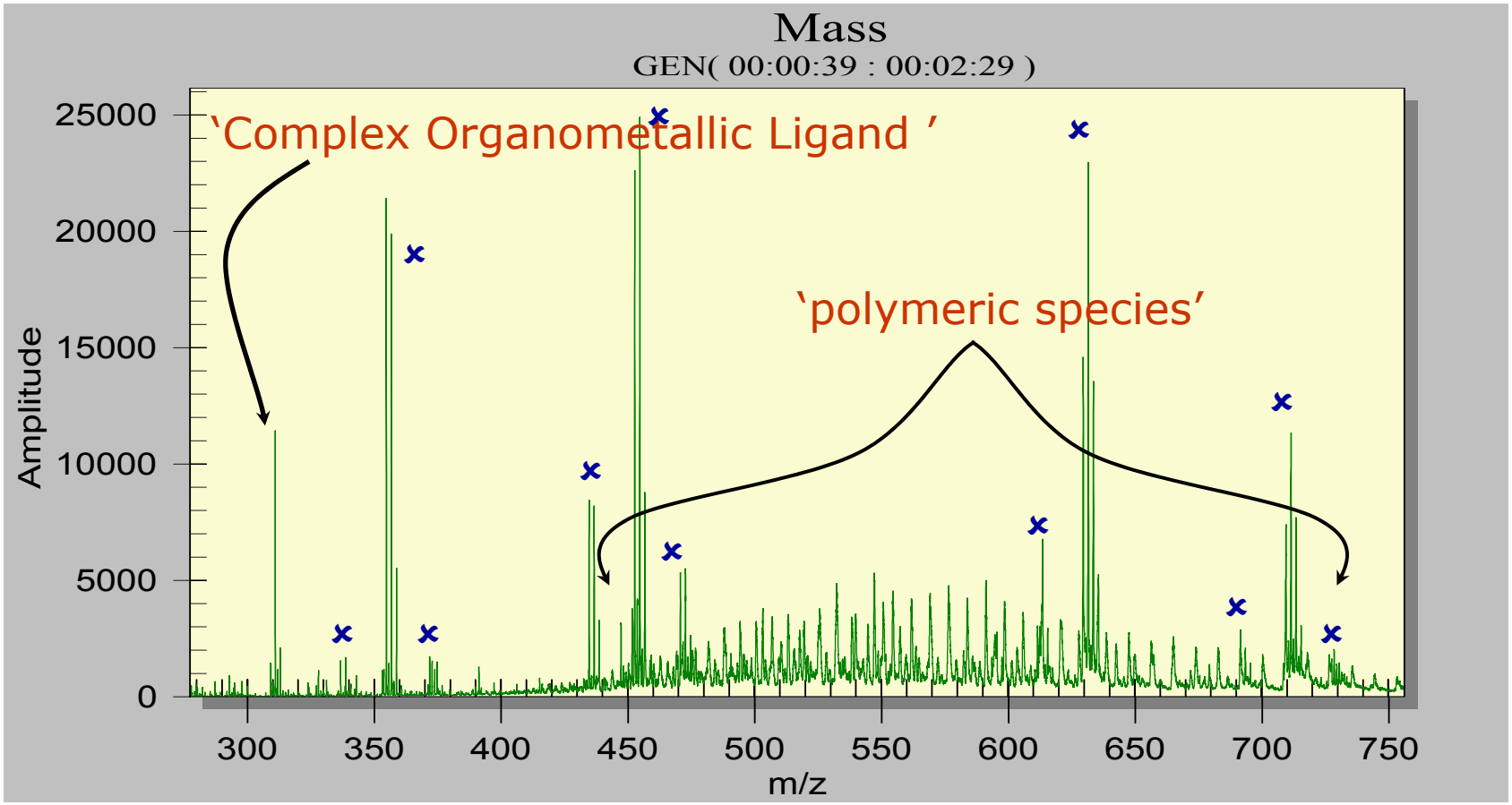
- 10 amps
- 1.635 V
- 2 Sabre anodes

Decomposition of the Accelerator *SPS* in an Aged Sample





Mass Spectrum of Complex Sample



× = Organometallic cluster ions

What is the Challenge?

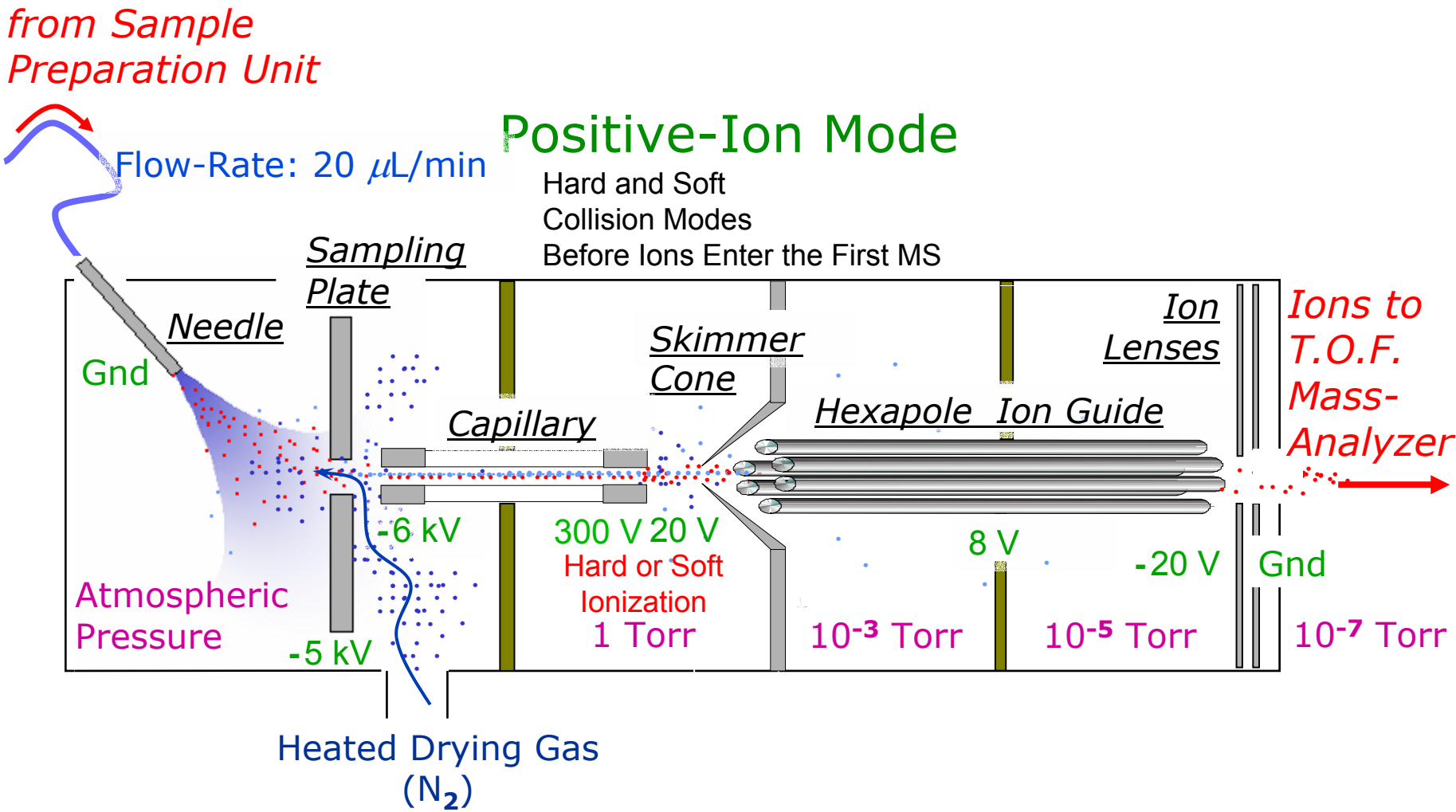
"The most critical challenge is to find ways to determine the effects of trace impurities on device performance and yield."

Reference: "Examining upcoming yield enhancement challenges in the 2001 roadmap"
-***Micro***, February 2002

Authors: Christopher Long, IBM;
Milton Godwin, Applied Materials;
Manuela Huber, Sematech/Infineon;
Richard Jarvis, Sematech/AMD
Fred Lakhani, Sematech

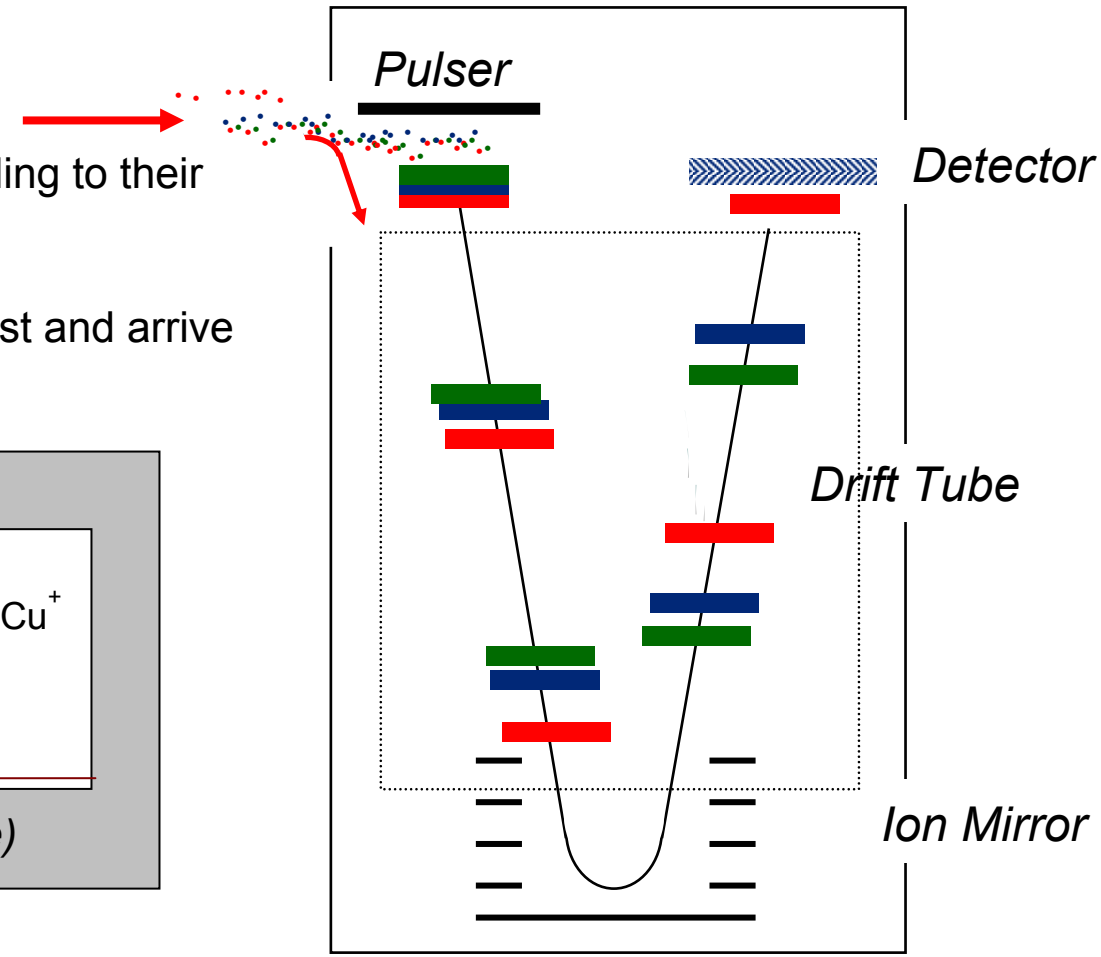
The Integrated System

Electrospray Ionization Interface



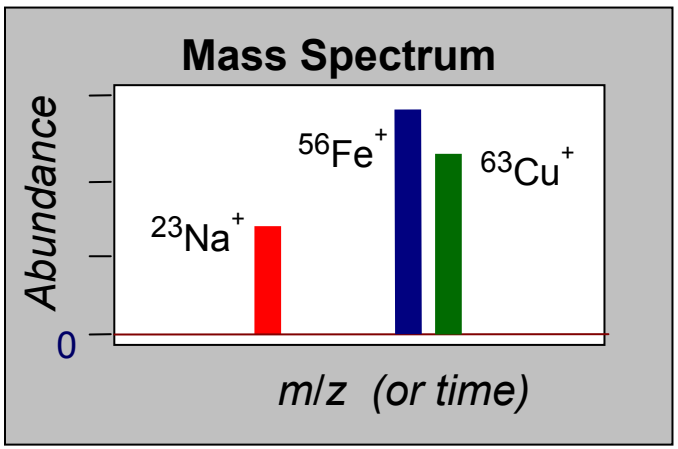
Time-of-Flight Mass Analyzer

Ions from Electrospray



- Ion packets separate according to their mass-to-charge ratio (*m*/*z*).

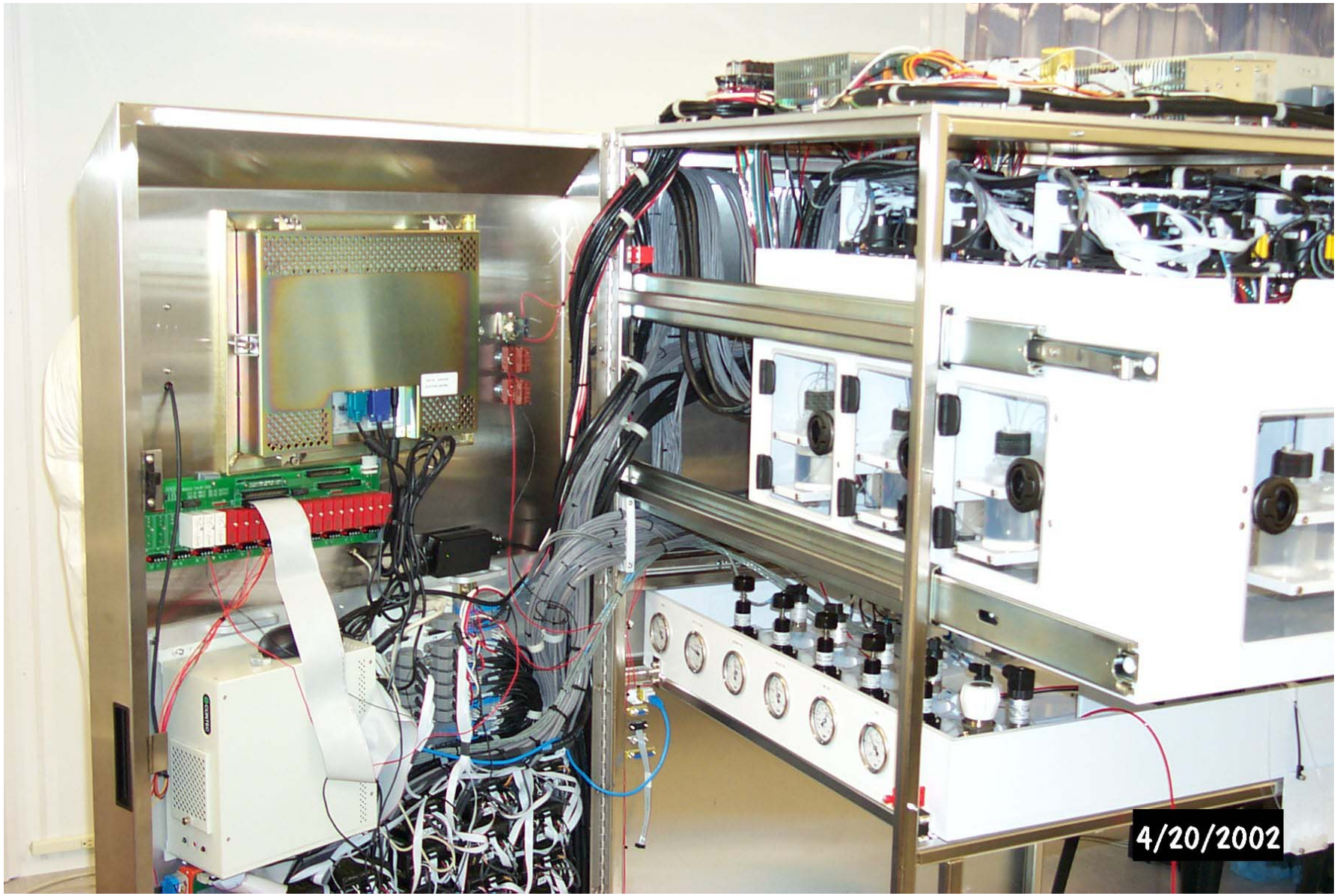
- The lightest ions travel fastest and arrive at the detector earliest.

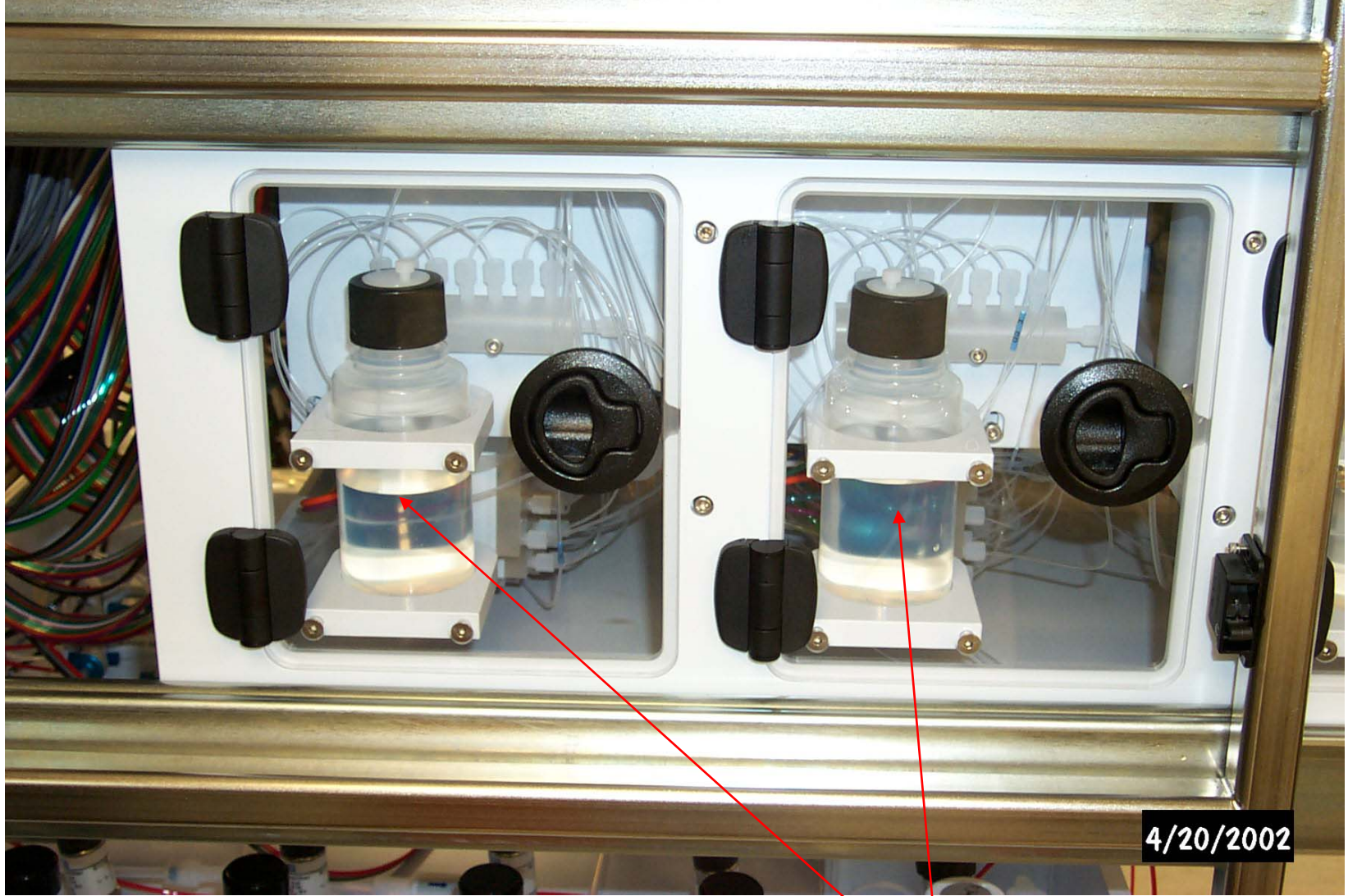


IPMS (ES-TOF) Vs. ICP-MS

Item	LMS-300 TCA	ICP-MS
Target Application	Real-time, In-line Trace contamination monitoring of standard aqueous semiconductor solutions	Lab applications
Sample Matrix	UPW, SC1, SC2, IPA, DHF, $HN0_3$, H_2O_2	UPW, SC1, SC2, IPA, DHF, $HN0_3$, H_2O_2
Monitors	16 (22) Trace Contaminants	Depends Upon Available Standards
	Cations (+) and anions (-)	Cations (+)
	Elements and species	Elements
	Inorganics and Organics	Inorganics
Sample Preparation	Automatic	Manual
Limit of Detection	< 20 ppt	< 20 ppt
Calibration and Quantitation Standards	Enriched isotope elemental standard (250 ppb)	Calibration Curves
	NIST natural isotope standard (10 ppm)	
Sample Volume	2 mL	5 mL
Technology	In-Process Mass Spectrometry (IPMS)	ICP-MS
Throughput	8 sample/hr (7.5 min/sample)	24 to 72 hours
Accuracy	± 25% at the quantitation limit	± 25% at the quantitation limit

Trace Contamination Analyzer (TCA) Semiconductor Solution Metrology

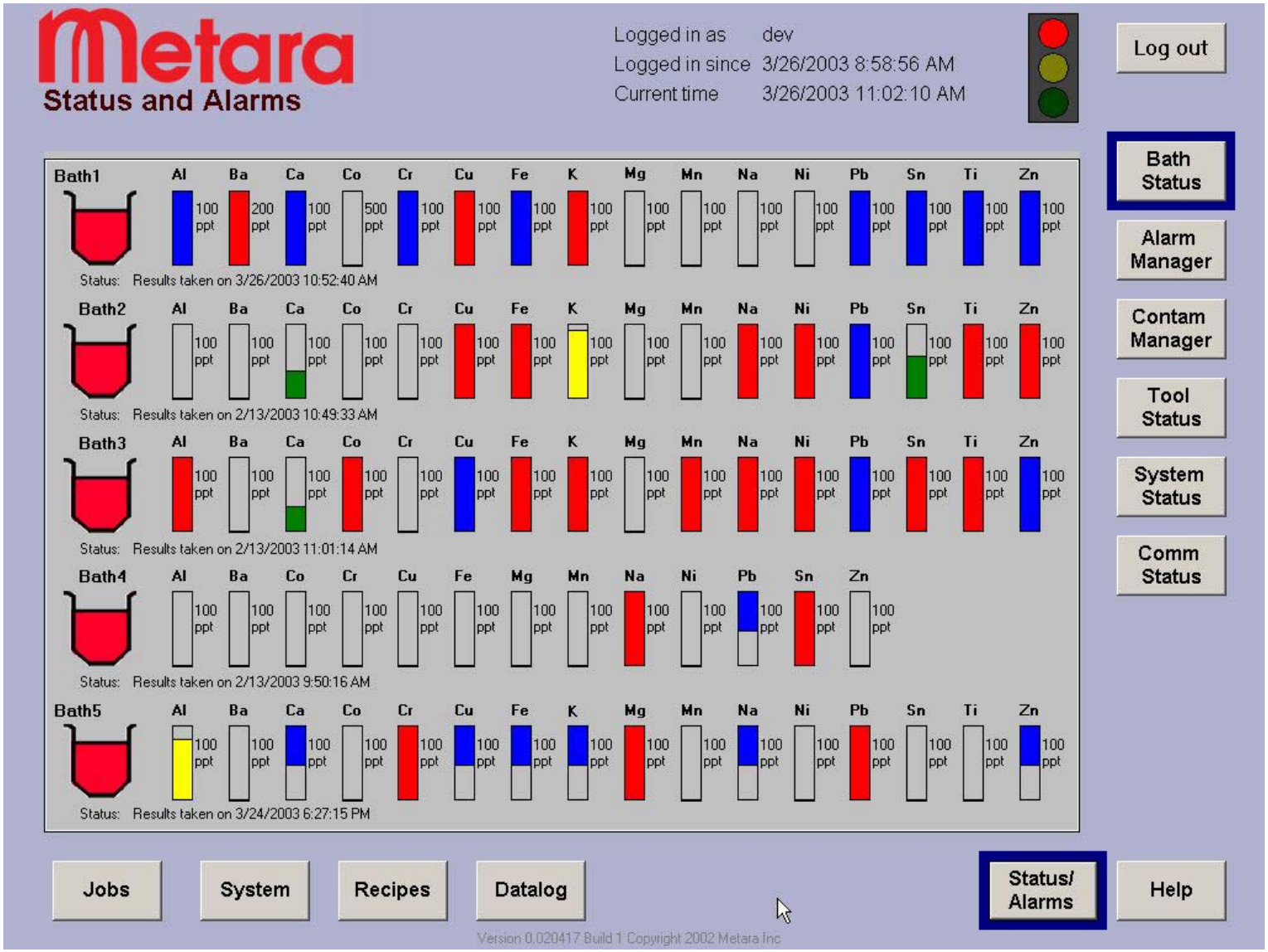

4/20/2002



"Enriched" Isotope Solutions Standards"

One semiconductor instrument being tested and one being assembled in clean room

Decision Information in Graphical User Interface (Beta) (Element selection individualized for a specific Fab)



Acknowledgements

Current and Former Research Group Member

Duquesne University

Dr. Ye Han
Ds. Helen Boylan
Ms. Sejal Iyer
Mr. Mizanur Rahman
Dr. Dan Taylor
Ms. Yusheng Lu
Dr. Dirk Link
Dr. Dengwei Huo
Dr. Stuart Chalk
Dr. Peter Walter
Dr. Robert Richter

Many others

Metara Inc.

Dr. Ye Han
Dr. Michael West
Dr. Marc Anderson
Mr. Larry Stewart
Dr. June Wang
Dr. Jason Wang
Dr. Harmish Seni
Mr. Bob Ormond
Dr. Kenneth Bhang
Mr. Rudy Mui
Mr. Patrick Franklin

programmers, engeneers…
Many others

Acknowledgments

Sponsors and Funding

Metara Inc.
SAIC & EPA
Environmental Standards
Allegheny Energy Supply Company
Duquesne University

Instrumentation Support

Metara Inc.
Milestone Inc.
Agilent Technologies
Fisons

Note:
Patents exist and are pending on portions of this research Nationally and Internationally

This is not your fathers kind of chemistry any more!

Micromachines of the future will be on an unprecedented scale with atomic and molecular domains where constituent and contaminant analysis must be on these same scales