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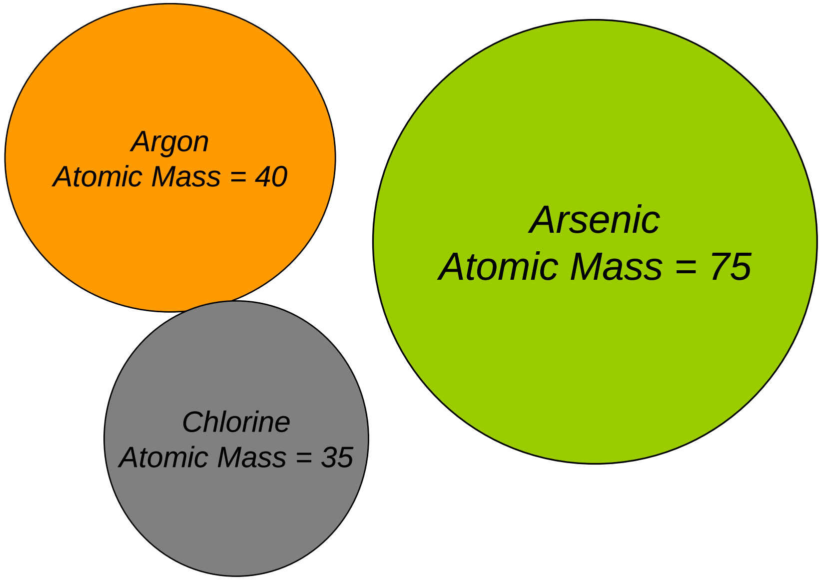
Application of ICP/MS Collision Cell Technology for the Analysis of Trace Metals in Marine Waters and other Challenging Matrices



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Abstract

Inductively Coupled Plasma Mass Spectrometry (ICP/MS) is the most widely used analytical technique for the measurement of trace metals in water. The technique uses characteristic isotopic masses to uniquely identify and quantify low concentrations of individual metal species. However, ICP/MS technology does suffer from interferences caused by polyatomic species that coincidentally have similar combined masses as the target metal species. These polyatomic interferences occur when there are high levels of contributing species such as Chloride (Cl), Calcium (Ca) or Carbon (C). High levels of these interfering species can impact the measurement of several environmentally important trace metals such as Arsenic (As), Chromium (Cr), Copper (Cu) and Zinc (Zn). Marine waters containing high levels of sodium chloride are examples of matrices that frequently create polyatomic interferences that result in compromised trace metal data. Other challenging matrices include brackish water, industrial effluents and wastewater streams. This presentation will focus on the use of ICP/MS sample preconditioning systems such as collision cells and dynamic reaction cells that effectively remove polyatomic interferences. The presentation will also include a discussion of the use of the improved low-level metals data in environmental monitoring and management.

Outline

- ICP/MS Technology
- Polyatomic Interferences
- Collision Cell Technology
- Laboratory Data

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- Baseline marine data – suspicious exceedences of CWQGs for Se and As
- Potential consequences of false positives

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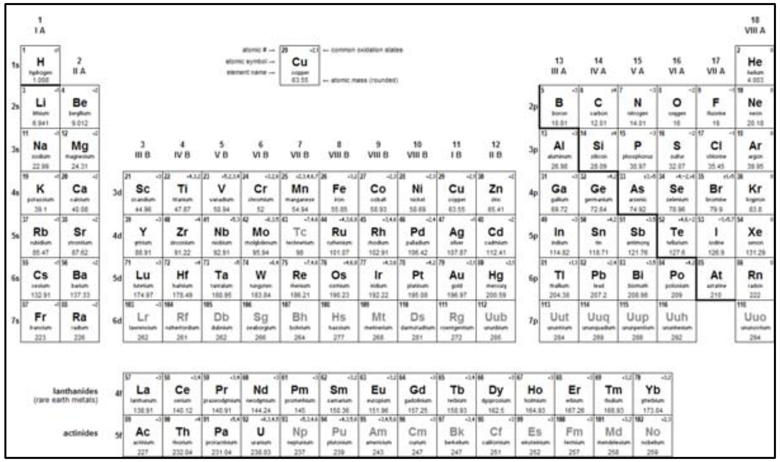
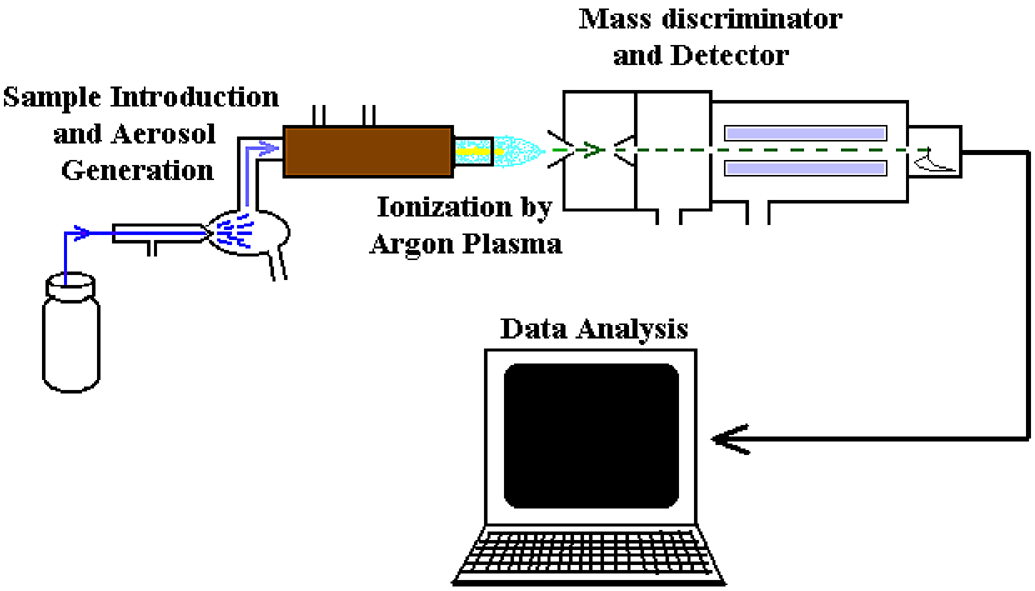
ICP/MS

Inductively Coupled Plasma Mass spectroscopy

- A measurement technique that allows for simultaneous identification and quantification of metals based on atomic mass.
  - Operating principle: A sample is vaporized into a plasma. The ions created in the plasma are accelerated and sorted by a mass spectrometer.





Stable Isotopes

Definition: *An isotope that does not spontaneously undergo radioactive decay*

Natural Abundance: *The typical % abundance occurring in nature*

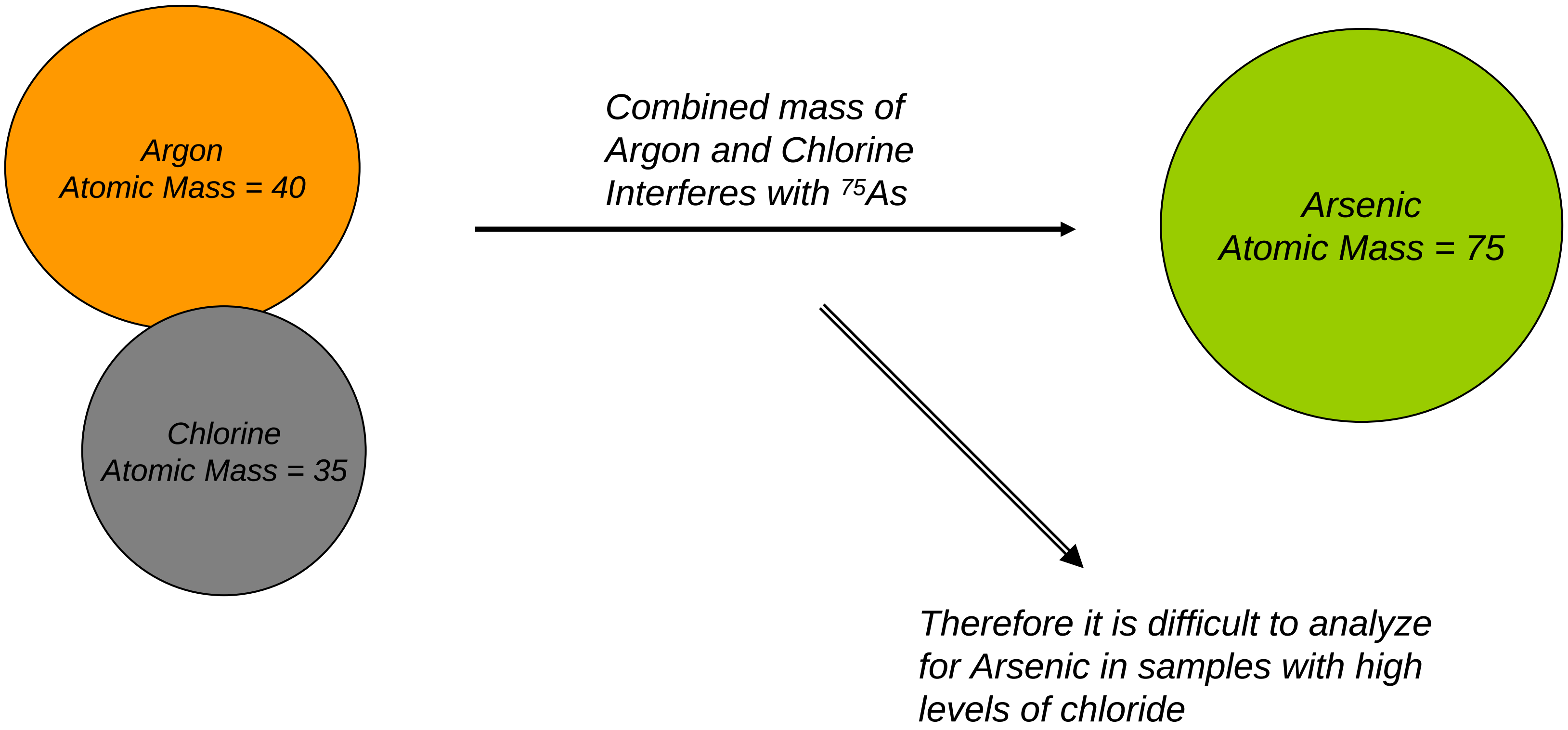
Zinc (Zn) Isotopes					64		66	67	68
Natural Abundance					*49%*		*28%*	*4%*	*19%*

Nickel (Ni) Isotopes	60	61	62		64				
Natural Abundance	*26%*	*1%*	*4%*		*1%*				

Implication: *Due to overlaps in isotopic mass, some elements can interfere with the measurement of other elements.*

Polyatomic Interferences

- Polyatomic Interferences when elemental (ionic) species combine to create a combined mass equivalent to the target mass.



Polyatomic Interferences

Isotope	Principal Interfering Species (Ca,Na,S,Cl,C)	Isoptope	Principal Interfering Species (Ca,Na,S,Cl,C)
51V	35Cl16O, 37Cl14N	*66Zn*	34S16O2, 32S34S, 33S2, 48Ca18O
52Cr	36Ar16O, 40Ar12C, 35Cl16OH, 37Cl14NH	*67Zn*	32S34SH, 33S2H, 48Ca18OH, 14N16O37Cl, 16O2, 35CL
53Cr	36Ar16OH, 40Ar13C, 37Cl16O, 35Cl18O, 40Ar12CH	*68Zn*	32S18O2, 34S2
54Fe	40Ar14N, 40Ca14N	*69Ga*	32S18O2H, 34S2H, 16O2, 37Cl
55Mn	37Cl18O, 23Na32S,	*70Zn*	34S18O2, 35Cl2
56Fe	40Ar16O, 40Ca16O	*71Ga*	34S18O2H
57Fe	40Ar16OH, 40Ca16OH	*72Ge*	40Ar32S, 35Cl37Cl, 40Ar16O2
58Ni	40Ar18O, 40Ca18O, 23Na35Cl	*73Ge*	40Ar33S, 35Cl37ClH, 40Ar16O2H
59Co	40Ar18OH, 43Ca16O	*74Ge*	40Ar34S, 37Cl2
60Ni	44Ca16O, 23Na37Cl	*75As*	40Ar34SH, 40Ar 35Cl, 40Ca 35Cl
61Ni	44Ca16OH, 38Ar23Na, 23Na37ClH	*77Se*	40Ar 37Cl, 40Ca 37Cl
63Cu	40Ar23Na, 12C16O35Cl, 12C14N37Cl	*78Se*	40Ar 38Ar
64Zn	32S16O2, 32S2, 36Ar12C16O, 38Ar12C14N, 48Ca16O,	*80Se*	40Ar2, 40Ca2, 40Ar40Ca, 40Ar
65Cu	32S16O2H, 32S2H, 14N16O35Cl, 48Ca16OH		

Sulfur, Calcium and Chloride interfere with Arsenic

Mathematical Reduction of Interferences

Example: Chloride interference on ^{75}As

1) Acquire data at masses 75, 77, 82 and 83
2) Assume the signal at mass 83 is from 83Kr and use this to estimate the signal from 82Kr
3) Subtract the estimated contribution from 82Kr from the signal at mass 82; the residual should be 82Se
4) Use the estimated 82Se signal to predict the size of the signal from 77Se on mass 77.
5) Subtract the estimated 77Se contribution from the signal at mass 77; the residual should be from 40Ar37Cl.
6) Use the calculated 40Ar37Cl signal to estimate the contribution on mass 75 from 40Ar35Cl
7) Subtract the estimated contribution from 40Ar35Cl on mass 75; the residual should be from 75As

What could possibly go wrong??

Physical or Chemical Reduction of Polyatomic Interferences

- Reaction Processes

  1. Used to remove plasma based interferences.
  2. Interference is removed by adding any reactive gas into a cell.
  3. Interference is removed by atom or charge transfer

- Collision Processes

  1. Used to remove sample based polyatomic interferences
  2. Collision process is most commonly used with an inert gas.
  3. Two majors processes used are:
     - Collisionally Induced Dissociation (CID)
     - Kinetic Energy Discrimination (KED)

Reaction Processes

- Interference is removed by atom or charge transfer

$$ArO^+ + H_2 \rightarrow H2O^+ + Ar$$

$$Ar+ + H2 \rightarrow ArH^+ + Ar$$

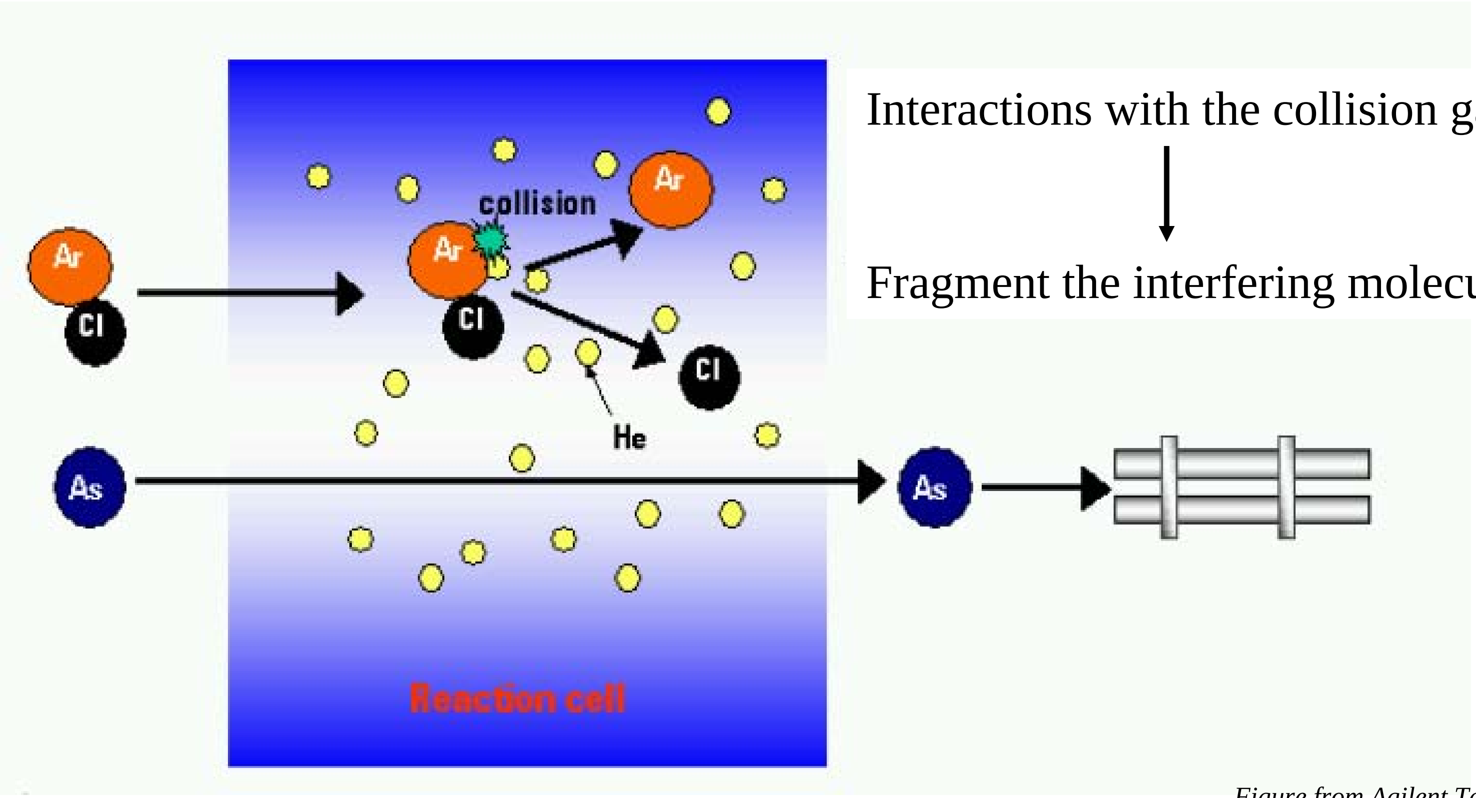
$$ArH^+ + NH_3 \rightarrow NH_4^+ + Ar$$

$$As + O_2 \rightarrow AsO + O$$

$$ArAr^+ + H2 \rightarrow ArH^+ + Ar + H$$

Collision Induced Dissociation (CID)

- Collision dissociation to break apart polyatomic species.



Interactions with the collision gas

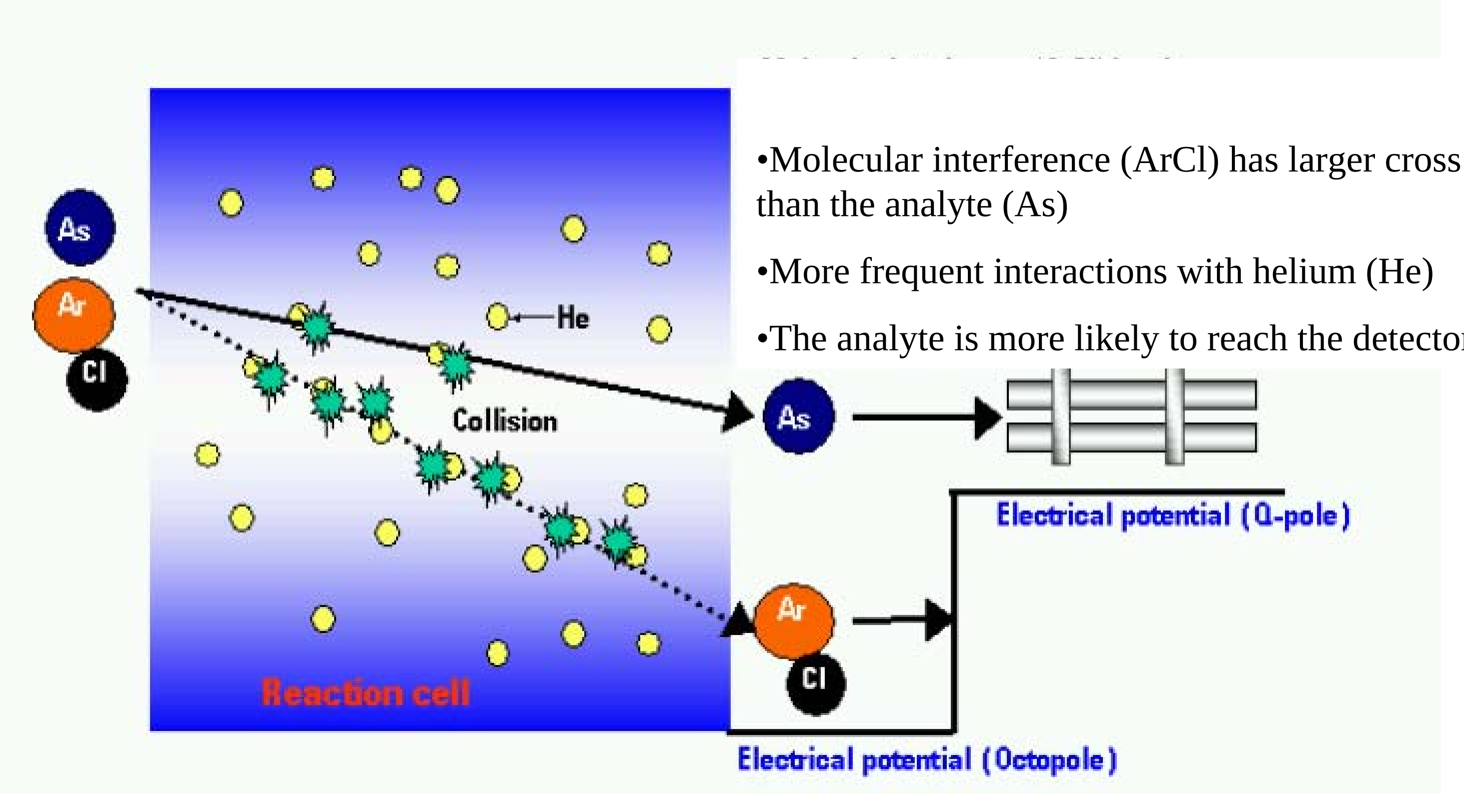
↓

Fragment the interfering molecule

Figure from Agilent Technologies

Kinetic Energy Discrimination (KED)

- Collisions impede transport of polyatomic species.



•Molecular interference (ArCl) has larger cross section than the analyte (As)

•More frequent interactions with helium (He)

•The analyte is more likely to reach the detector

Figure from Agilent Technologies

Laboratory Studies

Phase 1: Background detector response to interfering ions

Phase 2: Comparison of calibration behavior

Phase 3: Interference studies

Phase 4: Brine and brackish water samples

Phase 1 – Detector Response

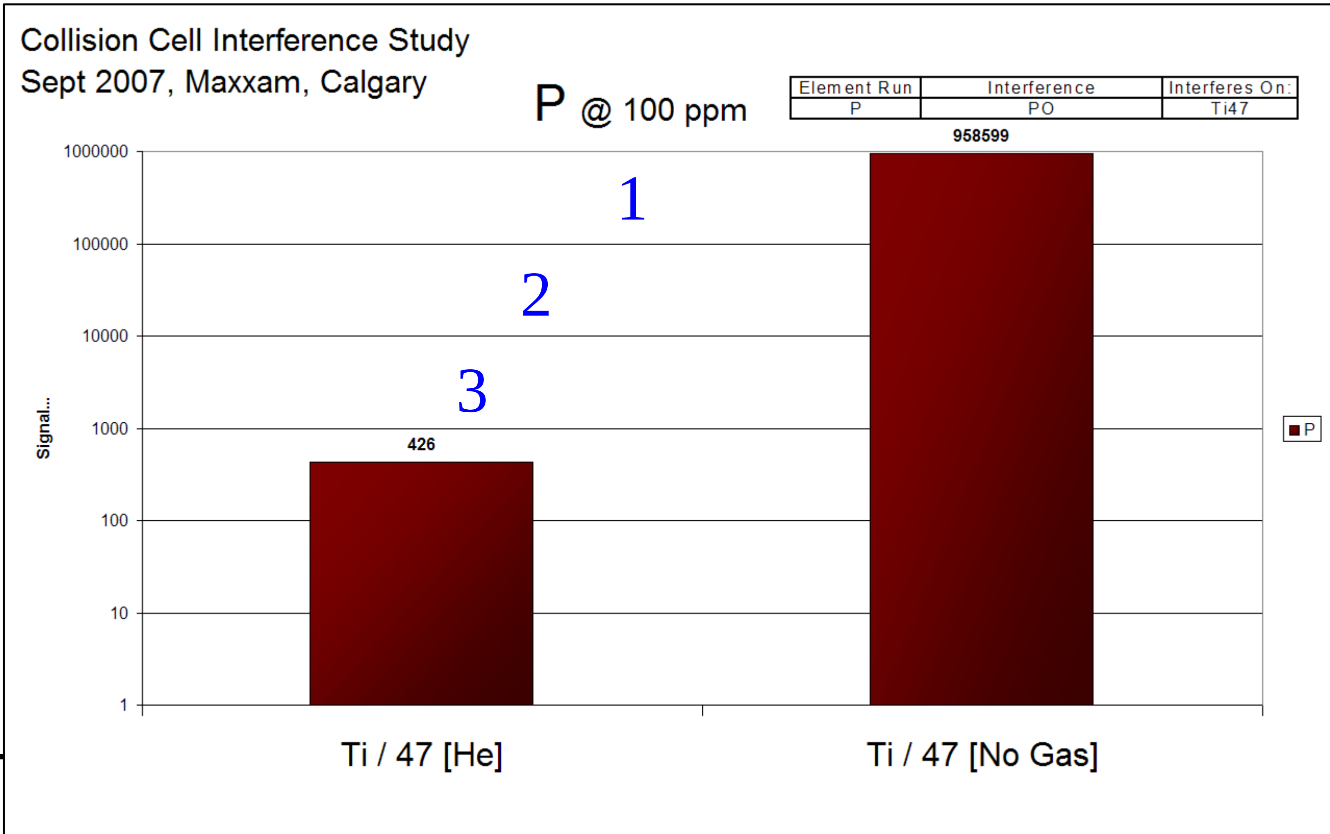
Example: Phosphorous (P) interference on Titanium (Ti)

- Deionized water was spiked with 100 ppm of various metals.
  - P, S, Br, C, Cl, Na and W
- Metals known to experience interference were monitored via detector response.

Observations

•Response always lower

•1 to 4 orders



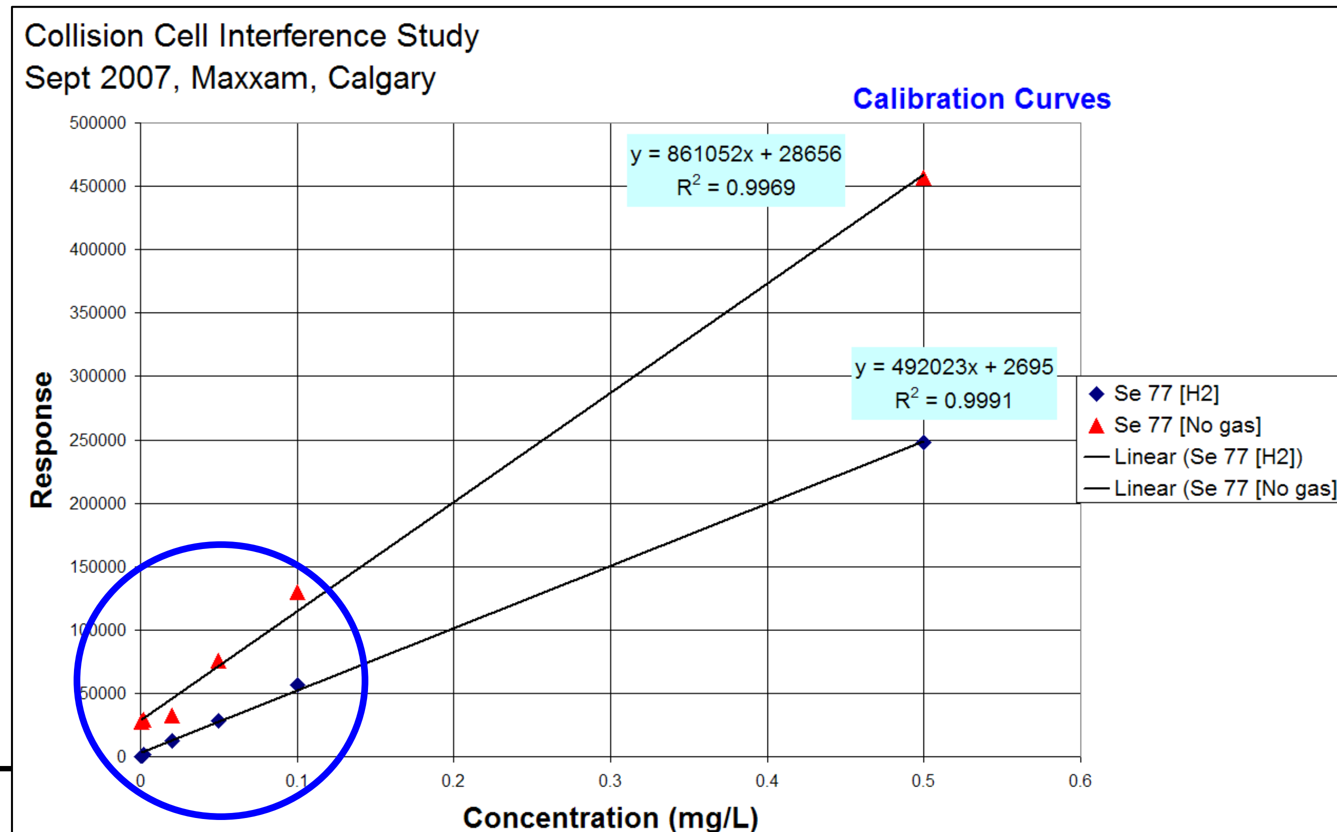
Phase 2 – Comparison of Calibration Behavior

Example: Selenium

- Data was collected under three modes of operation
  - He collision gas, H_2 collision gas and no gas

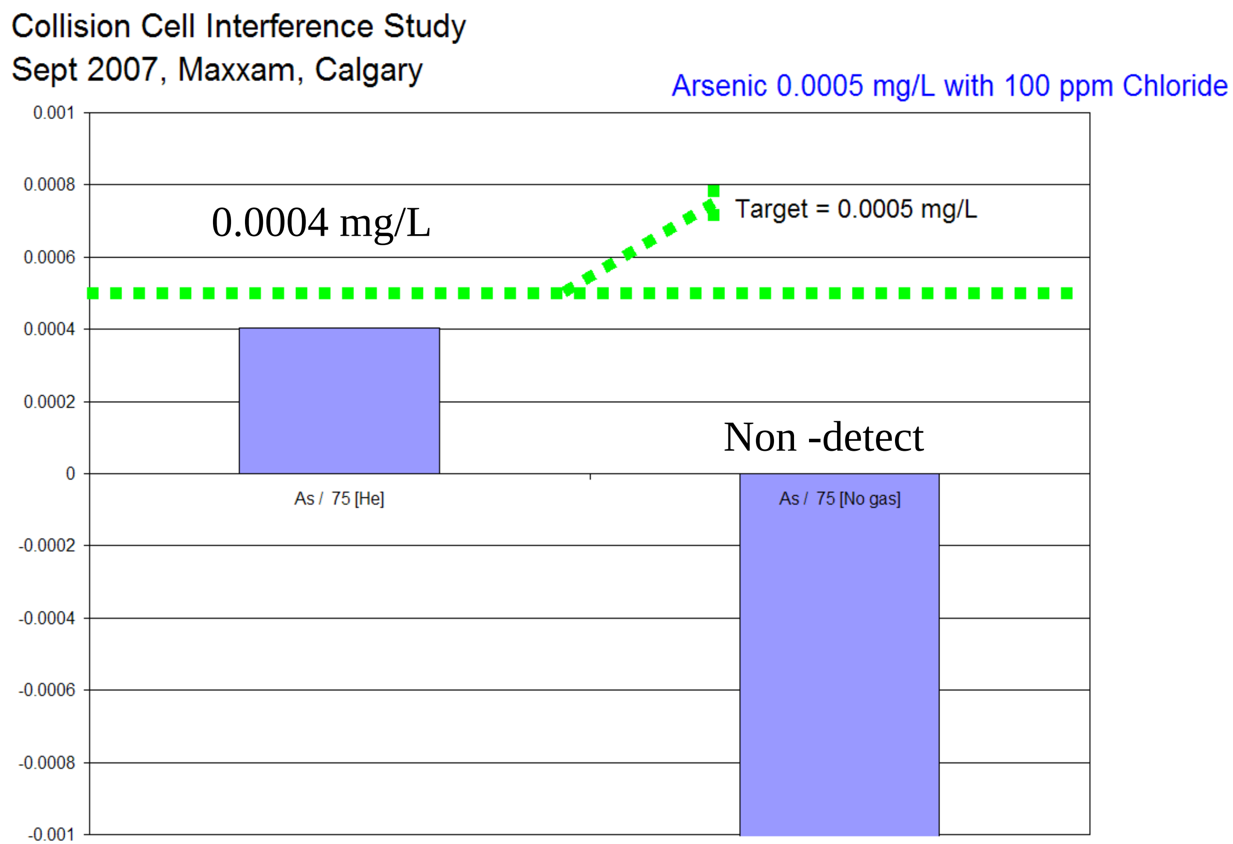
Observations

- Response always lower
  - 1 to 2 orders
- Improved y-intercept
- Reduced data scatter
  - Improved R^2 value



Phase 3 – Interference Studies

Example: Chloride Interference on Arsenic (^{75}As) LOW LEVEL SPIKE



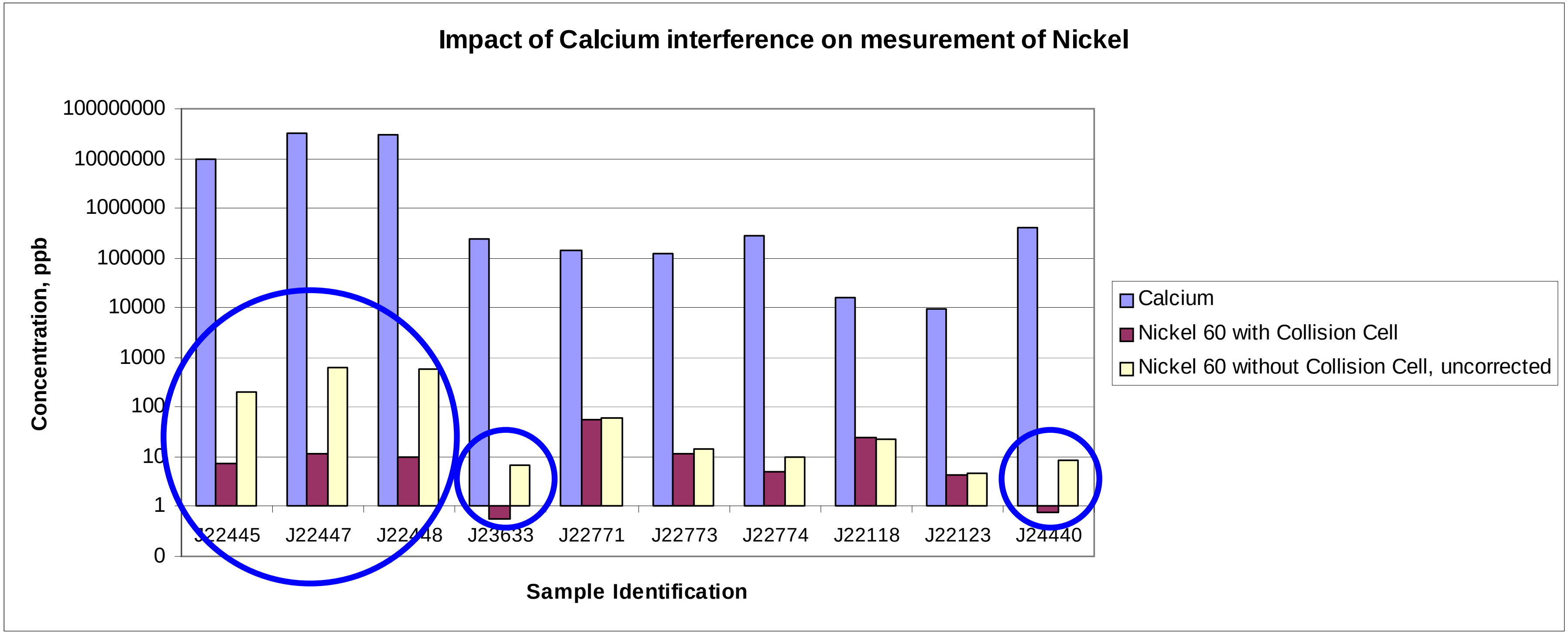
Observations

- Very close to target concentration using CC technology
- Report non-detect (ND) with standard technology
  - Over corrected

Phase 4 –Laboratory Studies
Impact of Calcium on Measurement of Nickel

Observations:

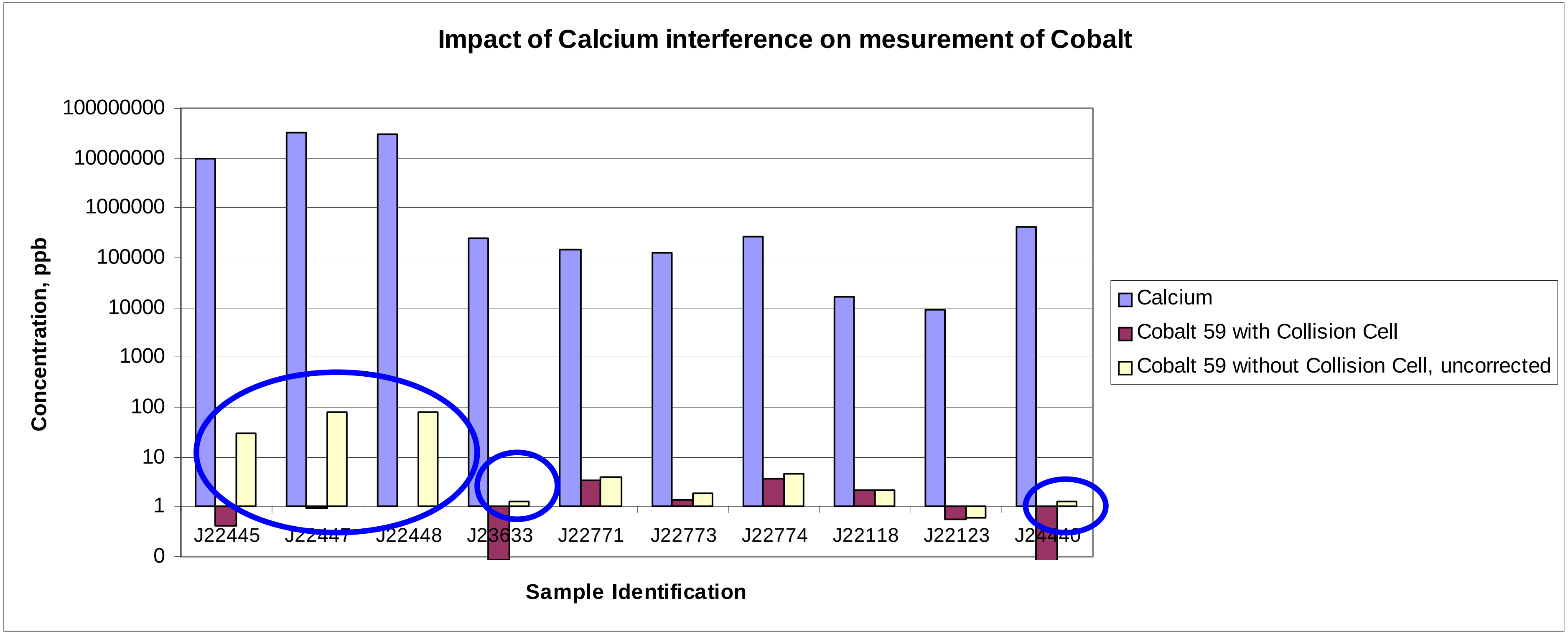
- Calcium concentrations above 100 mg/L have the potential to create false positive results for nickel
- When calcium is above 1000 mg/L the mathematical corrections may need to remove several hundred ppb of nickel interference



Phase 4 –Laboratory Studies
Impact of Calcium on Measurement of Cobalt

Observations:

- Calcium concentrations above 100 mg/L have the potential to create false positive results for cobalt.
- When calcium is above 1000 mg/L the mathematical corrections may need to remove up to 100 ppb of cobalt interference.

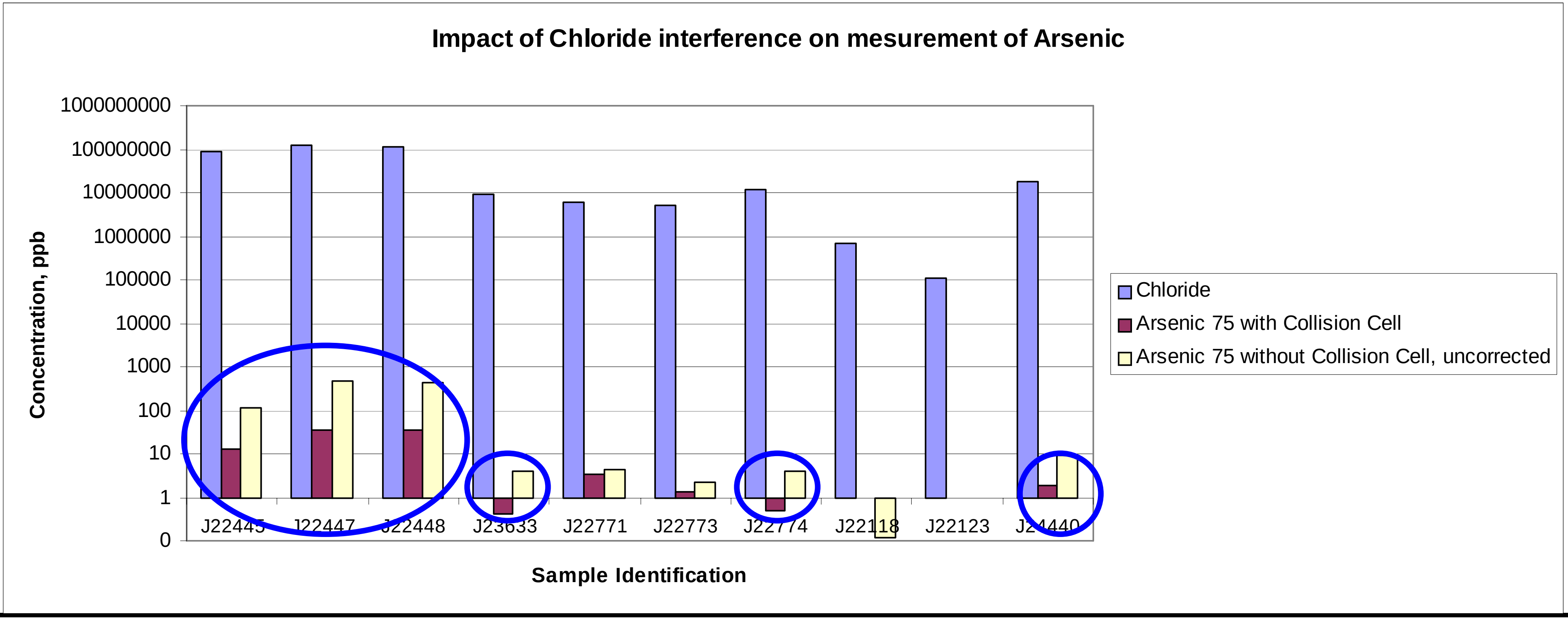


Phase 4 –Laboratory Studies

Impact of Chloride on Measurement of Arsenic

Observations:

- Chloride concentrations above 1,000 mg/L have the potential to create false positive results for Arsenic.
- When chloride is above 10,000 mg/L the mathematical corrections may need to remove up to several 100 ppb of arsenic interference.
  - In these extreme cases even the collision cell technology may not be entirely effective?

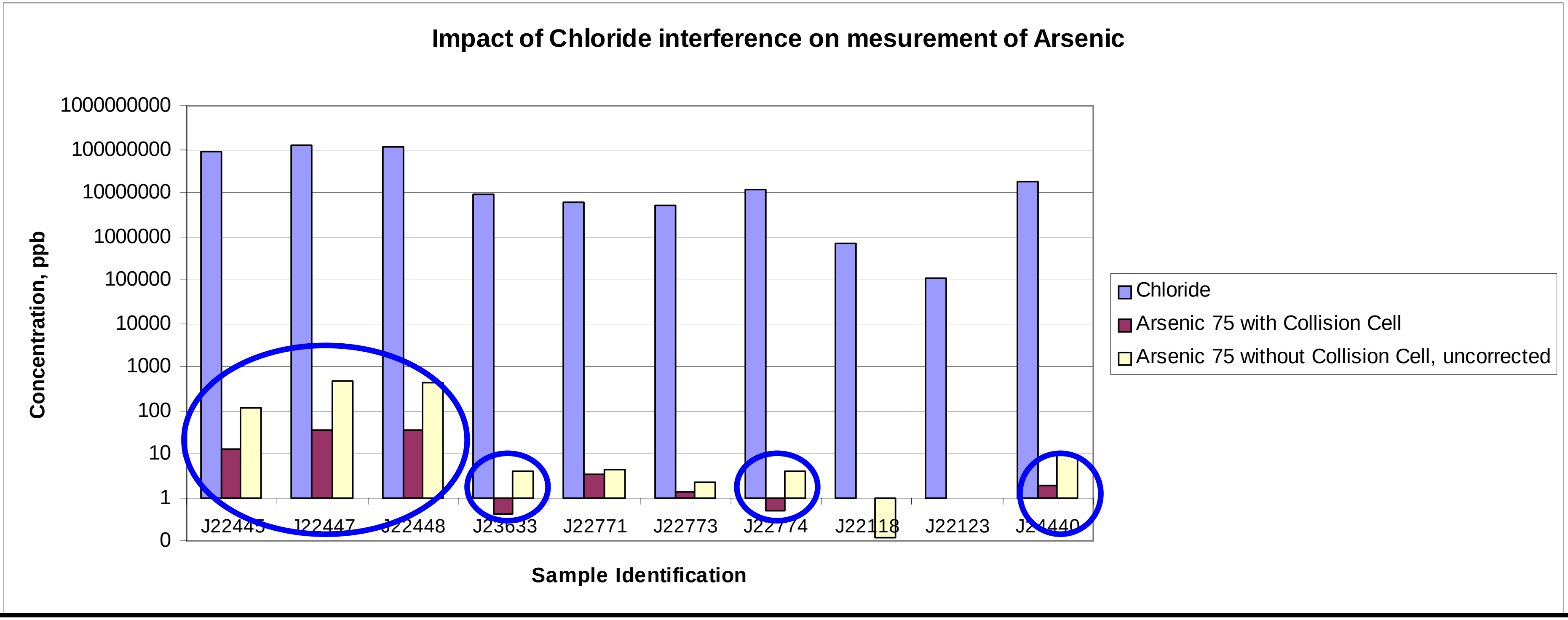


Phase 4 –Laboratory Studies

Impact of Chloride on Measurement of Arsenic

Observations:

- Chloride concentrations above 100 mg/L have the potential to create false positive results for Arsenic.
- When chloride is above 1000 mg/L the mathematical corrections may need to remove up to 100 ppb of Arsenic interference.
  - In these extreme cases even the collision cell technology may not be entirely effective?

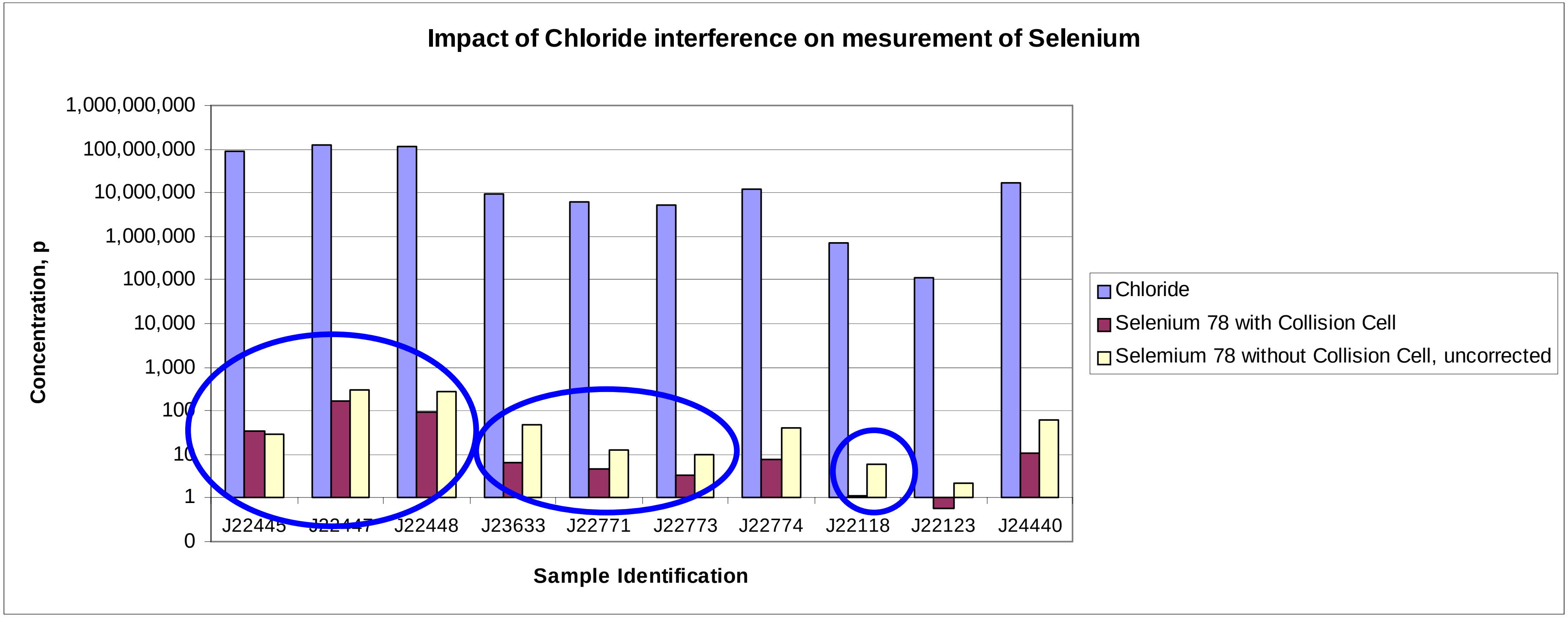


Phase 4 –Laboratory Studies

Impact of Chloride on Measurement of Selenium

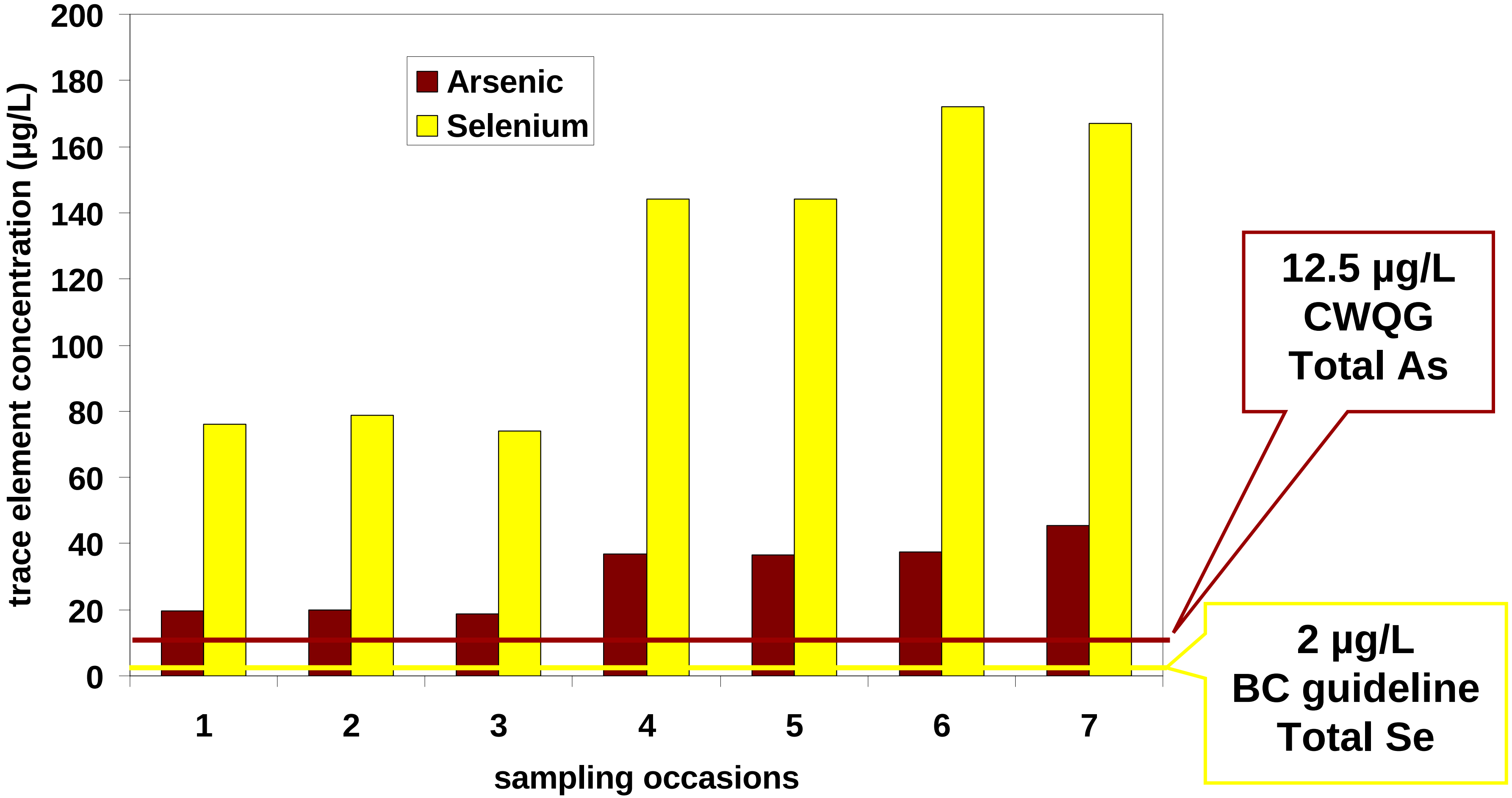
Observations:

- Chloride concentrations above 1,000 mg/L have the potential to create false positive results for Selenium.
- Chloride interference is substantially reduced using collision cell technology. Caution is still required in cases where chloride values exceed 1000 mg/L.



Real life scenarios: Selenium and Arsenic results for “pristine” marine waters

Selenium and arsenic concentrations in marine sites (baseline/pre-impact conditions) – all samples shown



Fish study

Maxxam Analytics Inc

Golder Associates

Resident marine fish healthy

Water monitoring during mine operation

Water monitoring during mining activities

Re-analysis of Selenium and Arsenic concentrations using ICP/MS Collision Cell Technology

- Total Selenium <2 µg/L
  (all measurements below the 2 µg/L BC guideline for protection of marine life)

- Total Arsenic <1 µg/L
  (all measurements below 12.5 µg/L CWQG for protection of marine life)

Summary

The importance of using the appropriate technique for water analysis cannot be over emphasized. False positive results for trace elements and metals such as selenium and arsenic due to interference by chloride are great enough to exceed the Canadian Water Quality Guidelines (CWQGs). The consequences of perceived exceedences of the CWQGs may include:

- Crippling constraints being put on the operation and management of tailing ponds in the mining industry.
- Confusion and inappropriate mitigation measures being employed in management and/or recovery plans;
- Installation of costly water treatment facilities.
- Initiation of expensive monitoring programs

Acknowledgements

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- The photographs were all taken by Golder Associates field crews.

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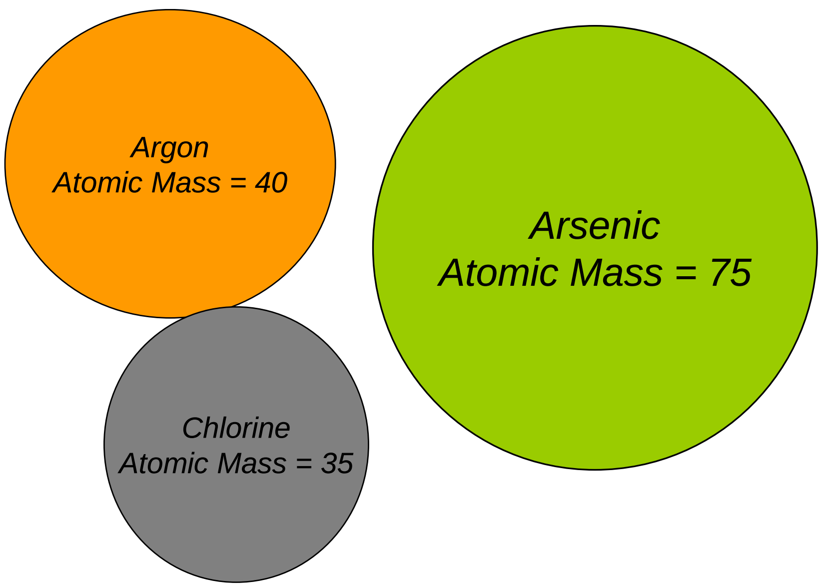

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