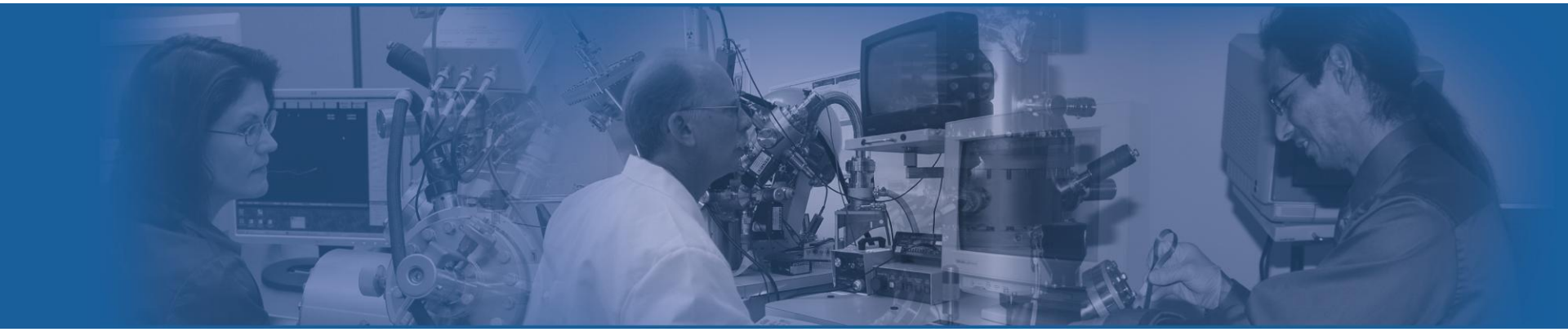

# The Evaluation and Characterization of Alternative Gases using Iron and Titanium Reference Materials

DeAnn Barnhart, Glyn Churchill, and Karol Putyera

EW-GDS
September 3-4, 2012
Kingston, UK

# Outline

- Introduction to alternative gases
- Analysis of titanium CRM BS-T2A in argon, krypton, neon, and nitrogen plasma gases
- Assessment of data reproducibility utilizing krypton as an alternative gas
- Alternative gas study to investigate the suppression of $MM^{+}$, $M^{++}$, $MG^{+}$, $GG^{+}$, and $G^{++}$ species
- Future endeavors
- Conclusions

The Astrum from Nu Instruments

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# Introduction

- Alternative gases have long been used in glow-discharge mass spectrometry (GDMS) to alleviate interferences that arise from the standard ionization gas of choice, in this instance argon.
- The research presented here explores:

1. The use of the alternative gases krypton, neon, and nitrogen with the Nu Astrum (Nu Instruments) and compares and contrasts the use of krypton as an alternative gas utilizing both the VG9000 and the Nu Astrum GDMS instruments.
2. The propensity for the different plasma gases to produce commonly seen potentially interfering species $M^{++}$, $MM^{+}$, $MG^{+}$, $G^{++}$, and $GG^{+}$ from the matrix (M) and gas (G) ions. The differences in concentrations seen for these interferences are investigated utilizing titanium and iron reference materials.
3. The behavior of oxygen in each plasma gas for both titanium and iron reference standards.

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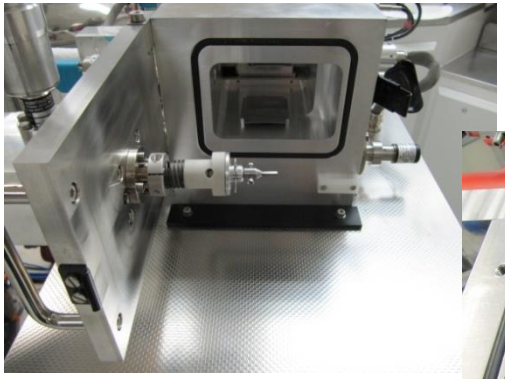
# Experimental Setup



- Materials:
  - Iron – CRM BS-56G
  - Titanium – CRM BS-T2A
  - Titanium 4N5 reproducibility material
  - Light acid etch for surface cleaning
- Gases:
  - Argon – 6N Praxiar fed through a MonoTorr PS4 rare gas getter, ~0.6 sccm
  - Krypton – 5N Linde fed through a MonoTorr PS3 rare gas getter, ~0.1 sccm
  - Neon – 5N Specialty Gases fed through a MonoTorr PS3 rare gas getter, ~0.3 sccm
  - Nitrogen – 5N Haun fed through a MonoTorr PS4 nitrogen getter, ~0.7 sccm
- Conditions: ~ 1 kV, ~3 mA
- Investigation:
  - The use of alternative gases to achieve better limits of detection for calcium, scandium, strontium, yttrium, and rhodium
  - The use of alternative gases to suppress the formation of $MM^{+}$, $M^{++}$, $MG^{+}$, $GG^{+}$, and $G^{++}$ species

*Gas Correction Factors for Thermal-based Mass Flow Controllers*. MKS Instruments, 2009, 1–6.

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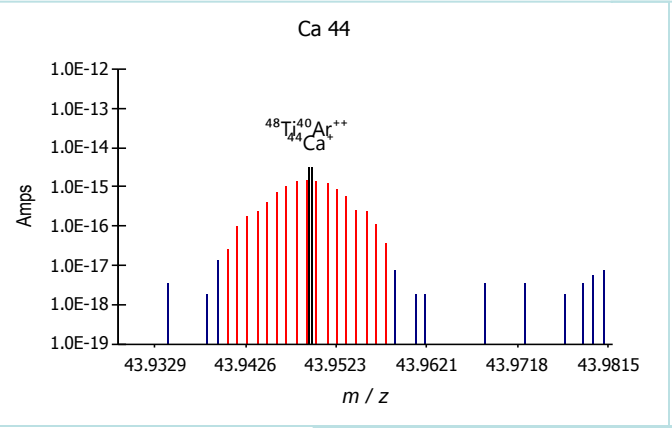
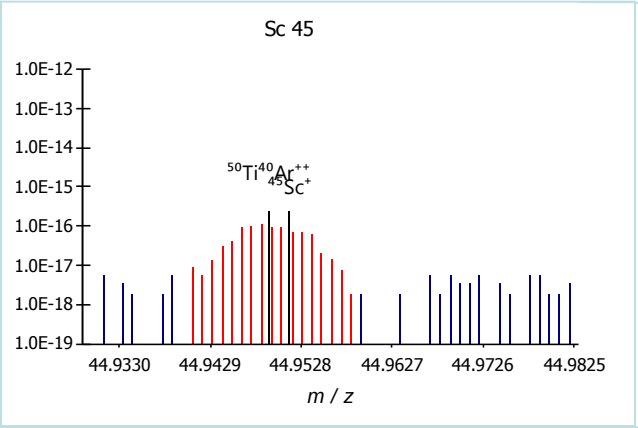
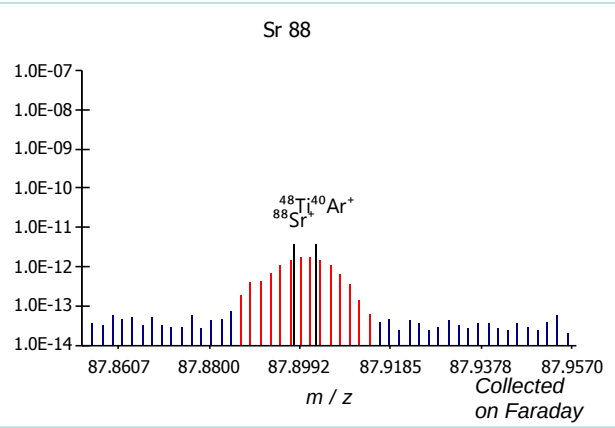
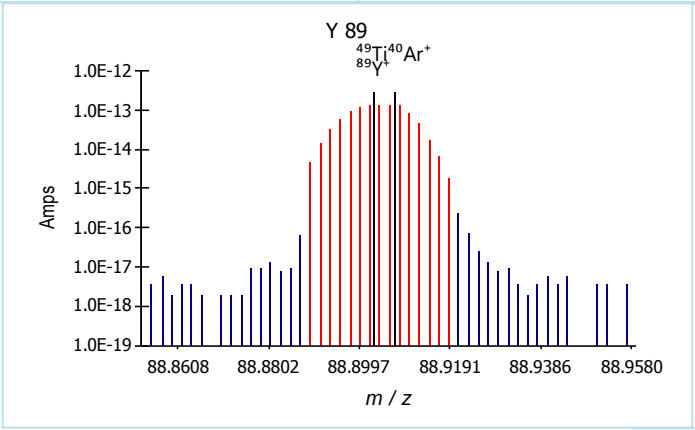
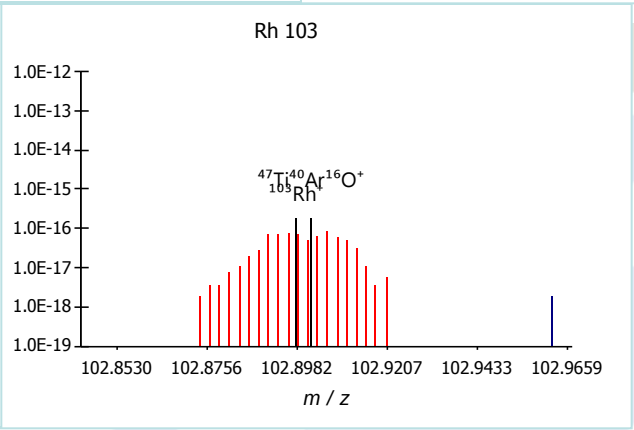
# Titanium BS-T2A in Argon




- $TiAr^{+}$, $TiAr^{++}$, and $TiArO^{+}$ interferences are superimposed on the isotopic peaks of interest
  - Peaks are unresolvable at 4000 ($M/\Delta M$ = RP5% valley definition)
  - Unable to approach certification of 4N5 purity

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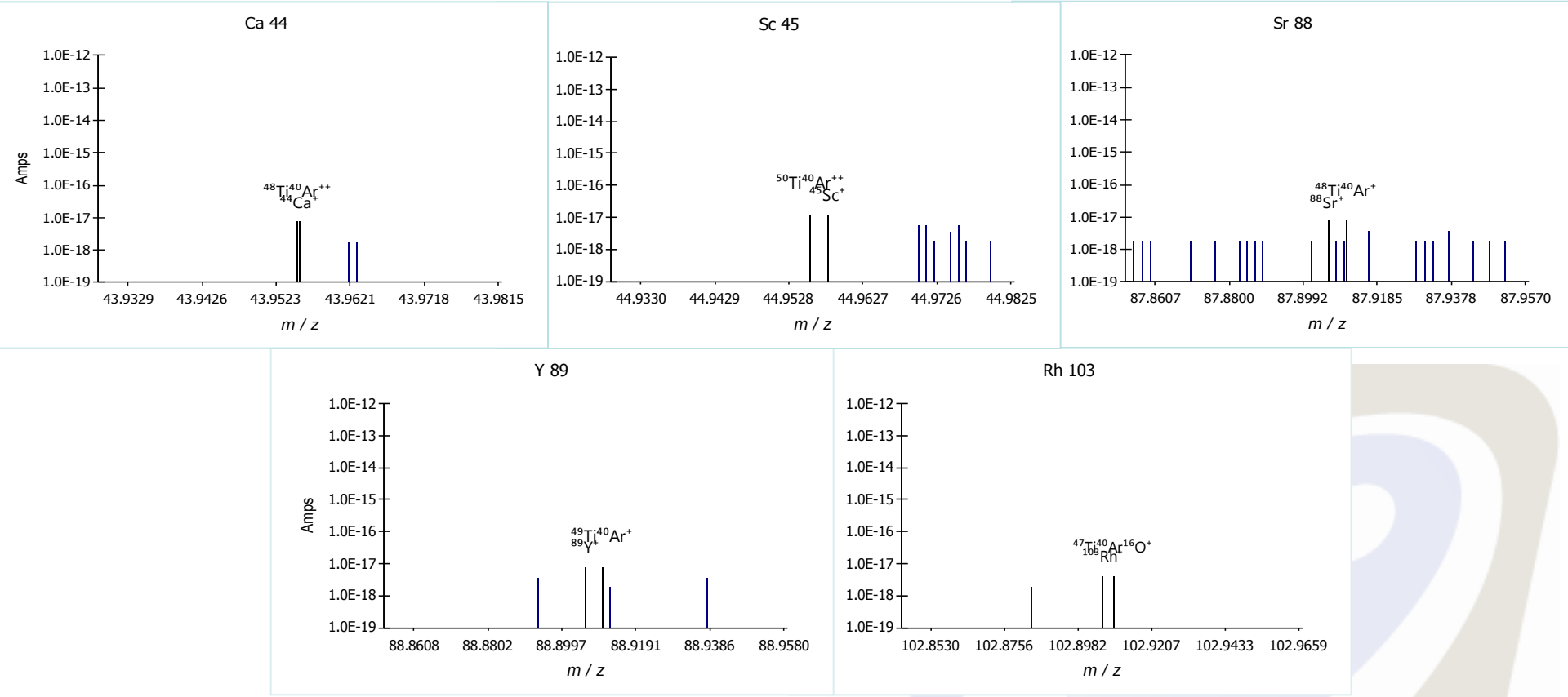
# Titanium BS-T2A in Krypton




- $TiAr^{+}$, $TiAr^{++}$, and $TiArO^{+}$ interferences are alleviated by using krypton as an alternative gas
  - Detection limits for calcium, scandium, strontium, yttrium, and rhodium are now achievable
  - Allows for approach of 4N5 purity

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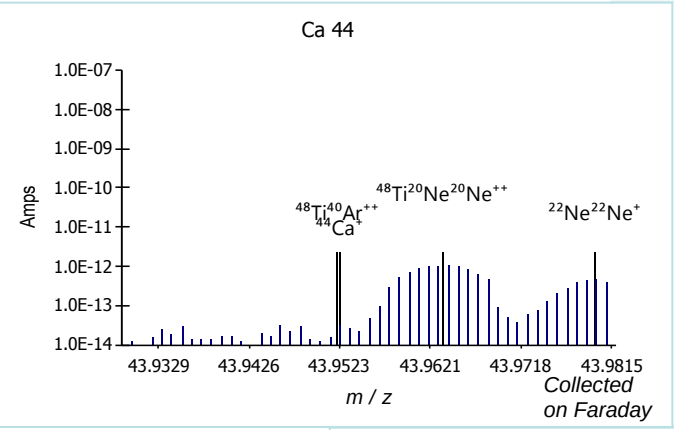
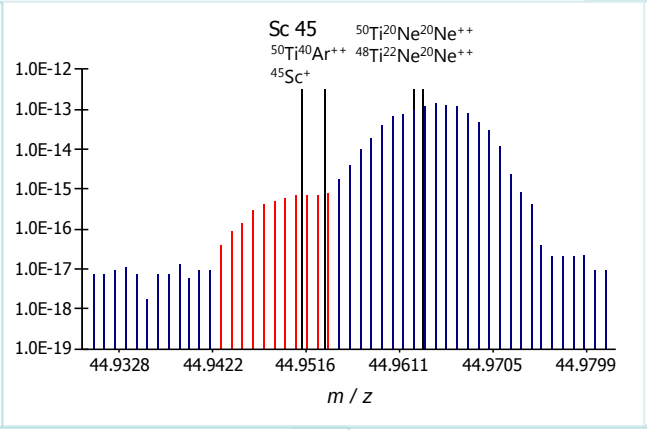
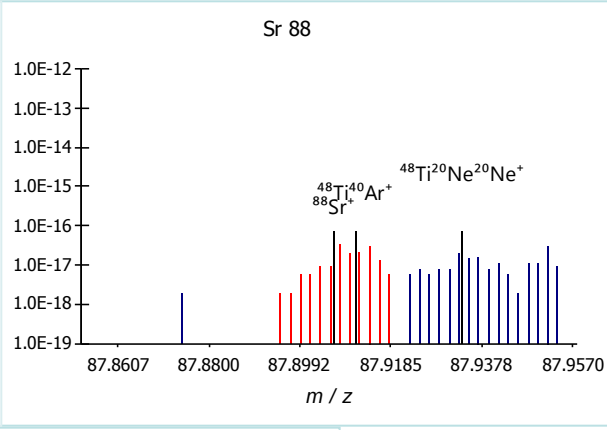
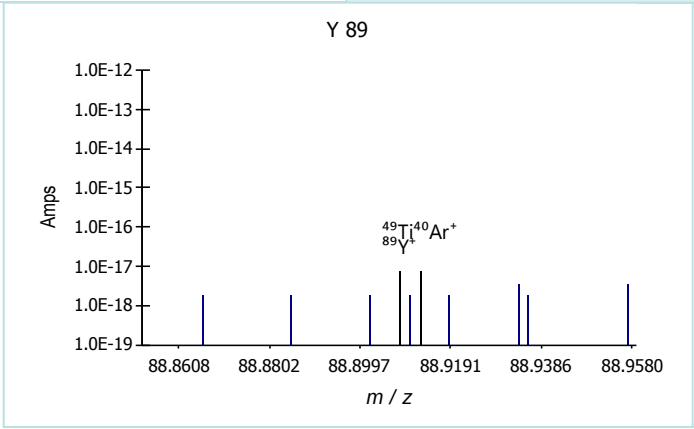
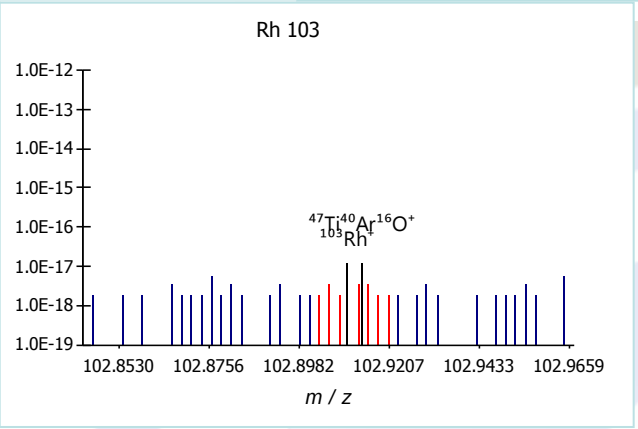
# Titanium BS-T2A in Neon




- Interferences from neon are superimposed on the calcium and scandium peaks
  - These peaks of interest are unresolvable in neon
  - Unable to approach certification of 4N5 purity

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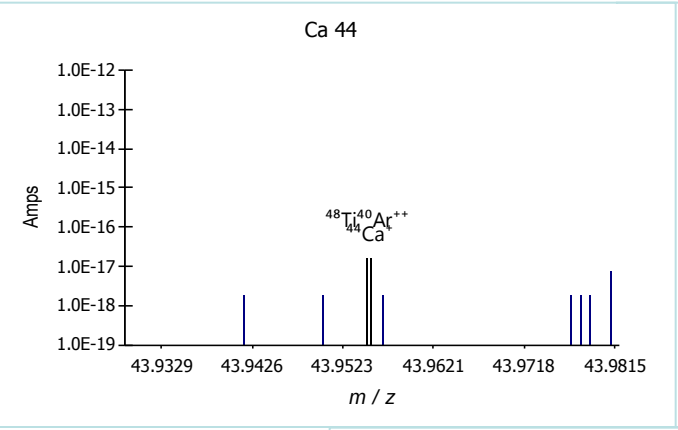
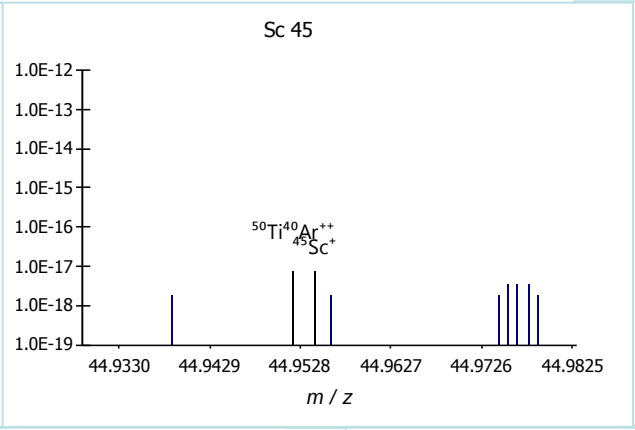
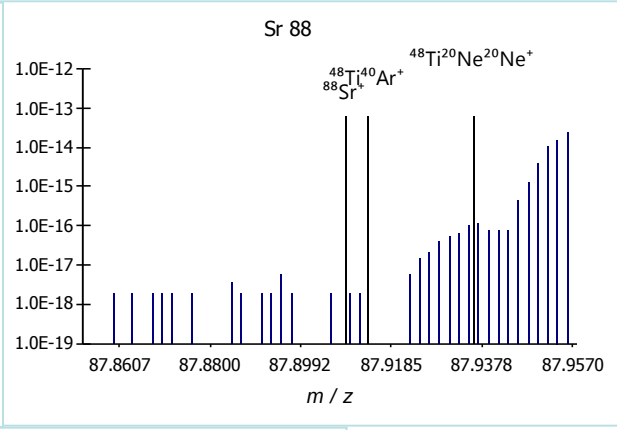
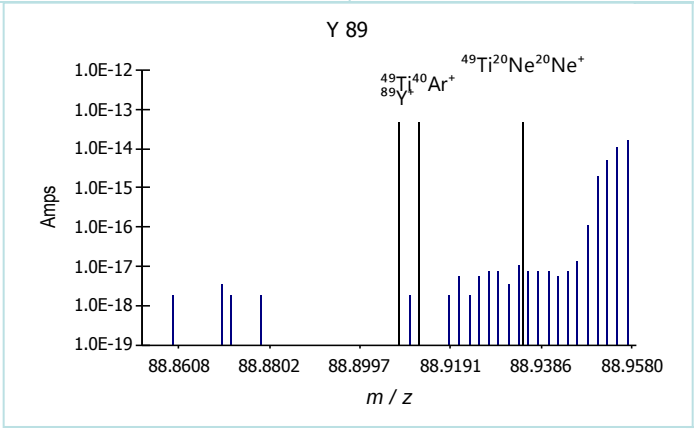
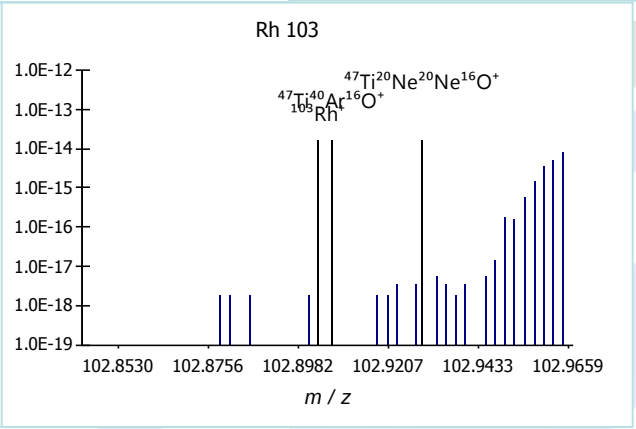
# Titanium BS-T2A in Nitrogen




- $TiAr^{+}$, $TiAr^{++}$, and $TiArO^{+}$ interferences are alleviated by using nitrogen as an alternative gas
  - Detection limits for calcium, scandium, strontium, yttrium, and rhodium are now achievable
  - Nitrogen has potential as a viable alternative to krypton gas

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# Titanium Data (Argon)

- Data (µg $g^{-1}$) from the Astrum and historical analyses are shown on the left and right hand sides of the table, respectively
- BS-T2A data from the Astrum is in good agreement with the CRM values
- 4N5 reproducibility material data from the Astrum is in good agreement with values ca.1995 VG9000 analysis (n = 2)
- The standard relative sensitivity factor (RSF) set used for VG9000 data is also applicable to data from the Astrum

| | Ti BS-T2A | | Ti 4N5 | |
|---|---|---|---|---|
| *Data from:* | *Astrum* | *CRM values* | *Astrum* | *VG9000* |
| Al | 59 | 50 | 1.5 | 1.4 |
| Si | 8.8 | 20 | 0.19 | 0.12 |
| V | 2.8 | < 20 | 1.3 | 1.5 |
| Cr | 190 | 180 | 0.98 | 0.28 |
| Mn | 26 | 30 | 0.07 | < 0.005 |
| Fe | 1230 | 1560 | 2.5 | 2.7 |
| Ni | 170 | 210 | 0.04 | 0.02 |

Vieth, W. and Huneke, J.C. (1991). Relative sensitivity factors in glow discharge mass spectrometry. *Spectrochimica Acta*, *46B*(2), 137–153.

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# Titanium Data (Krypton/Argon)

| µg g$^{-1}$ | Ti BS-T2A | Ti 4N5 | Ti6Al4V | Ti Ratio Ave. | Ti Ratio St. Dev. | Ti Ratio Ave. | Ti Ratio St. Dev. | Fe Ratio BS-56G |
|---|---|---|---|---|---|---|---|---|
| Al | 103 / 59 | 2.8 / 1.5 | 121000 / 72000 | 1.8 | 0.1 | 2.5 | 0.6 | 2.9 |
| Si | 6.5 / 8.8 | 0.46 / 0.19 | 160 / 93 | 1.6 | 0.9 | 1.9 | 0.5 | 0.55 |
| V | 2.2 / 2.8 | 1.2 / 1.3 | 38000/ 36000 | 0.91 | 0.14 | 1.1 | 0.5 | 1.2 |
| Cr | 420 / 190 | 2.3 / 0.98 | 320 / 83 | 2.8 | 0.9 | 2.5 | 0.4 | 2.7 |
| Mn | 52 / 26 | 0.14 / 0.07 | 29 / 11 | 2.2 | 0.3 | 2.2 | 0.3 | 3.0 |
| Fe | 940 / 1230 | 1.7 / 2.5 | 1600 / 1700 | 0.80 | 0.14 | 1.2 | 0.7 | Matrix |
| Ni | 250 / 170 | 0.05 / 0.04 | 200 / 92 | 1.7 | 0.5 | 2.2 | 0.3 | 2.0 |
| *Data from:* | *Astrum n = 3* | | | | | *VG9000, ca. 2001 n = 10* | | *Astrum n = 1* |

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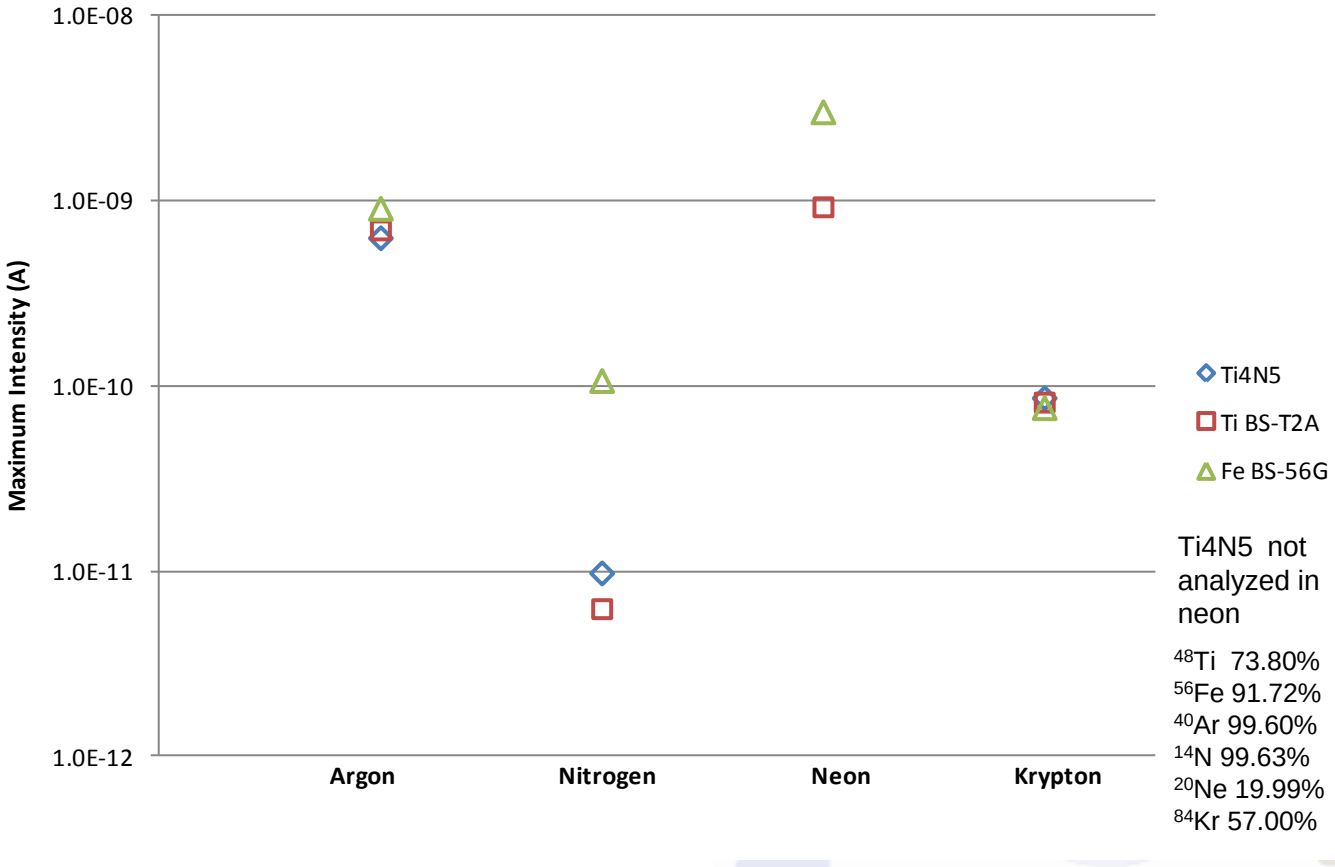
# Alternative Gas Study




- Intensities of titanium and iron with the different plasma gases
  - Neon > Argon >> Krypton ≥ Nitrogen

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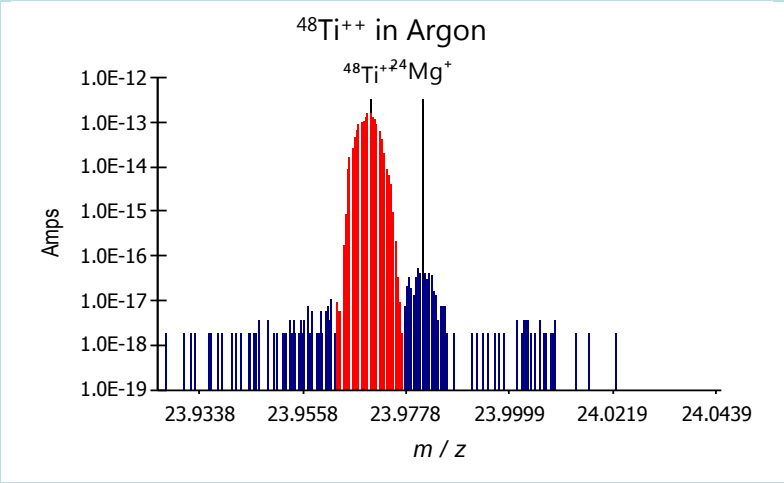
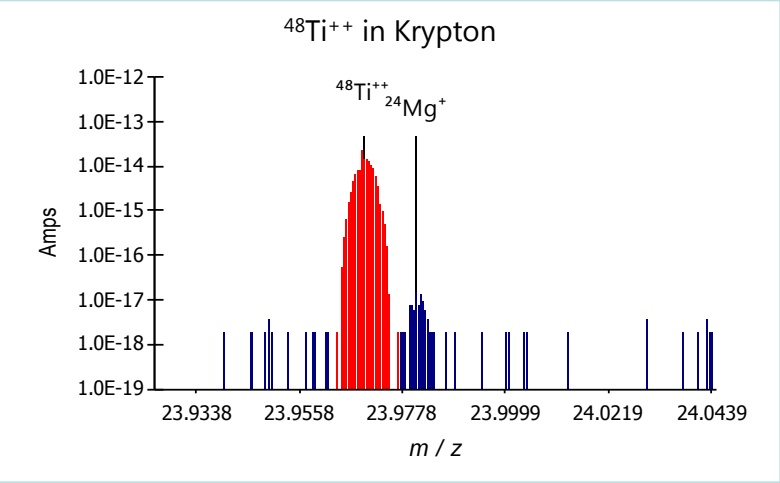
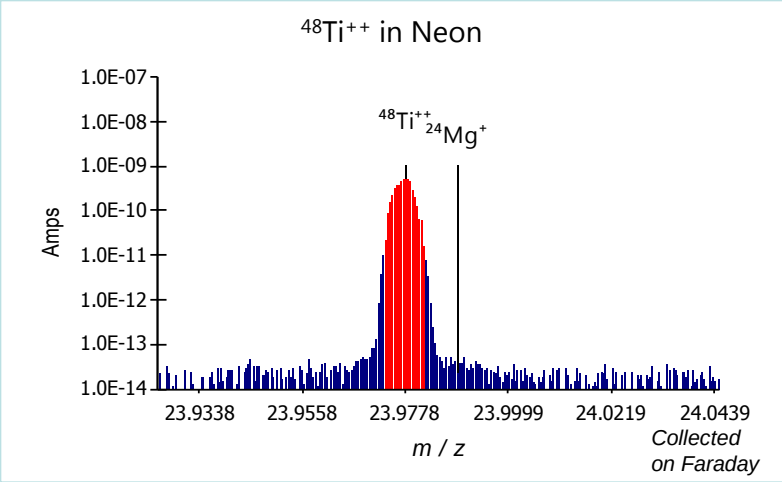
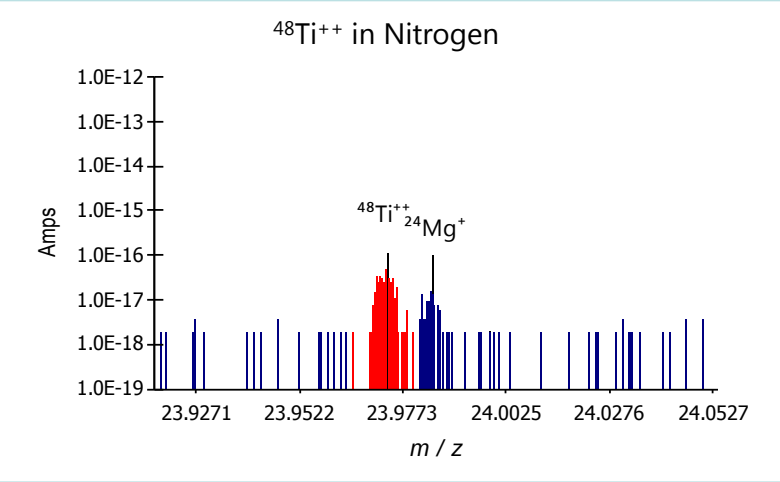
# Alternative Gas Study




- Titanium-48 doubly ionized peak acquired with each discharge gas
  - Neon >> Argon > Krypton >> Nitrogen
  - $MM^{+}$, $M^{++}$, $MG^{+}$, $GG^{+}$, and $G^{++}$

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# Alternative Gas Study

- To calculate the concentrations (µg $g^{-1}$):
  - Divide the integrated intensity of the interference peak by the abundance
    - Abundance is calculated as the product of the natural abundance percentages
    - *e.g.* $^{48}Ti^{40}Ar^{+}$ abundance = 73.80% x 99.60%
  - Set the matrix
    - Use the integrated intensity from either the matrix or the gas peak
    - Divide this number by the natural abundance
  - Divide the number from the first part by the number from the second part

$$\frac{\dfrac{\text{int}:^{48}Ti^{40}Ar^{+}}{abund:^{48}Ti^{40}Ar^{+}}}{\dfrac{\text{int}:^{48}Ti^{+}}{abund:^{48}Ti^{+}}} =$$

*Element concentration of $^{48}Ti^{40}Ar^{+}$ in a titanium matrix*

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# Alternative Gas Study

| | | Element Concentrations (µg $g^{-1}$) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Gas | $G^{++}/G^{+}$ | $GG^{+}/G^{+}$ | $G^{++}/M^{+}$ | $GG^{+}/M^{+}$ | $G^{+}/M^{+}$ | $M^{++}/M^{+}$ | $MM^{+}/M^{+}$ | $MG^{+}/M^{+}$ | $MG^{+}/G^{+}$ | $O^{+}/M^{+}$ | $O^{+}/G^{+}$ |
| Ti4N5 | Ar | 150973 | 22620 | 494288 | 74057 | 3274022 | 227 | 17 | 2592 | 792 | 1.2 | 1.5 |
| Ti4N5 | N | 26 | 810772 | 573 | 18077343 | 22296445 | 7 | 246 | 58800 | 2637 | 6.7 | 0.50 |
| Ti4N5 | Ne | - | - | - | - | - | - | - | - | - | - | - |
| Ti4N5 | Kr | 149416 | 11608 | 646814 | 50248 | 4328939 | 177 | 10 | 2308 | 533 | 10 | 2.0 |
| Ti BS-T2A | Ar | 142449 | 21351 | 387861 | 58134 | 2722805 | 212 | 27 | 2171 | 797 | 8.7 | 3.4 |
| Ti BS-T2A | N | 22 | 629636 | 387 | 10981672 | 17441313 | 7 | 183 | 55266 | 3169 | 35 | 2.2 |
| Ti BS-T2A | Ne | 72491 | 14503 | 187579 | 37529 | 2587627 | 566706 | 5 | 79 | 31 | 92 | 30 |
| Ti BS-T2A | Kr | 171362 | 14005 | 692338 | 56585 | 4040218 | 191 | 14 | 2805 | 694 | 58 | 16 |
| Fe BS-56G | Ar | 107813 | 21048 | 491477 | 95948 | 4558625 | 811 | 111 | 6133 | 1345 | 1.0 | 0.20 |
| Fe BS-56G | N | 30 | 5885 | 88 | 16501 | 2804030 | --- | 19816 | 4273 | 11982 | 7.9 | 3.0 |
| Fe BS-56G | Ne | 79443 | 19717 | 138449 | 34362 | 1742761 | 3413 | 4 | 2 | 1 | 11 | 8.2 |
| Fe BS-56G | Kr | 29443 | 21351 | 210908 | 152943 | 7163332 | 15978 | 46 | 3360 | 469 | 546 | 105 |

- Element concentrations from all the interfering species with either titanium or iron ($M^{+}$) or the plasma gas ($G^{+}$) as the matrix
  - The titanium 4N5 material was not analyzed in neon

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# Alternative Gas Study

| | | Element Concentrations (µg $g^{-1}$) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Gas | $G^{++}/ G^{+}$ | $GG^{+}/ G^{+}$ | $G^{++}/ M^{+}$ | $GG^{+}/ M^{+}$ | $G^{+}/ M^{+}$ | $M^{++}/ M^{+}$ | $MM^{+}/ M^{+}$ | $MG^{+}/ M^{+}$ | $MG^{+}/ G^{+}$ | $O^{+}/ M^{+}$ | $O^{+}/ G^{+}$ |
| Ti4N5 | Ar | 150973 | 22620 | 494288 | 74057 | 3274022 | 227 | 17 | 2592 | 792 | 1.2 | 1.5 |
| Ti4N5 | N | 26 | 810772 | 573 | 18077343 | 22296445 | 7 | 246 | 58800 | 2637 | 6.7 | 0.50 |
| Ti4N5 | Ne | - | - | - | - | - | - | - | - | - | - | - |
| Ti4N5 | Kr | 149416 | 11608 | 646814 | 50248 | 4328939 | 177 | 10 | 2308 | 533 | 10 | 2.0 |
| Ti BS-T2A | Ar | 142449 | 21351 | 387861 | 58134 | 2722805 | 212 | 27 | 2171 | 797 | 8.7 | 3.4 |
| Ti BS-T2A | N | 22 | 629636 | 387 | 10981672 | 17441313 | 7 | 183 | 55266 | 3169 | 35 | 2.2 |
| Ti BS-T2A | Ne | 72491 | 14503 | 187579 | 37529 | 2587627 | 566706 | 5 | 79 | 31 | 92 | 30 |
| Ti BS-T2A | Kr | 171362 | 14005 | 692338 | 56585 | 4040218 | 191 | 14 | 2805 | 694 | 58 | 16 |
| Fe BS-56G | Ar | 107813 | 21048 | 491477 | 95948 | 4558625 | 811 | 111 | 6133 | 1345 | 1.0 | 0.20 |
| Fe BS-56G | N | 30 | 5885 | 88 | 16501 | 2804030 | --- | 19816 | 4273 | 11982 | 7.9 | 3.0 |
| Fe BS-56G | Ne | 79443 | 19717 | 138449 | 34362 | 1742761 | 3413 | 4 | 2 | 1 | 11 | 8.2 |
| Fe BS-56G | Kr | 29443 | 21351 | 210908 | 152943 | 7163332 | 15978 | 46 | 3360 | 469 | 546 | 105 |

- The $O^{+}/ M^{+}$ concentrations evaluated the behavior of oxygen with each plasma gas
  - The $O^{+}/ G^{+}$ concentrations were not graphed, they were calculated to corroborate the $O^{+}/ M^{+}$ values

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# Alternative Gas Study

Element Concentrations (µg $g^{-1}$)

| Sample | Gas | $G^{++}/G^{+}$ | $GG^{+}/G^{+}$ | $G^{++}/M^{+}$ | $GG^{+}/M^{+}$ | $G^{+}/M^{+}$ | $M^{++}/M^{+}$ | $MM^{+}/M^{+}$ | $MG^{+}/M^{+}$ | $MG^{+}/G^{+}$ | $O^{+}/M^{+}$ | $O^{+}/G^{+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ti4N5 | Ar | 150973 | 22620 | 494288 | 74057 | 3274022 | 227 | 17 | 2592 | 792 | 1.2 | 1.5 |
| Ti4N5 | N | 26 | 810772 | 573 | 18077343 | 22296445 | 7 | 246 | 58800 | 2637 | 6.7 | 0.50 |
| Ti4N5 | Ne | - | - | - | - | - | - | - | - | - | - | - |
| Ti4N5 | Kr | 149416 | 11608 | 646814 | 50248 | 4328939 | 177 | 10 | 2308 | 533 | 10 | 2.0 |
| Ti BS-T2A | Ar | 142449 | 21351 | 387861 | 58134 | 2722805 | 212 | 27 | 2171 | 797 | 8.7 | 3.4 |
| Ti BS-T2A | N | 22 | 629636 | 387 | 10981672 | 17441313 | 7 | 183 | 55266 | 3169 | 35 | 2.2 |
| Ti BS-T2A | Ne | 72491 | 14503 | 187579 | 37529 | 2587627 | 566706 | 5 | 79 | 31 | 92 | 30 |
| Ti BS-T2A | Kr | 171362 | 14005 | 692338 | 56585 | 4040218 | 191 | 14 | 2805 | 694 | 58 | 16 |
| Fe BS-56G | Ar | 107813 | 21048 | 491477 | 95948 | 4558625 | 811 | 111 | 6133 | 1345 | 1.0 | 0.20 |
| Fe BS-56G | N | 30 | 5885 | 88 | 16501 | 2804030 | --- | 19816 | 4273 | 11982 | 7.9 | 3.0 |
| Fe BS-56G | Ne | 79443 | 19717 | 138449 | 34362 | 1742761 | 3413 | 4 | 2 | 1 | 11 | 8.2 |
| Fe BS-56G | Kr | 29443 | 21351 | 210908 | 152943 | 7163332 | 15978 | 46 | 3360 | 469 | 546 | 105 |

- The $G^{+}/M^{+}$ concentrations investigated the intensities of the different plasma gases with each matrix
  - Concentrations were not graphed as the results were similar

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# Alternative Gas Study

Element Concentrations (µg $g^{-1}$)

| Sample | Gas | $G^{++}/G^{+}$ | $GG^{+}/G^{+}$ | $G^{++}/M^{+}$ | $GG^{+}/M^{+}$ | $G^{+}/M^{+}$ | $M^{++}/M^{+}$ | $MM^{+}/M^{+}$ | $MG^{+}/M^{+}$ | $MG^{+}/G^{+}$ | $O^{+}/M^{+}$ | $O^{+}/G^{+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ti4N5 | Ar | 150973 | 22620 | 494288 | 74057 | 3274022 | 227 | 17 | 2592 | 792 | 1.2 | 1.5 |
| Ti4N5 | N | 26 | 810772 | 573 | 18077343 | 22296445 | 7 | 246 | 58800 | 2637 | 6.7 | 0.50 |
| Ti4N5 | Ne | - | - | - | - | - | - | - | - | - | - | - |
| Ti4N5 | Kr | 149416 | 11608 | 646814 | 50248 | 4328939 | 177 | 10 | 2308 | 533 | 10 | 2.0 |
| Ti BS-T2A | Ar | 142449 | 21351 | 387861 | 58134 | 2722805 | 212 | 27 | 2171 | 797 | 8.7 | 3.4 |
| Ti BS-T2A | N | 22 | 629636 | 387 | 10981672 | 17441313 | 7 | 183 | 55266 | 3169 | 35 | 2.2 |
| Ti BS-T2A | Ne | 72491 | 14503 | 187579 | 37529 | 2587627 | 566706 | 5 | 79 | 31 | 92 | 30 |
| Ti BS-T2A | Kr | 171362 | 14005 | 692338 | 56585 | 4040218 | 191 | 14 | 2805 | 694 | 58 | 16 |
| Fe BS-56G | Ar | 107813 | 21048 | 491477 | 95948 | 4558625 | 811 | 111 | 6133 | 1345 | 1.0 | 0.20 |
| Fe BS-56G | N | 30 | 5885 | 88 | 16501 | 2804030 | --- | 19816 | 4273 | 11982 | 7.9 | 3.0 |
| Fe BS-56G | Ne | 79443 | 19717 | 138449 | 34362 | 1742761 | 3413 | 4 | 2 | 1 | 11 | 8.2 |
| Fe BS-56G | Kr | 29443 | 21351 | 210908 | 152943 | 7163332 | 15978 | 46 | 3360 | 469 | 546 | 105 |

- $G^{++}/G^{+}$, $GG^{+}/G^{+}$, $G^{++}/M^{+}$ and $GG^{+}/M^{+}$ concentrations were compared to ascertain differences in:
  - Plasma gas behavior with either titanium or iron ($M^{+}$) or the plasma gas ($G^{+}$) as the matrix
  - Doubly ionized versus singly ionized dimer species

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# Alternative Gas Study

Element Concentrations (µg $g^{-1}$)

| Sample | Gas | $G^{++}/G^{+}$ | $GG^{+}/G^{+}$ | $G^{++}/M^{+}$ | $GG^{+}/M^{+}$ | $G^{+}/M^{+}$ | $M^{++}/M^{+}$ | $MM^{+}/M^{+}$ | $MG^{+}/M^{+}$ | $MG^{+}/G^{+}$ | $O^{+}/M^{+}$ | $O^{+}/G^{+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ti4N5 | Ar | 150973 | 22620 | 494288 | 74057 | 3274022 | 227 | 17 | 2592 | 792 | 1.2 | 1.5 |
| Ti4N5 | N | 26 | 810772 | 573 | 18077343 | 22296445 | 7 | 246 | 58800 | 2637 | 6.7 | 0.50 |
| Ti4N5 | Ne | - | - | - | - | - | - | - | - | - | - | - |
| Ti4N5 | Kr | 149416 | 11608 | 646814 | 50248 | 4328939 | 177 | 10 | 2308 | 533 | 10 | 2.0 |
| Ti BS-T2A | Ar | 142449 | 21351 | 387861 | 58134 | 2722805 | 212 | 27 | 2171 | 797 | 8.7 | 3.4 |
| Ti BS-T2A | N | 22 | 629636 | 387 | 10981672 | 17441313 | 7 | 183 | 55266 | 3169 | 35 | 2.2 |
| Ti BS-T2A | Ne | 72491 | 14503 | 187579 | 37529 | 2587627 | 566706 | 5 | 79 | 31 | 92 | 30 |
| Ti BS-T2A | Kr | 171362 | 14005 | 692338 | 56585 | 4040218 | 191 | 14 | 2805 | 694 | 58 | 16 |
| Fe BS-56G | Ar | 107813 | 21048 | 491477 | 95948 | 4558625 | 811 | 111 | 6133 | 1345 | 1.0 | 0.20 |
| Fe BS-56G | N | 30 | 5885 | 88 | 16501 | 2804030 | --- | 19816 | 4273 | 11982 | 7.9 | 3.0 |
| Fe BS-56G | Ne | 79443 | 19717 | 138449 | 34362 | 1742761 | 3413 | 4 | 2 | 1 | 11 | 8.2 |
| Fe BS-56G | Kr | 29443 | 21351 | 210908 | 152943 | 7163332 | 15978 | 46 | 3360 | 469 | 546 | 105 |

- $G^{++}/M^{+}$ and $M^{++}/M^{+}$ concentrations were compared to $GG^{+}/M^{+}$ and $MM^{+}/M^{+}$ to ascertain differences in doubly ionized versus singly ionized dimer species

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# Alternative Gas Study

| Sample | Gas | Element Concentrations (µg $g^{-1}$) $G^{++}/G^{+}$ | $GG^{+}/G^{+}$ | $G^{++}/M^{+}$ | $GG^{+}/M^{+}$ | $G^{+}/M^{+}$ | $M^{++}/M^{+}$ | $MM^{+}/M^{+}$ | $MG^{+}/M^{+}$ | $MG^{+}/G^{+}$ | $O^{+}/M^{+}$ | $O^{+}/G^{+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ti4N5 | Ar | 150973 | 22620 | 494288 | 74057 | 3274022 | 227 | 17 | 2592 | 792 | 1.2 | 1.5 |
| Ti4N5 | N | 26 | 810772 | 573 | 18077343 | 22296445 | 7 | 246 | 58800 | 2637 | 6.7 | 0.50 |
| Ti4N5 | Ne | - | - | - | - | - | - | - | - | - | - | - |
| Ti4N5 | Kr | 149416 | 11608 | 646814 | 50248 | 4328939 | 177 | 10 | 2308 | 533 | 10 | 2.0 |
| Ti BS-T2A | Ar | 142449 | 21351 | 387861 | 58134 | 2722805 | 212 | 27 | 2171 | 797 | 8.7 | 3.4 |
| Ti BS-T2A | N | 22 | 629636 | 387 | 10981672 | 17441313 | 7 | 183 | 55266 | 3169 | 35 | 2.2 |
| Ti BS-T2A | Ne | 72491 | 14503 | 187579 | 37529 | 2587627 | 566706 | 5 | 79 | 31 | 92 | 30 |
| Ti BS-T2A | Kr | 171362 | 14005 | 692338 | 56585 | 4040218 | 191 | 14 | 2805 | 694 | 58 | 16 |
| Fe BS-56G | Ar | 107813 | 21048 | 491477 | 95948 | 4558625 | 811 | 111 | 6133 | 1345 | 1.0 | 0.20 |
| Fe BS-56G | N | 30 | 5885 | 88 | 16501 | 2804030 | --- | 19816 | 4273 | 11982 | 7.9 | 3.0 |
| Fe BS-56G | Ne | 79443 | 19717 | 138449 | 34362 | 1742761 | 3413 | 4 | 2 | 1 | 11 | 8.2 |
| Fe BS-56G | Kr | 29443 | 21351 | 210908 | 152943 | 7163332 | 15978 | 46 | 3360 | 469 | 546 | 105 |

- The $MG^{+}/M^{+}$ concentrations evaluated the behavior of the $MG^{+}$ species in each plasma gas
  - The $MG^{+}/G^{+}$ concentrations were not graphed, they were calculated to corroborate the $MG^{+}/M^{+}$ values

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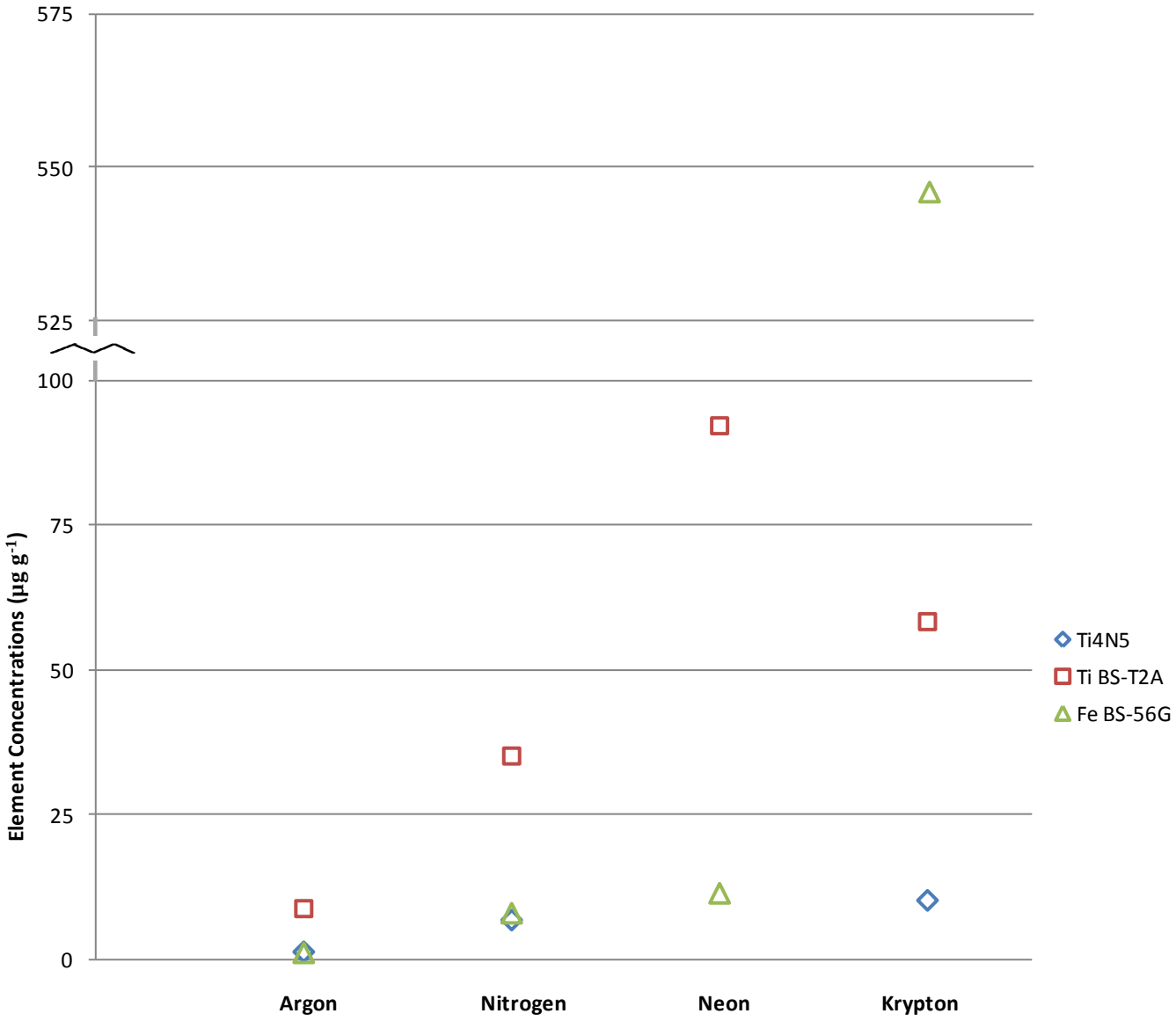
# Alternative Gas Study




- $O^+/ M^+$
- Historically from VG9000 data (Ti matrix), oxygen levels are ~10x greater than their argon counterparts
- Ti 4N5 – an elevated level of oxygen is seen with the krypton
- Ti BS-T2A – the elevated level of oxygen with krypton is more prominent, the neon value being an outlier
- Fe BS-56G – significantly elevated level of oxygen with krypton

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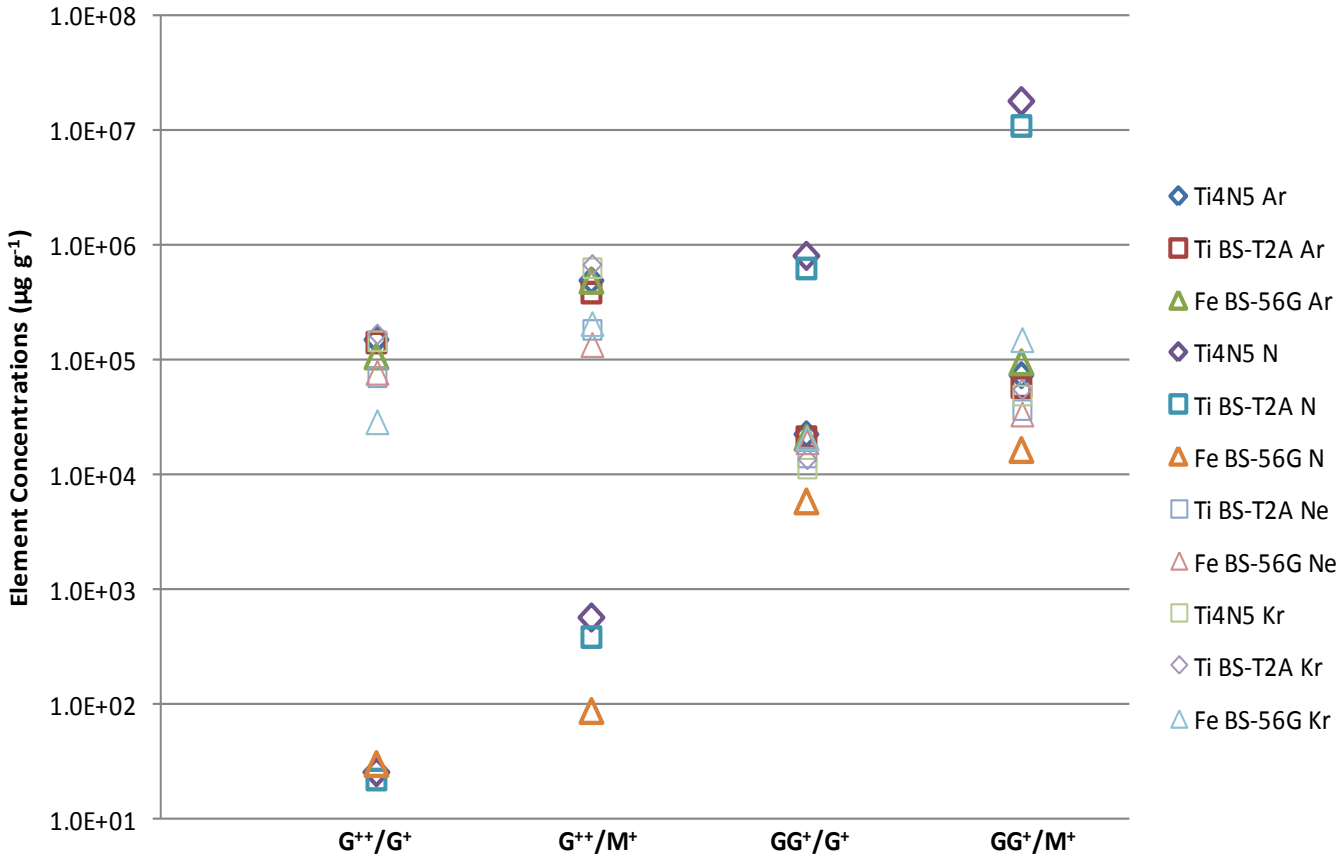
# Alternative Gas Study




- Concentrations normalized by $G^+$ are less than concentrations normalized by $M^+$ (Intensity: G > M)
- $G^{++}$ > $GG^+$ with the exception of values from nitrogen plasma gas

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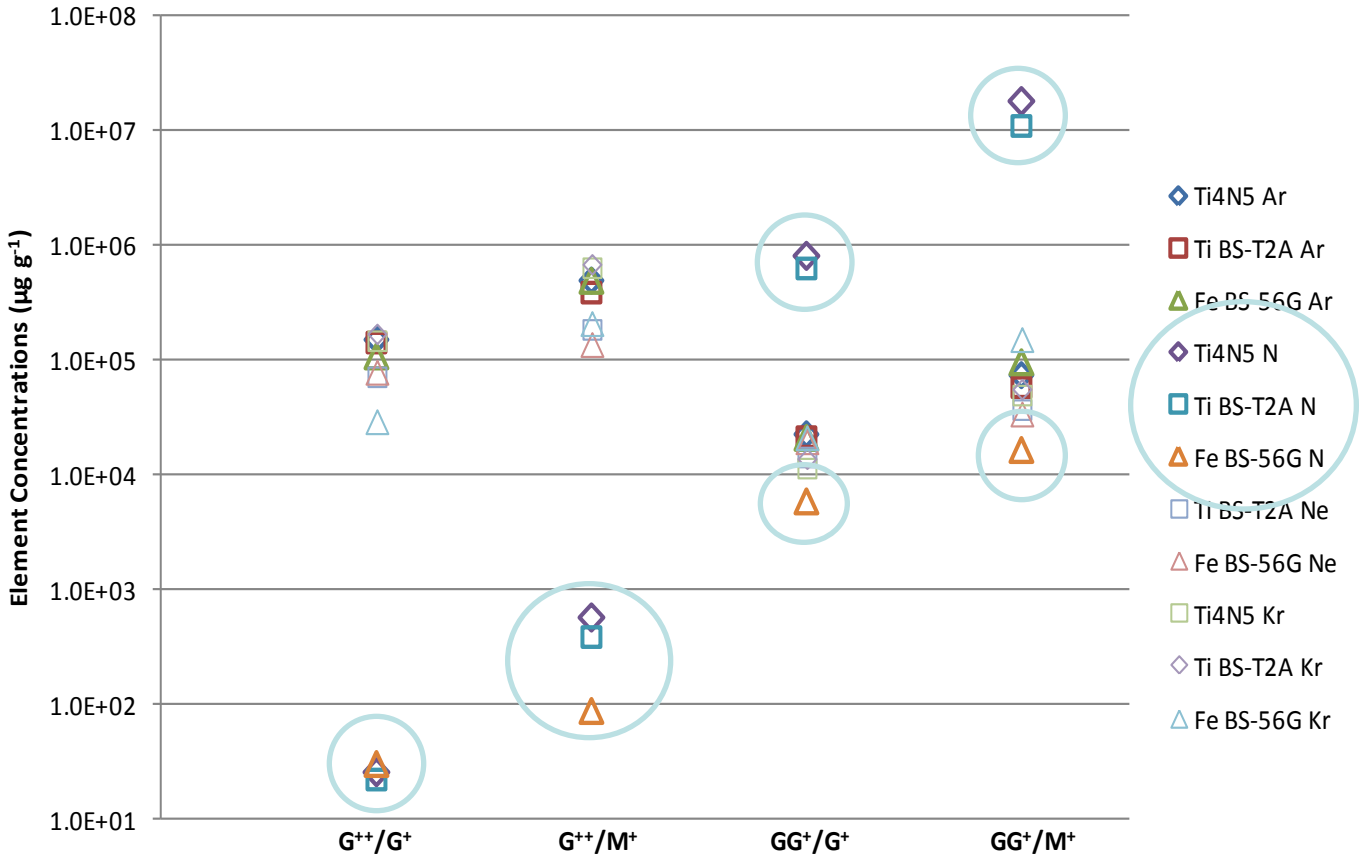
# Alternative Gas Study




- Concentrations normalized by $G^+$ are less than concentrations normalized by $M^+$
- Values from nitrogen plasma gas are not consistent with values from other plasma gases
  - Significantly less doubly ionized species (Ti and Fe matrices), more singly ionized dimer species (Ti matrix)

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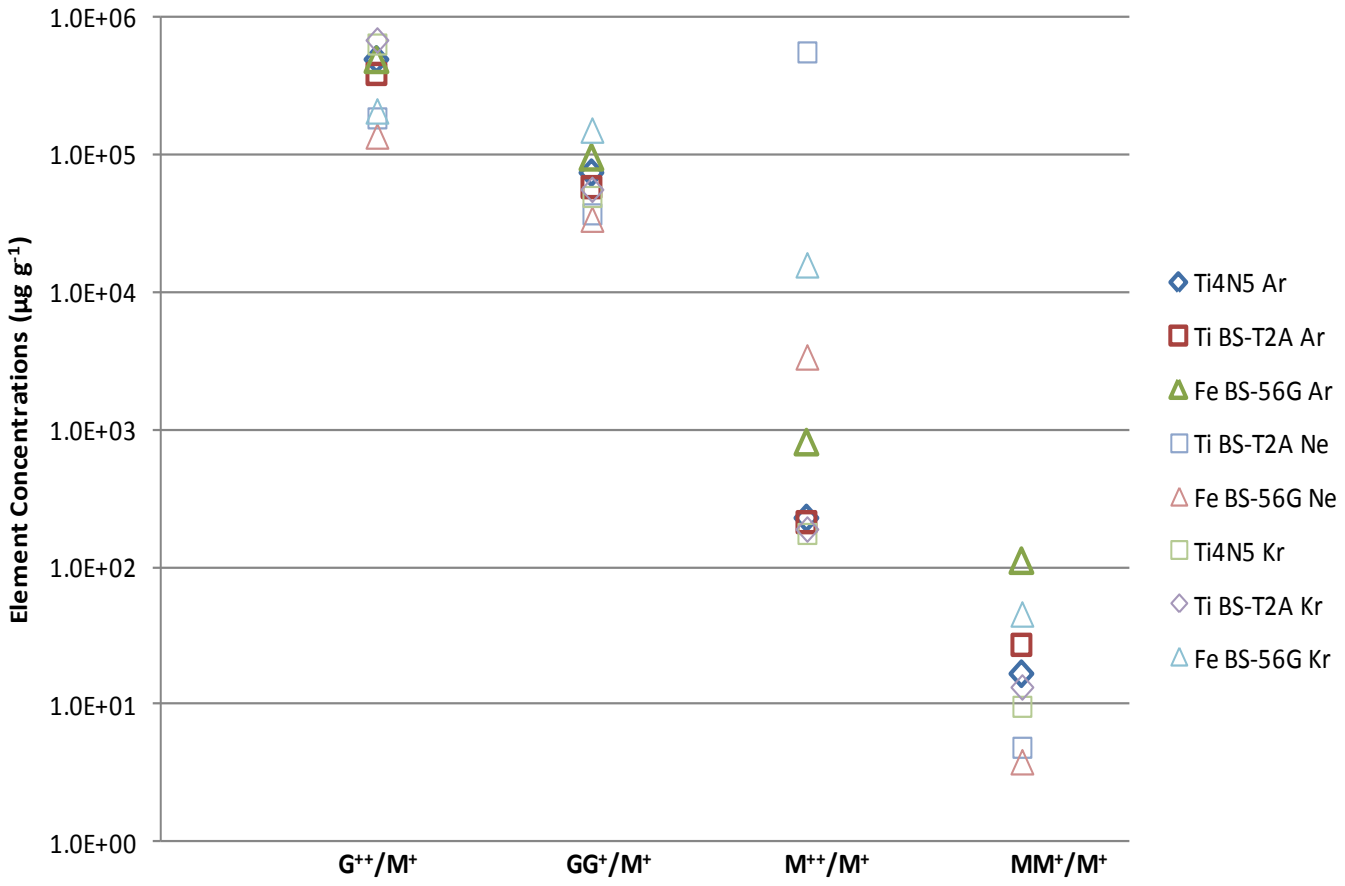
# Alternative Gas Study




- Concentrations from doubly ionized species are slightly greater than concentrations from singly ionized dimers
- Values from nitrogen do not fit this profile

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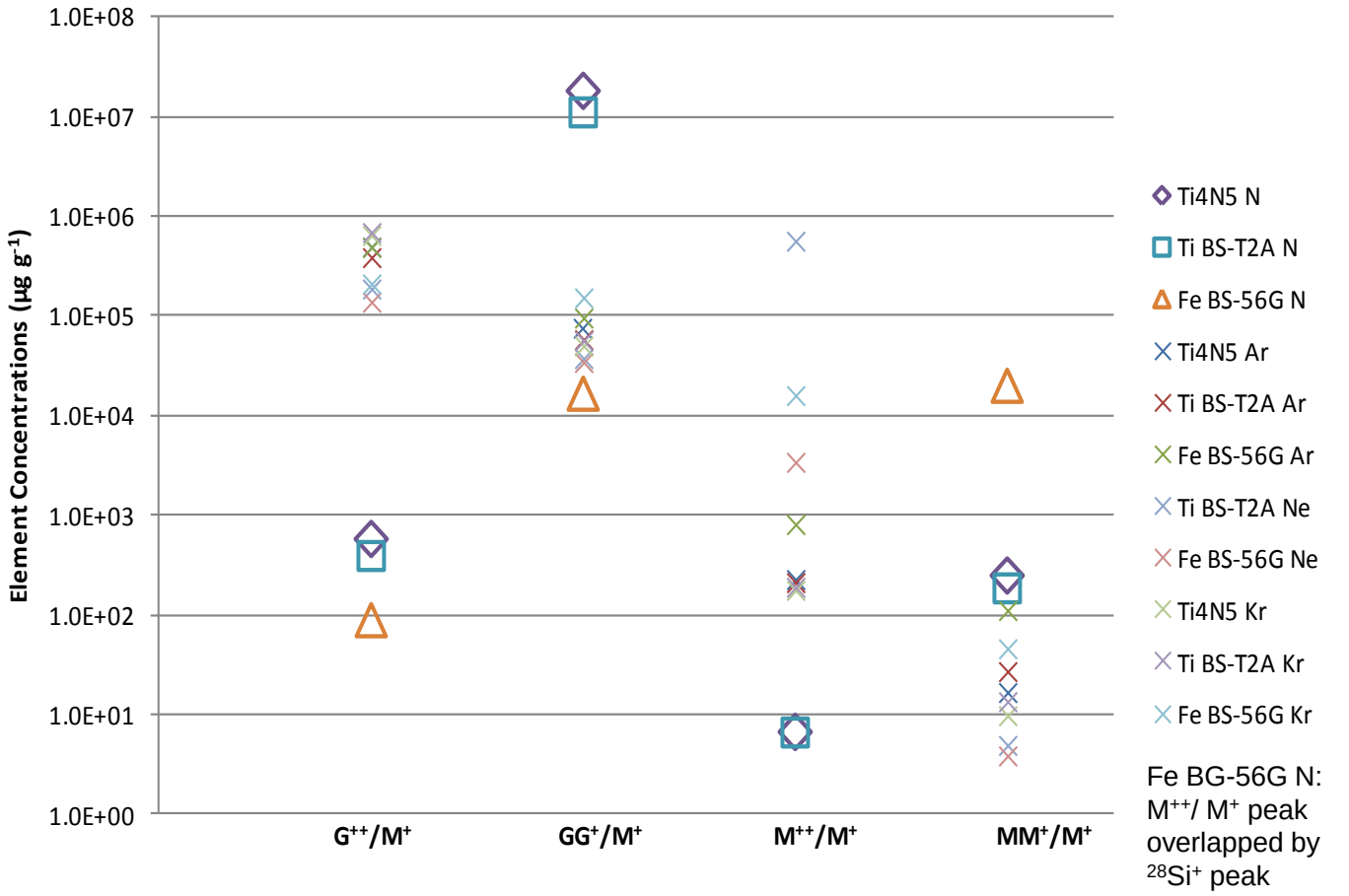
# Alternative Gas Study




- For the nitrogen data, concentrations from doubly ionized species are less than concentrations from singly ionized dimers
  - Increase in singly ionized dimers, significant decrease in doubly ionized species

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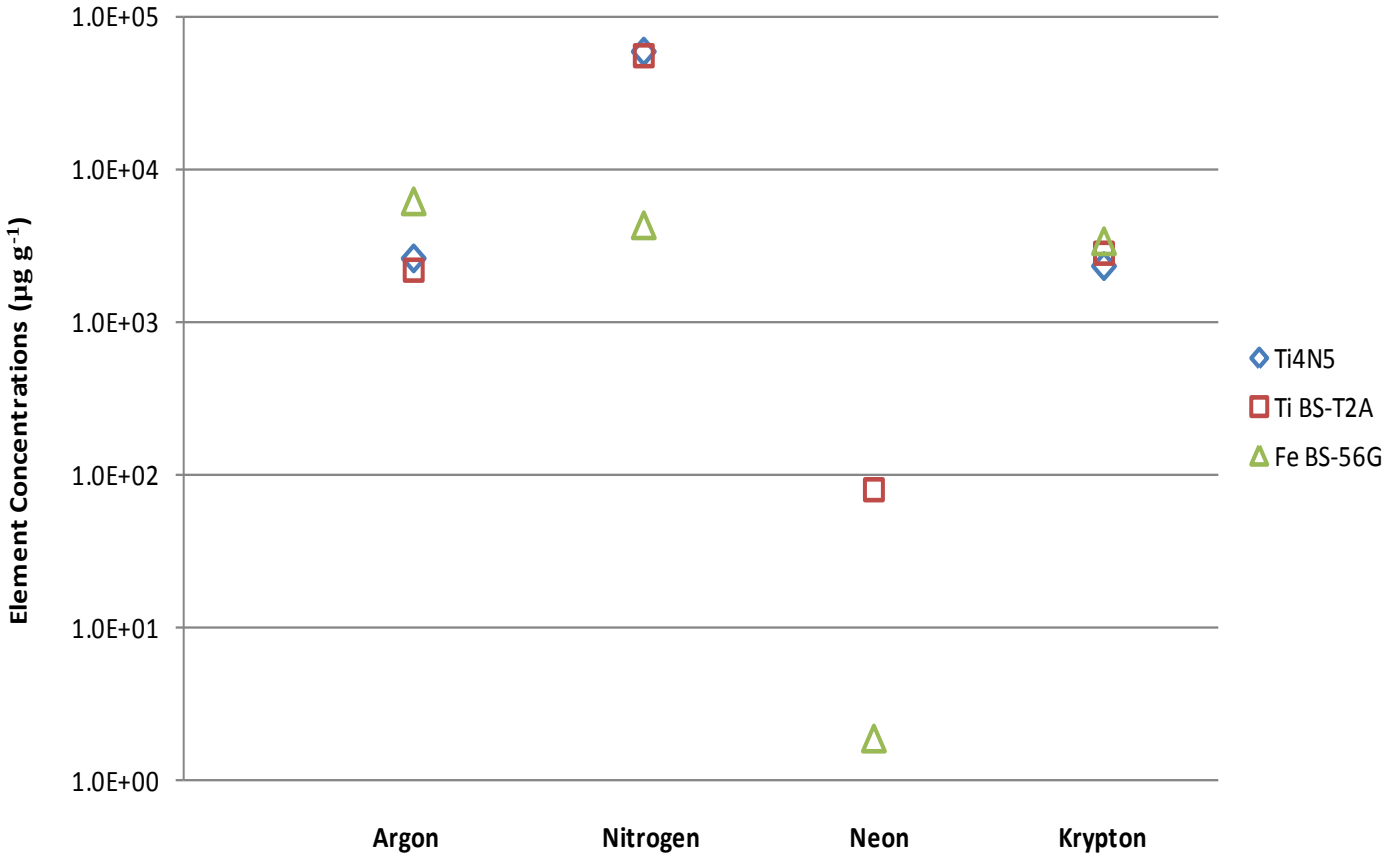
# Alternative Gas Study




- $MG^+/ M^+$
- In neon, the $MG^+/ M^+$ concentrations are less than in the other plasma gases

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# Conclusions

- $TiAr^{+}$, $TiAr^{++}$, and $TiArO^{+}$ interferences can be alleviated by using nitrogen, as well as krypton, as an alternative gas, allowing for suitable LOD's for calcium, scandium, strontium, yttrium, and rhodium and thus allowing for the approach of 4N5 purity
- Data from the titanium BS-2TA and 4N5 reproducibility material showed that the standard relative sensitivity factor (RSF) set used for VG9000 data is also applicable to data from the Astrum
- Data from analysis of titanium utilizing krypton as an alternative gas is both comparable and reproducible on the VG9000 and the Astrum
- From the titanium and iron analysis, oxygen levels detected utilizing krypton as a plasma gas are consistently higher than the oxygen levels detected using argon
- Data collected in nitrogen exhibited concentrations from doubly ionized species ($M^{++}/ M^{+}$ and $G^{++}/ M^{+}$) which were significantly less than the concentrations seen in the other plasma gases
- In neon, the $MG^{+}/M^{+}$ concentrations were less than those in the other plasma gases

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# Future Projects

- Analysis of another iron reference material for comparison
- Analysis of copper standards, acquiring both $^{63}Cu$ and $^{65}Cu$ as matrix isotopes to confirm similar results
- Analysis utilizing helium as an alternative gas
- Comparison of these results to GD-OES data

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# Acknowledgments

- Organizing Committee of the European Working Group on Glow Discharge Spectroscopy (EW-GDS)
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- Colleagues at Evans Analytical Group
  - Karol Putyera, Glyn Churchill, Darya Dunn, David Schumm


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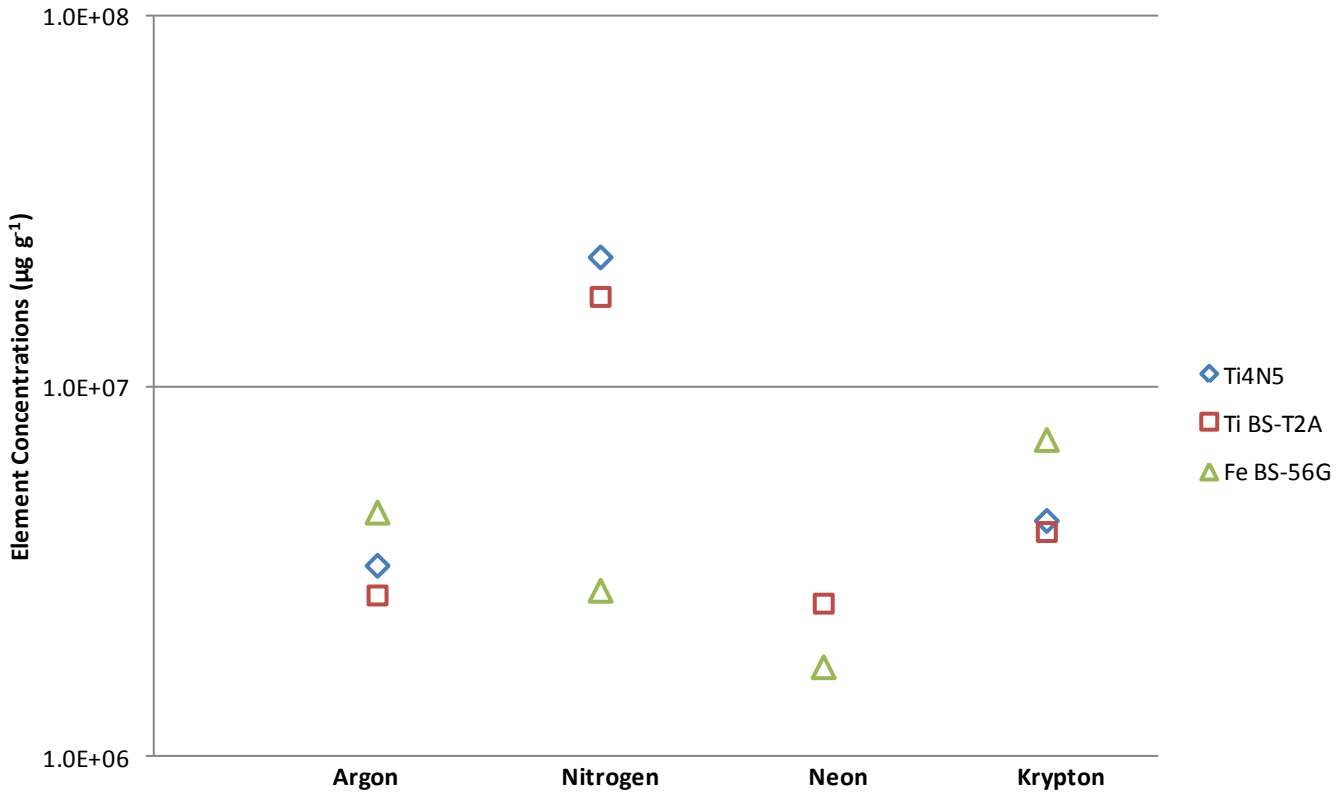
# Alternative Gas Study




- $G^+/ M^+$
- All gases have similar intensities
- Concentrations are mostly clustered together with the exception of titanium in nitrogen

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# Ionization Energies

| First Ionization Energy (eV) | | Second Ionization Energy (eV) | |
|---|---|---|---|
| Ti | 6.8281 | Ti | 13.5755 |
| Fe | 7.9024 | Fe | 16.1878 |
| O | 13.61806 | Kr | 24.35985 |
| Kr | 13.9996 | Ar | 27.62967 |
| N | 14.53414 | N | 29.6013 |
| Ar | 15.75962 | O | 35.1173 |
| Ne | 21.5646 | Ne | 40.96328 |

Lide, D.R. (Ed.). (2003). *CRC Handbook of Chemistry and Physics, 84th Edition*. Section 10 Atomic, Molecular, and Optical Physics: Ionization Potentials of Atoms and Atomic Ions. CRC Press: Boca Raton, Florida.
Bogaerts , A. and Gijbels, R. (1999). New developments and applications in GDMS. *Fresenius J .Anal. Chem*., 364 , 367–375.

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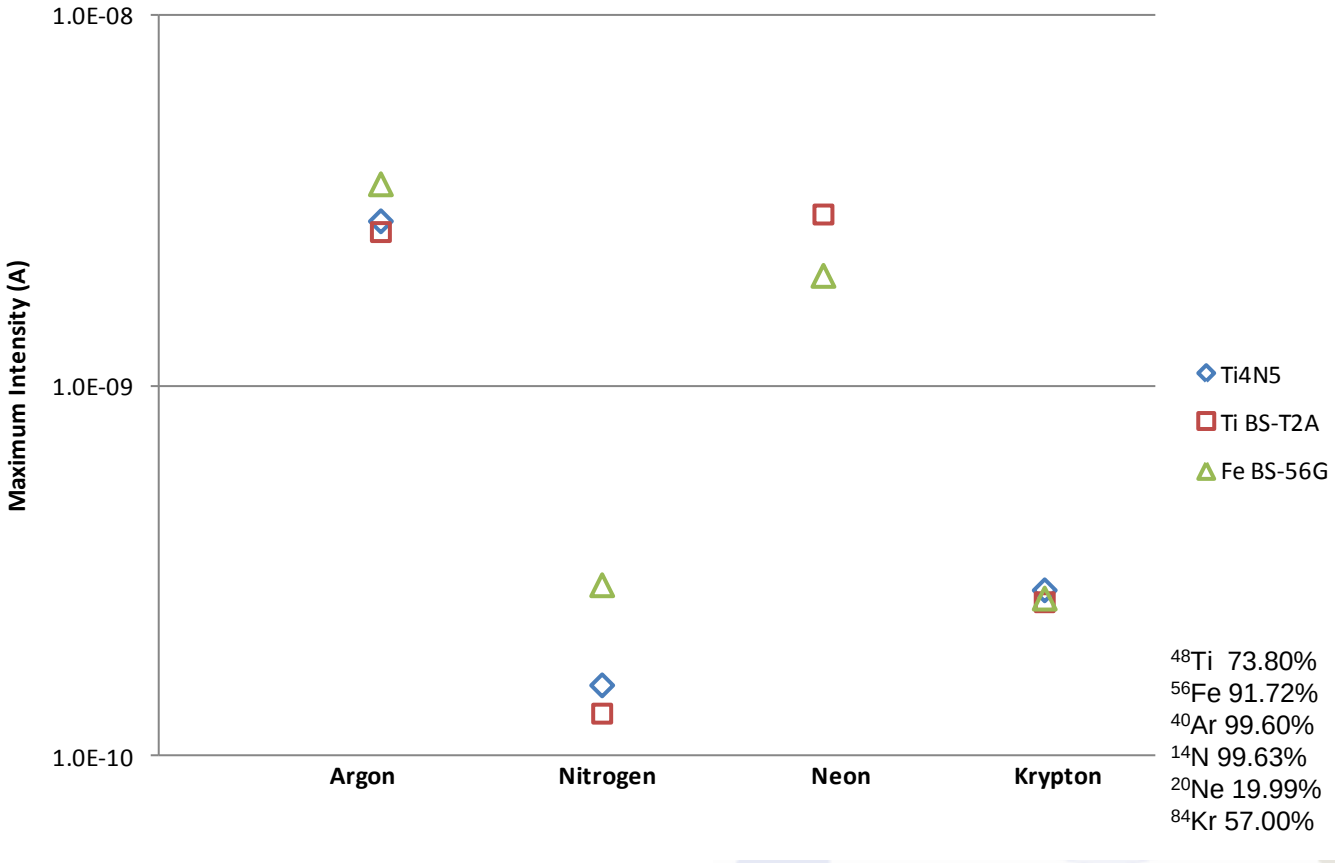
# Plasma Gas Intensity




- Plasma gas intensity with titanium and iron cathodes
  - Argon > Neon >> Krypton ≥ Nitrogen

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# Ionization

- Electron impact ionization and excitation

$$Ar^0 + e^- \rightarrow Ar^+ + 2e^-$$

$$Ar^0 + e^- \rightarrow Ar^* + e^-$$

- Penning ionization

$$M^0 + Ar^*_m \rightarrow M^+ + Ar^0 + e^-$$

- Asymmetric charge transfer

$$M^0 + Ar^+ \rightarrow (M^+)^* + Ar^0$$

Bogaerts , A. and Gijbels, R. (2001). Modeling of a microsecond pulsed glow discharge: behavior of the argon excited levels and of the sputtered copper atoms and ions. *JAAS*, 16, 239–249.
Bogaerts , A.. (2001). *Mathematical modeling of a direct current glow discharge in argon* .

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