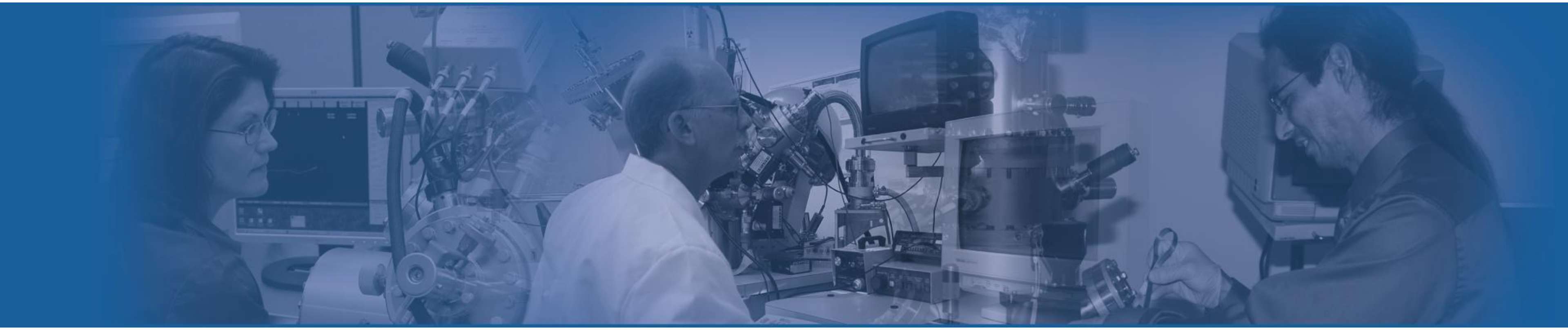

The Evaluation and Characterization of Alternative Gases using Iron and Titanium Reference Materials

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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

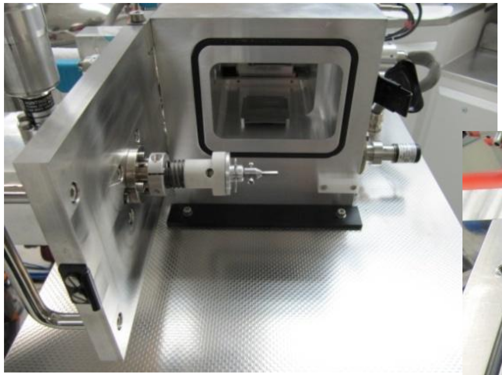

The Astrum from Nu Instruments

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.

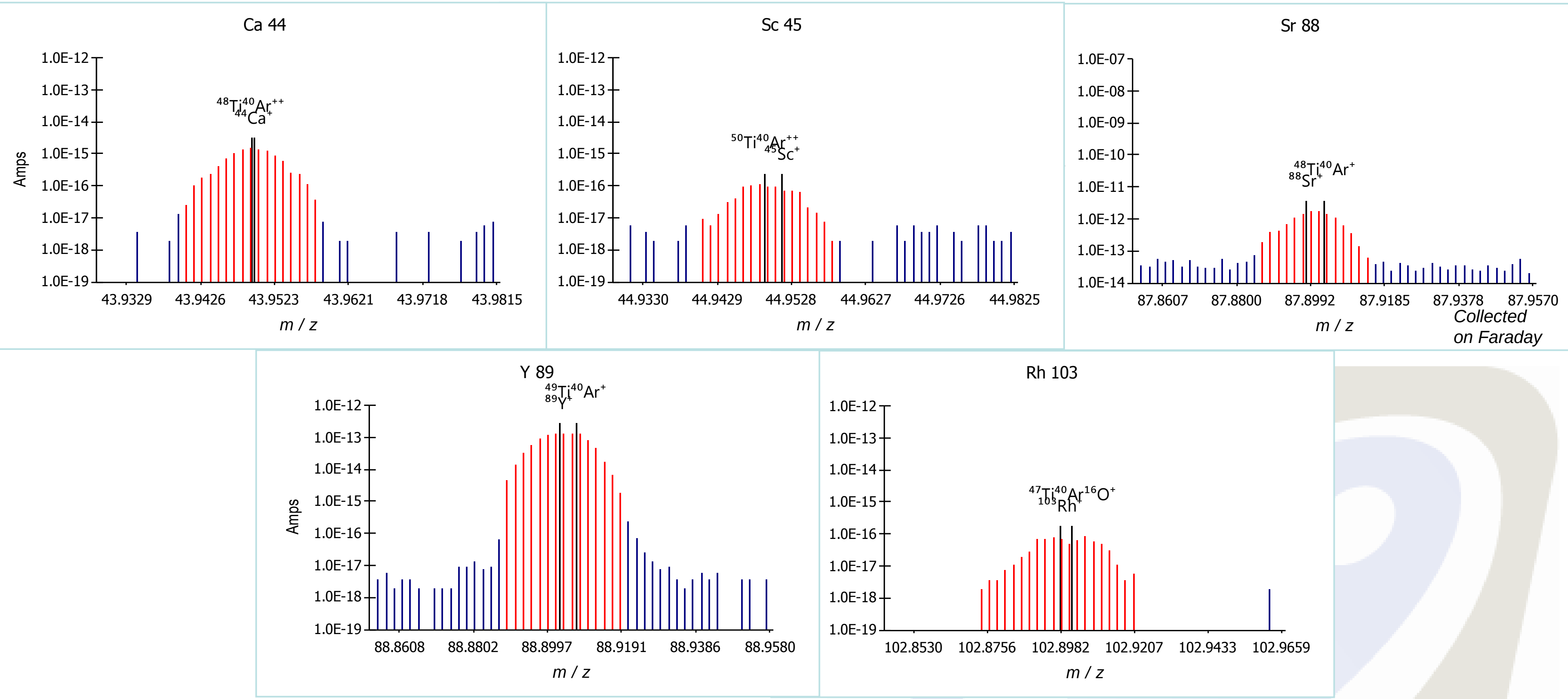
Experimental Setup



- 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

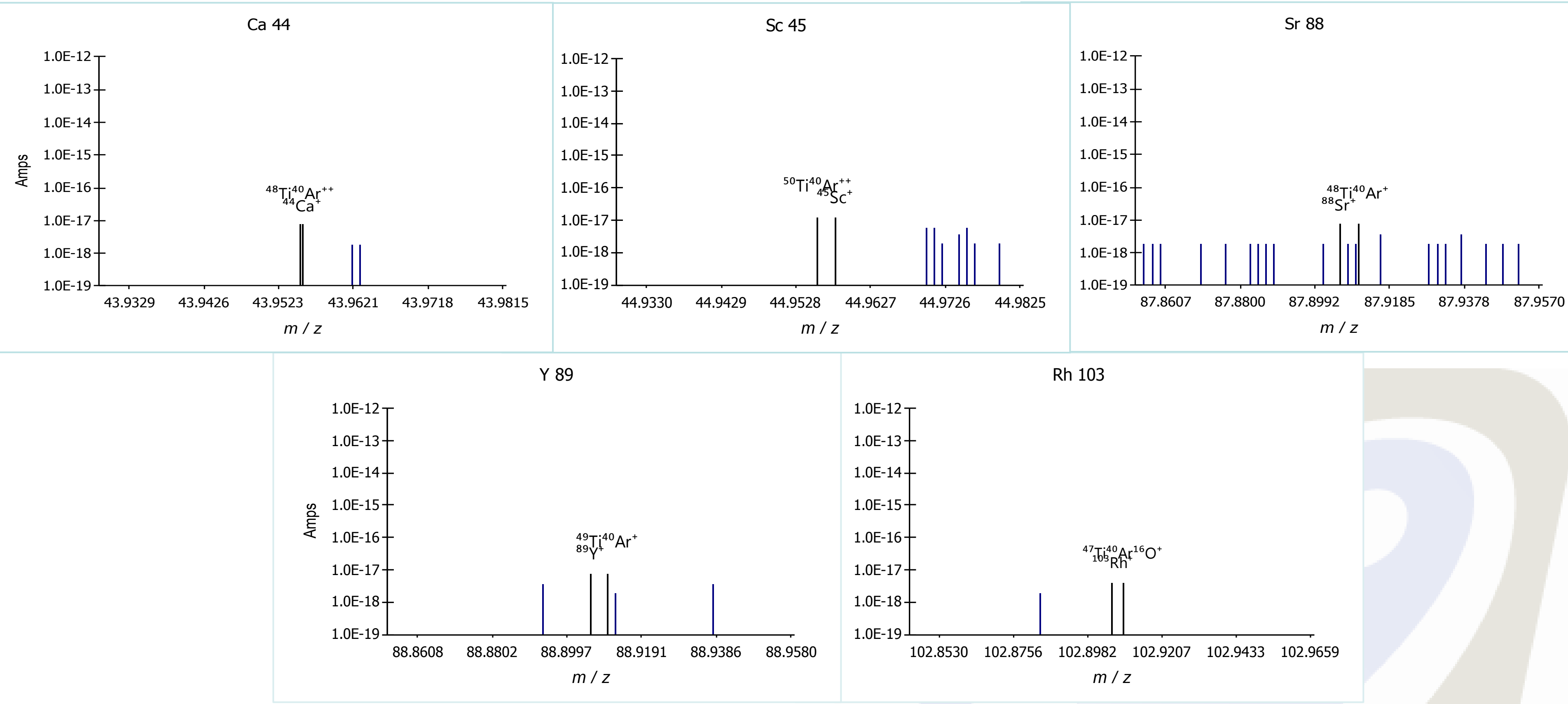
Gas Correction Factors for Thermal-based Mass Flow Controllers. MKS Instruments, 2009, 1–6.

Titanium BS-T2A in Argon



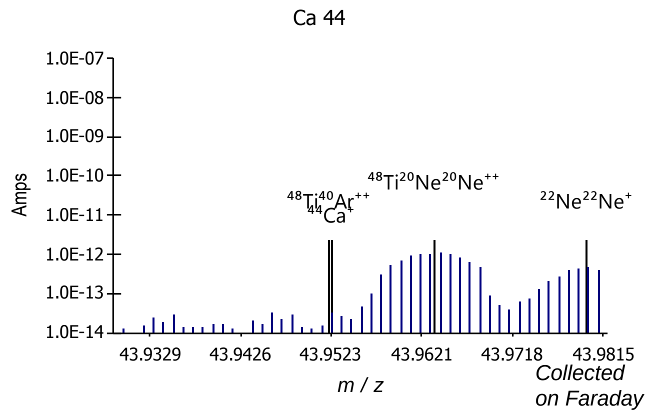
- TiAr^{+}, TiAr^{++}, and TiArO^{+} interferences are superimposed on the isotopic peaks of interest
  - Peaks are unresolvable at 4000 (M/ΔM = RP5% valley definition)
  - Unable to approach certification of 4N5 purity

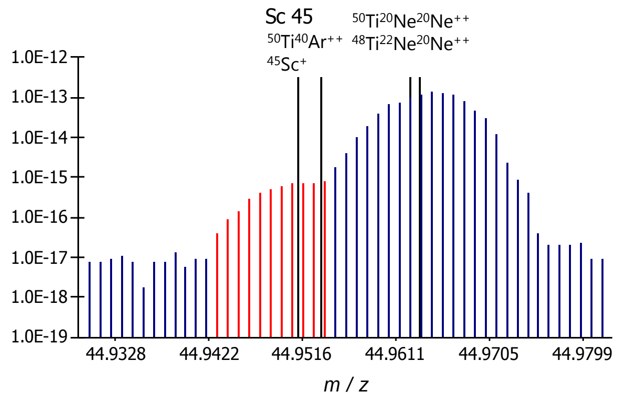
Titanium BS-T2A in Krypton

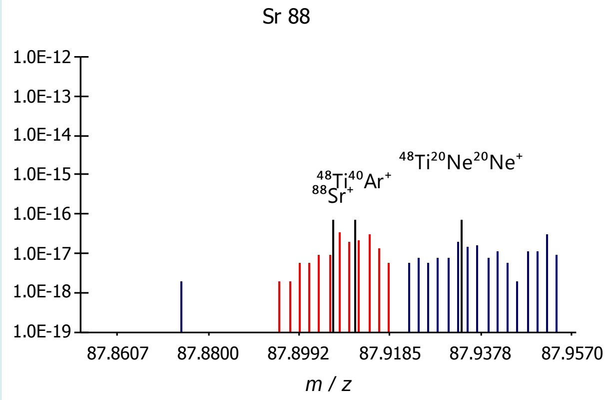


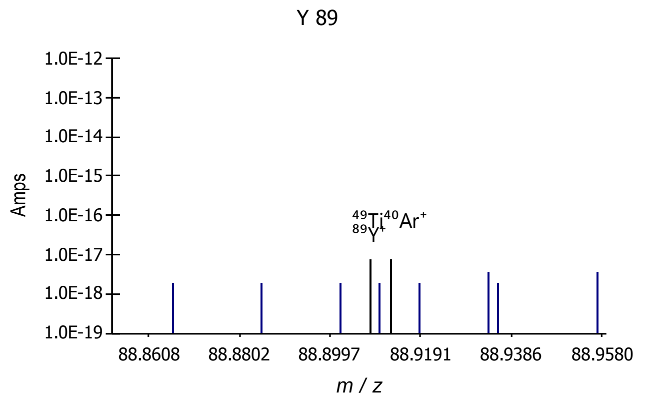
- $TiAr^{+}$, $TiAr^{++}$, and $TiArO^{+}$ interferences are alleviated by using krypton as an alternative gas
  - Detection limits for calcium, scandium, strontium, yttrium, and rhodium are now achievable
  - Allows for approach of 4N5 purity

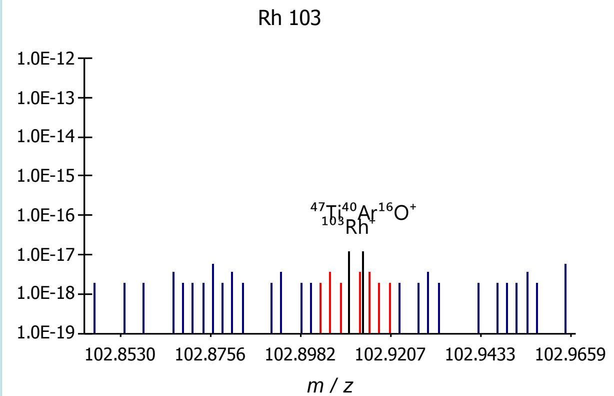
Titanium BS-T2A in Neon





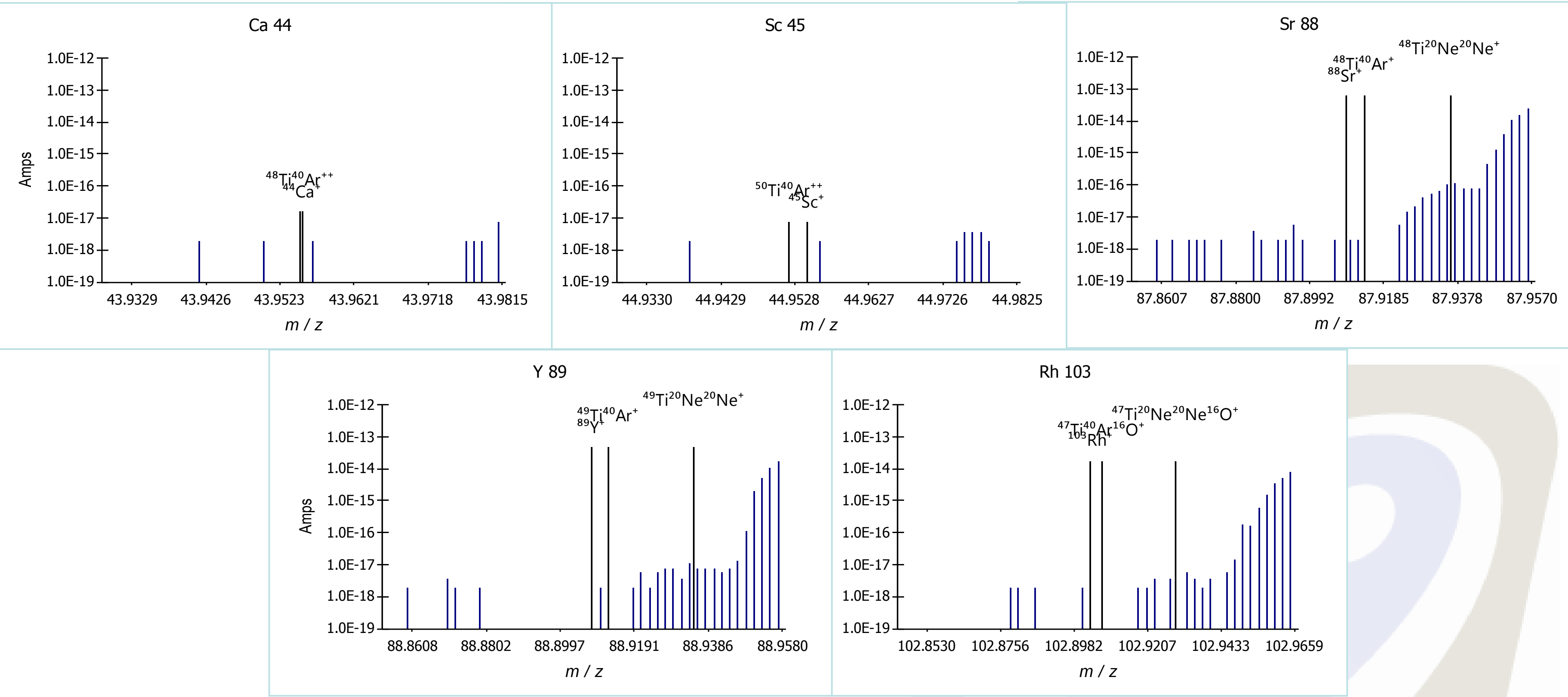






- Interferences from neon are superimposed on the calcium and scandium peaks
  - These peaks of interest are unresolvable in neon
  - Unable to approach certification of 4N5 purity

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

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

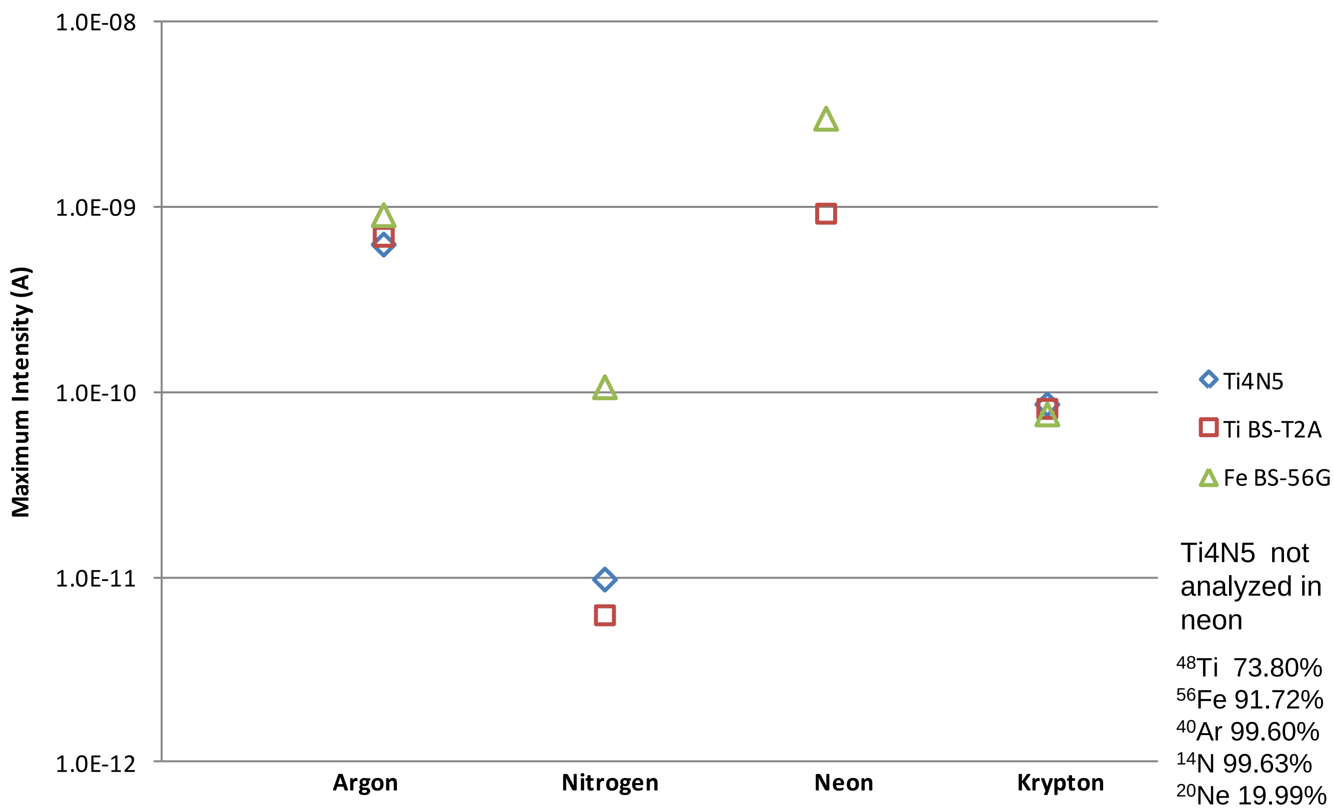
Vieth, W. and Huneke, J.C. (1991). Relative sensitivity factors in glow discharge mass spectrometry. *Spectrochimica Acta*, *46B*(2), 137–153.

EAG 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*

Alternative Gas Study

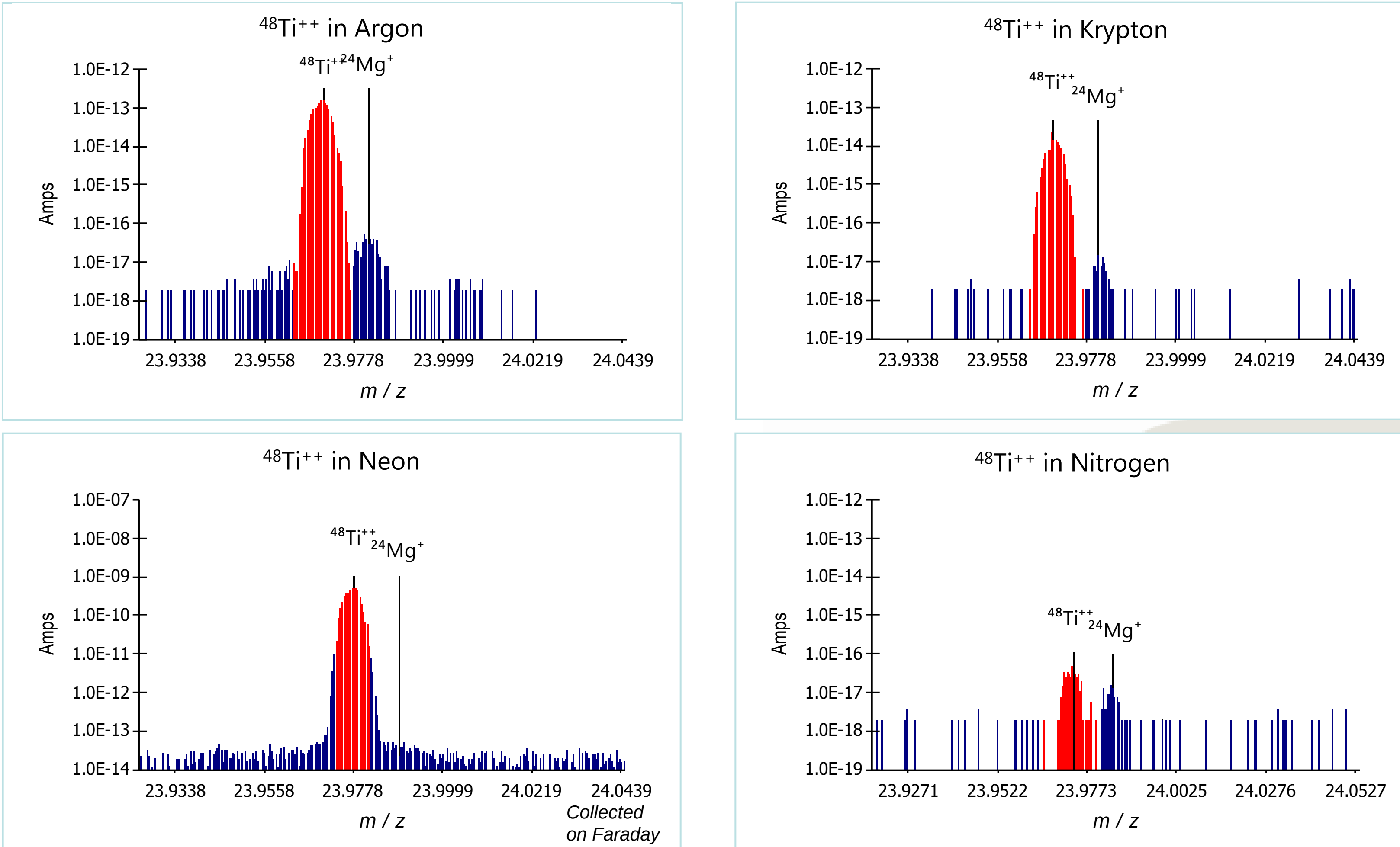


Ti4N5 not analyzed in neon

^{48}Ti 73.80%
^{56}Fe 91.72%
^{40}Ar 99.60%
^{14}N 99.63%
^{20}Ne 19.99%
^{84}Kr 57.00%

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

Alternative Gas Study



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

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

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

- 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

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^{+}
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Ti4N5	Ne	-	-	-	-	-	-	-	-	-	-	-
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- 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

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^{+}
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Ti4N5	Ne	-	-	-	-	-	-	-	-	-	-	-
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- The G^{+}/M^{+} concentrations investigated the intensities of the different plasma gases with each matrix
  - Concentrations were not graphed as the results were similar

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^{+}
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- 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

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^{+}
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- 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

Alternative Gas Study

Sample	Gas	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^{+}
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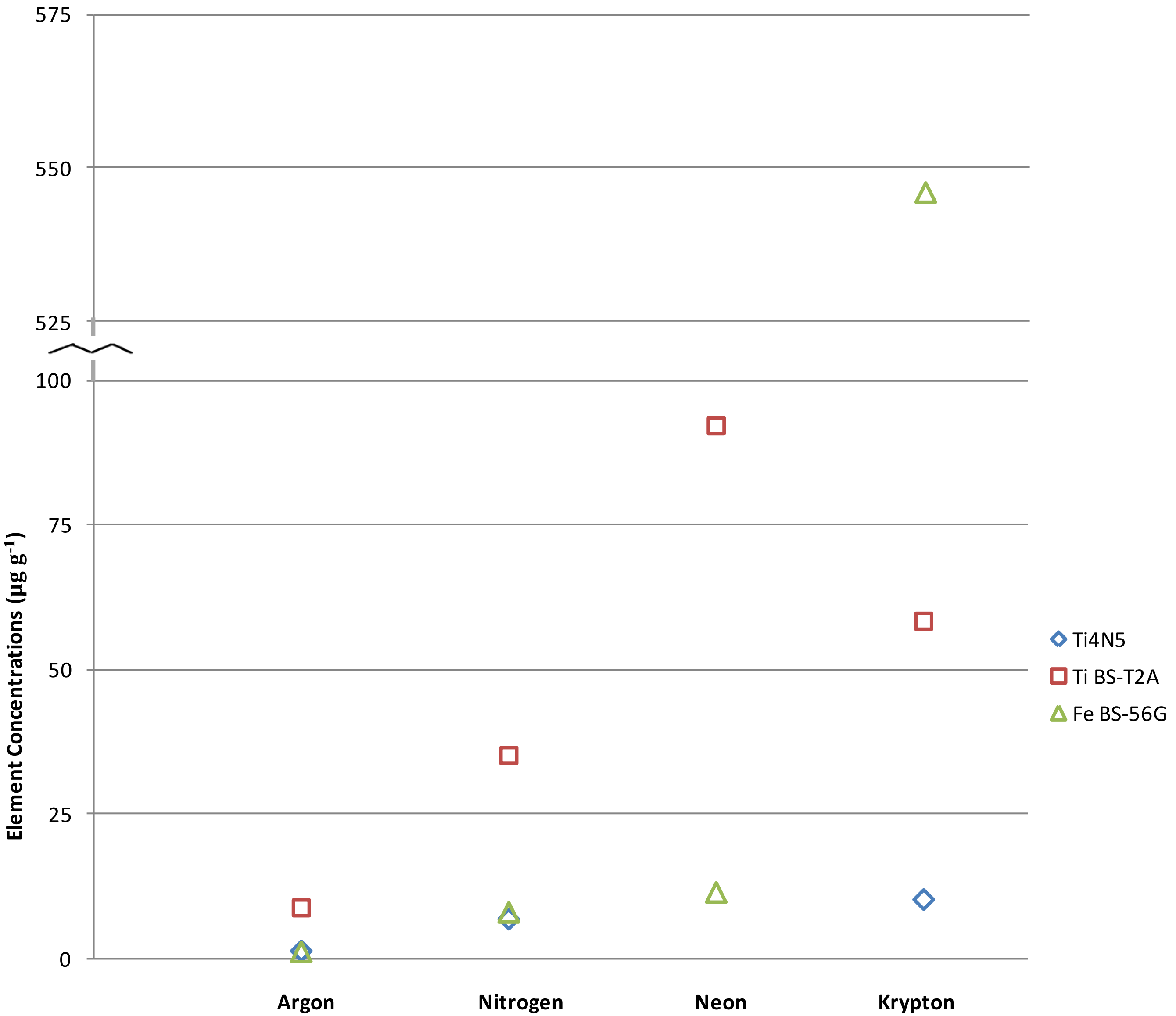
Fe BS-56G	Kr	29443	21351	210908	152943	7163332	15978	46	3360	469	546	105

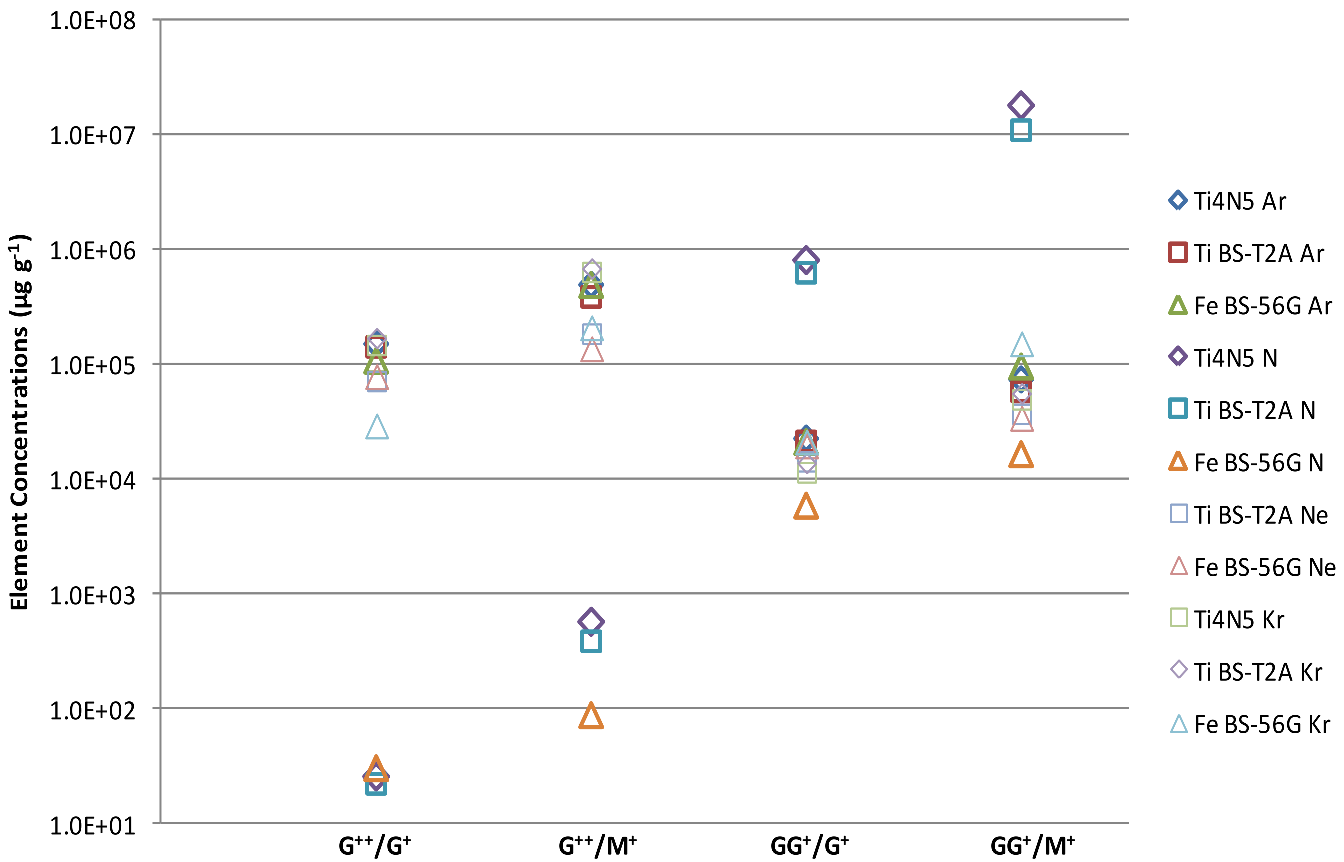
- The MG^{+}/M^{+} concentrations evaluated the behavior of the MG^{+} species in each plasma gas
  - The MG^{+}/G^{+} concentrations were not graphed, they were calculated to corroborate the MG^{+}/M^{+} values

Alternative Gas Study



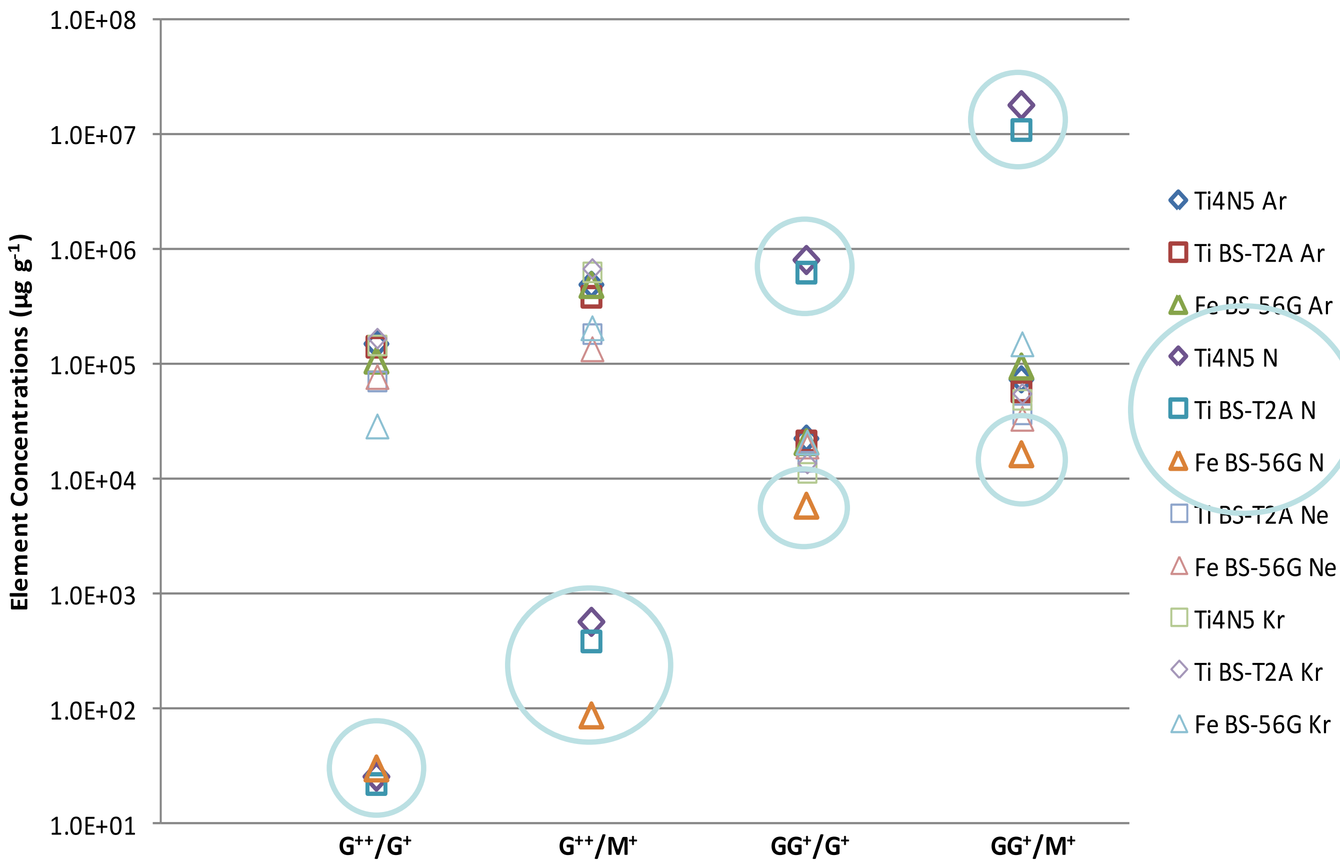
- O^+/M^+
- Historically from VG9000 data (Ti matrix), oxygen levels are ~10x greater than their argon counterparts
- Ti 4N5 – an elevated level of oxygen is seen with the krypton
- Ti BS-T2A – the elevated level of oxygen with krypton is more prominent, the neon value being an outlier
- Fe BS-56G –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

Alternative Gas Study



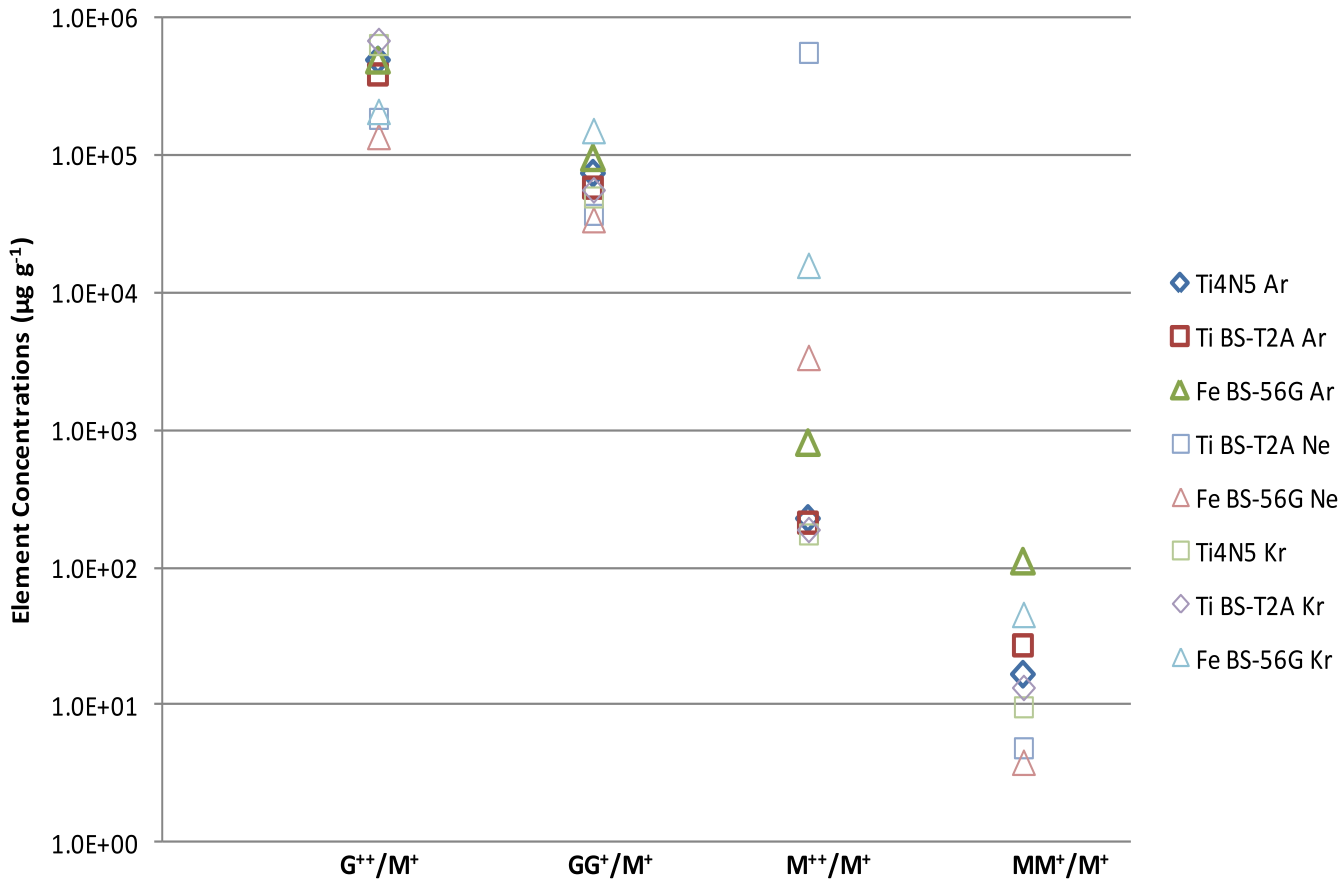
- Concentrations normalized by G^+ are less than concentrations normalized by M^+ (Intensity: G > M)
- $G^{++} > GG^+$ with the exception of values from nitrogen plasma gas

Alternative Gas Study



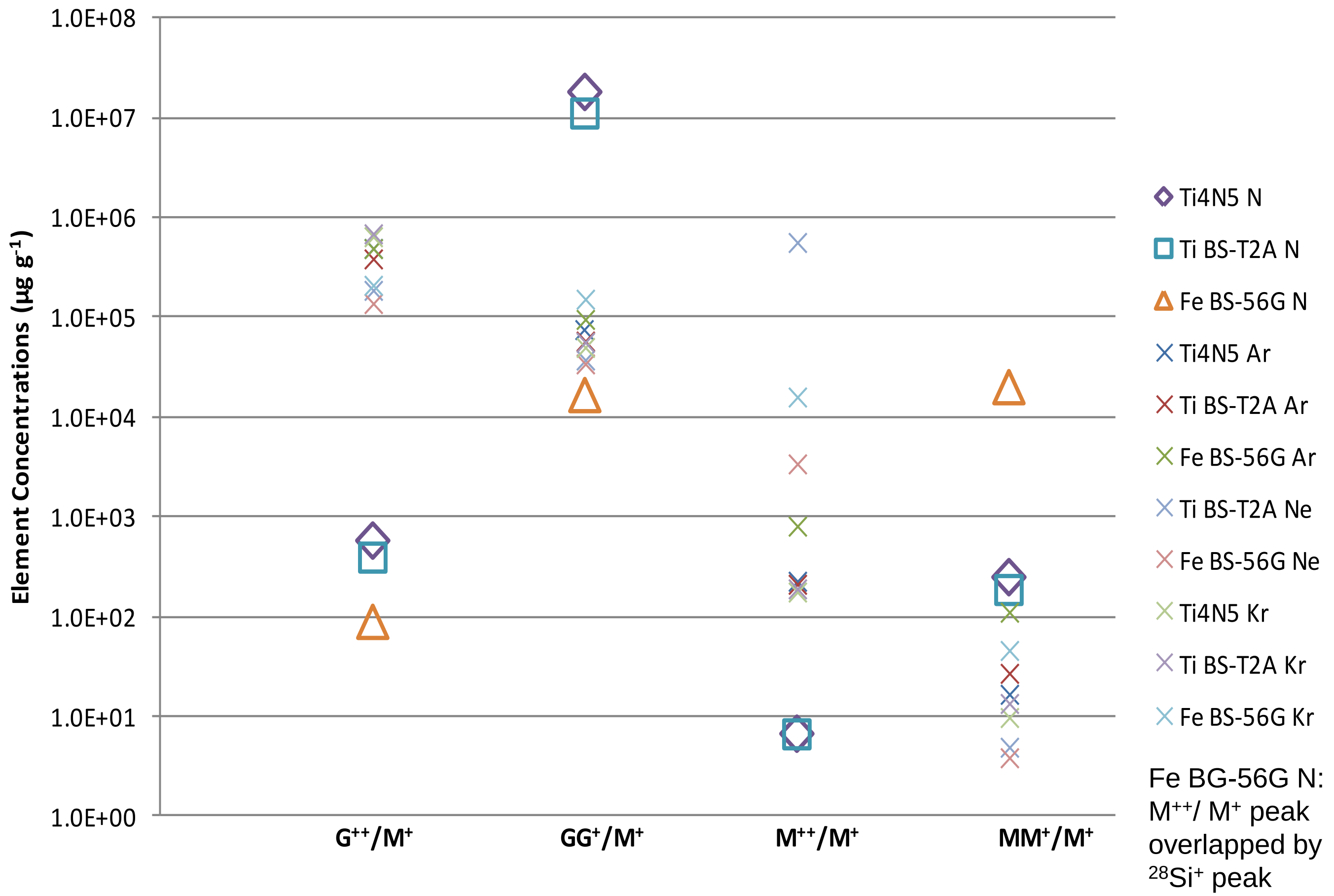
- Concentrations normalized by G^+ are less than concentrations normalized by M^+
- Values from nitrogen plasma gas are not consistent with values from other plasma gases
  - Significantly less doubly ionized species (Ti and Fe matrices), more singly ionized dimer species (Ti matrix)

Alternative Gas Study



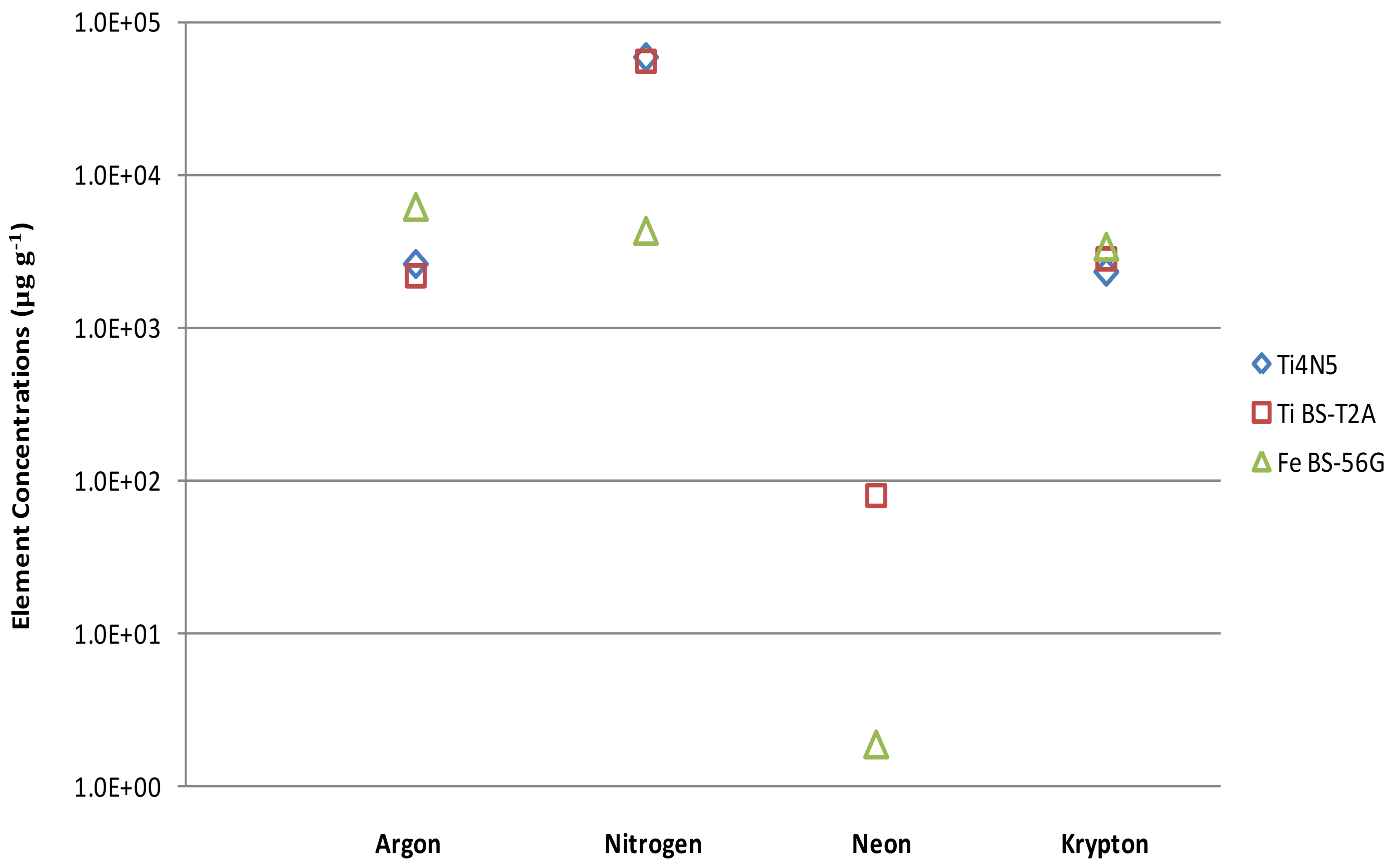
- Concentrations from doubly ionized species are slightly greater than concentrations from singly ionized dimers
- Values from nitrogen do not fit this profile

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

Alternative Gas Study



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

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

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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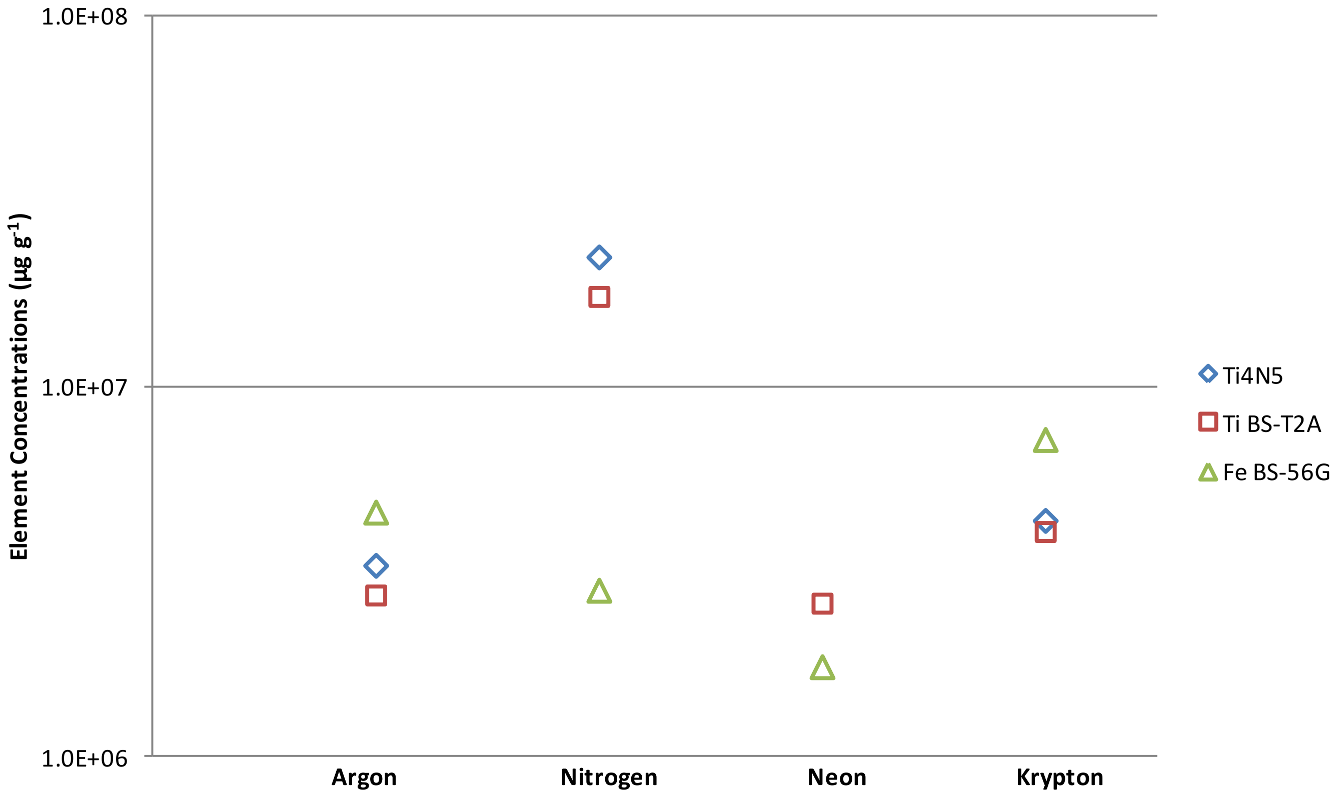
Alternative Gas Study



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

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

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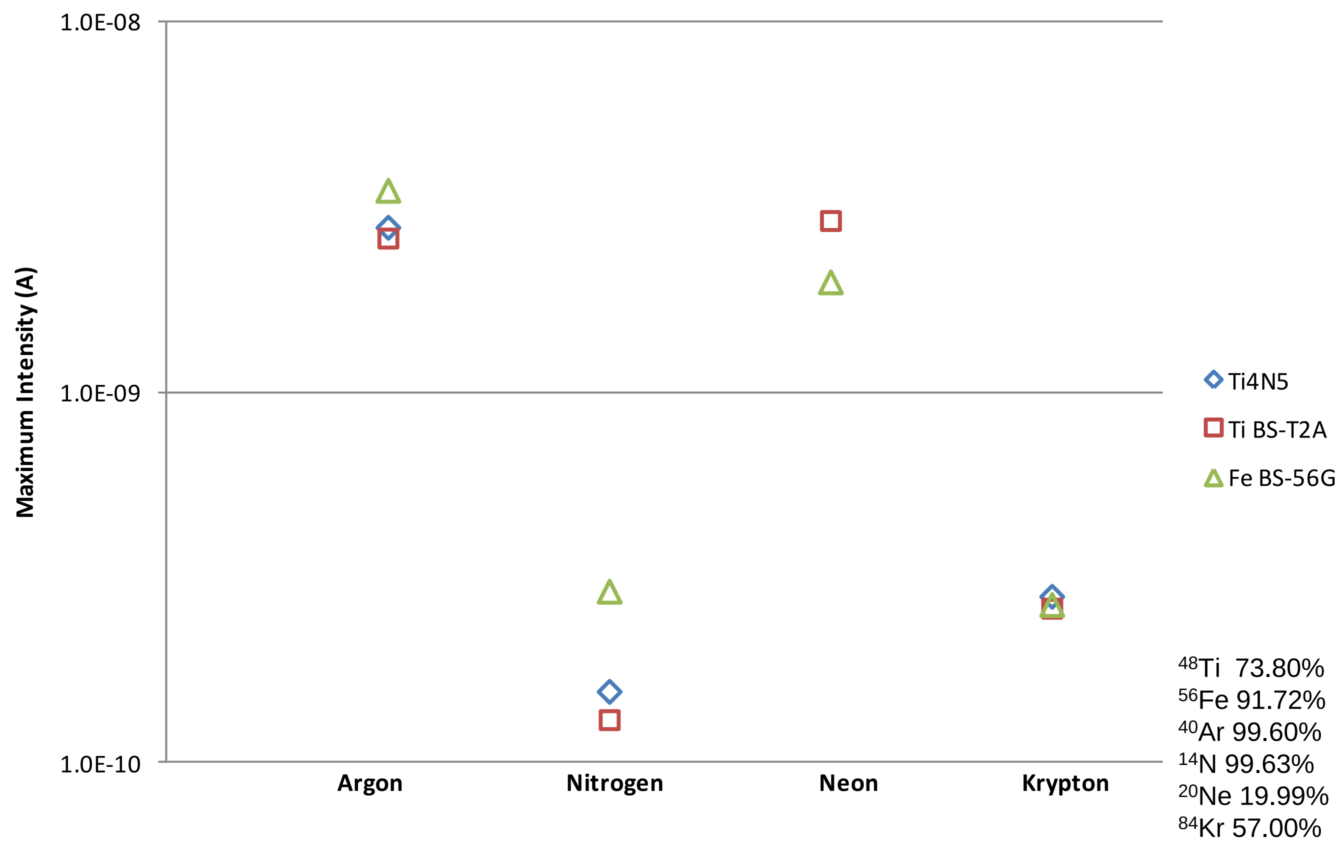
Plasma Gas Intensity



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

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

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

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