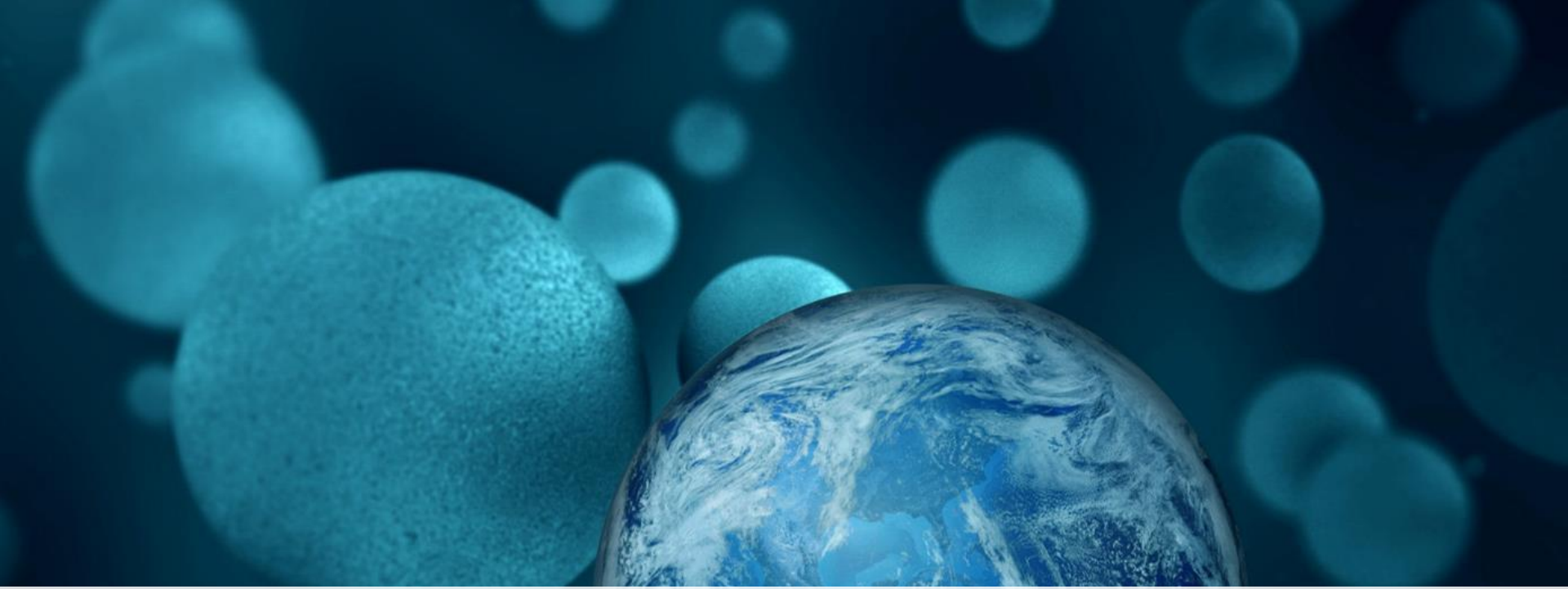

Gallium Analysis Using µs-Pulsed Fast Flow Glow Discharge Mass Spectrometry

GDS Anwendertreffen Freiberg, Germany. 26. – 27. September 2019
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Problem statement: Gallium Kit development

Goal:
Analysis of 6N+ high purity Gallium on the Element GD Plus

Problem:
Gallium has a melting point of 29.8 ºC. During discharge/analysis, the sample heats up and may melt on fast flow GD-MS.

Current Situation:
Element GD Plus can cool to -25 ºC and run gallium: need higher signal, better cooling and sophisticated sample prep for best performance.

What we need:
- Stronger cooling by electronics, hardware and software modifications; clean samples and sample prep knowledge.
- Implement a dedicated workflow solution for sophisticated Gallium analysis

Why now?
Thin-film solar cells: Increased demand as QC control tool for incoming goods

Problem statement: Previous work

DC mode: Ga analysis not possible without melting. Similar behavior as Aluminum: extra high discharge current to obtain full ion signal in the MS
Expected 60mA/800V = 50W; not possible with current cooling capacity

Pulsed mode: early trials on 2011 WPC successful
Much lower plasma power 1kV/5mA = 5W
Cooling default to ~-20 to -25ºC gets close to maximum signal

Current development: cooling to -35ºC in pulsed mode enables full sensitivity Ga analysis for the Fast Flow GD source
1 x 10^{10} cps Medium Resolution (1.6 nA) sensitivity for both matrix isotopes
Sufficient for sub ppb detection power

Problem statement: Previous work

Historical data: 2011 WPC

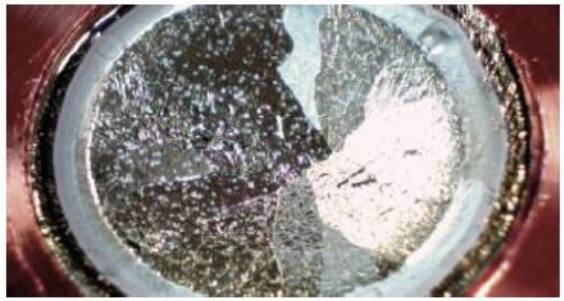
FIGURE 4. Results for a) Gallium and b) Tellurium. All mass fractions are in ppbw units using the Standard RSF set. For Ga, a second sample with high levels of impurities was available. The background picture shows the actual Ga sputter crater.

a)

Element	Isot.	Resol.	NRCC Values	Gallium sample #1
B	11	MR	< 2	2
Sc	45	MR	< 0.6	0.2
Fe	56	MR	2	2
Co	59	MR	< 0.3	0.2
Zn	66	MR	< 3	2.7
Ge	72	HR	< 20	14
Ag	107	HR	< 65	9
Cd	114	MR	3	3
In	115	MR	110	117
Sn	117	MR	< 2	1.6
La	139	MR	< 0.2	0.1
Ce	140	MR	< 20	0.1
Pb	208	MR	1	0.6
U	238	MR	< 0.1	0.05
				sample #2
Cu	63	MR	15,000	18,000
Zn	66	MR	110,000	100,000

b)

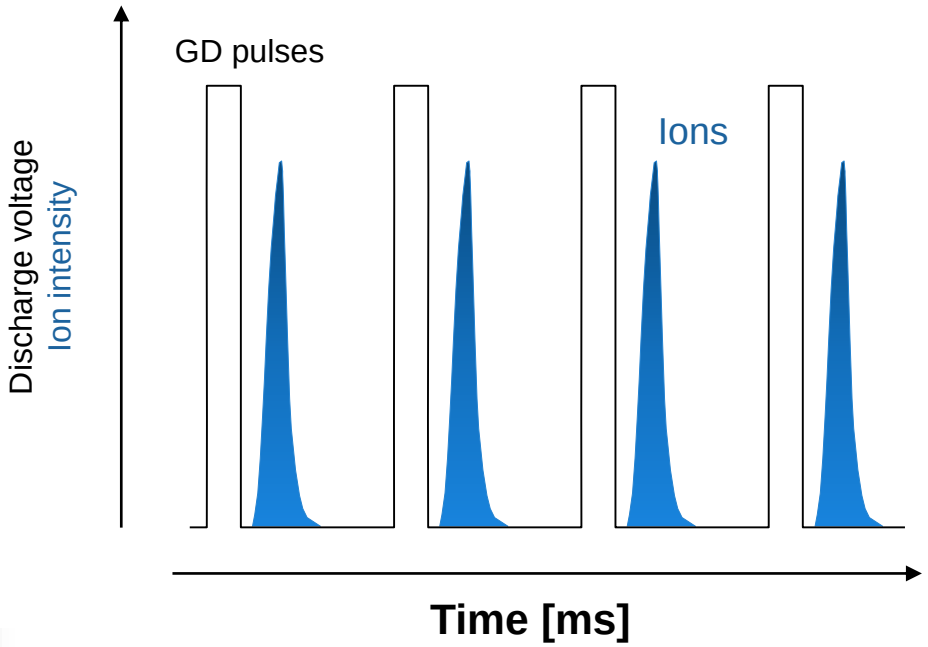
Element	Isot.	Resol.	Tellurium sample
Ti	48	MR	0.3
V	51	MR	0.2
Cr	52	MR	0.9
Mn	55	MR	0.9
Fe	56	MR	2
Co	59	MR	0.6
Ni	58	MR	1.6
Cu	63	MR	13
Zn	66	MR	5



Acknowledgement: The authors thank Brad Methven (National Research Council Canada (NRCC), Ottawa, Canada) for supplying the Gallium samples and experimental values.

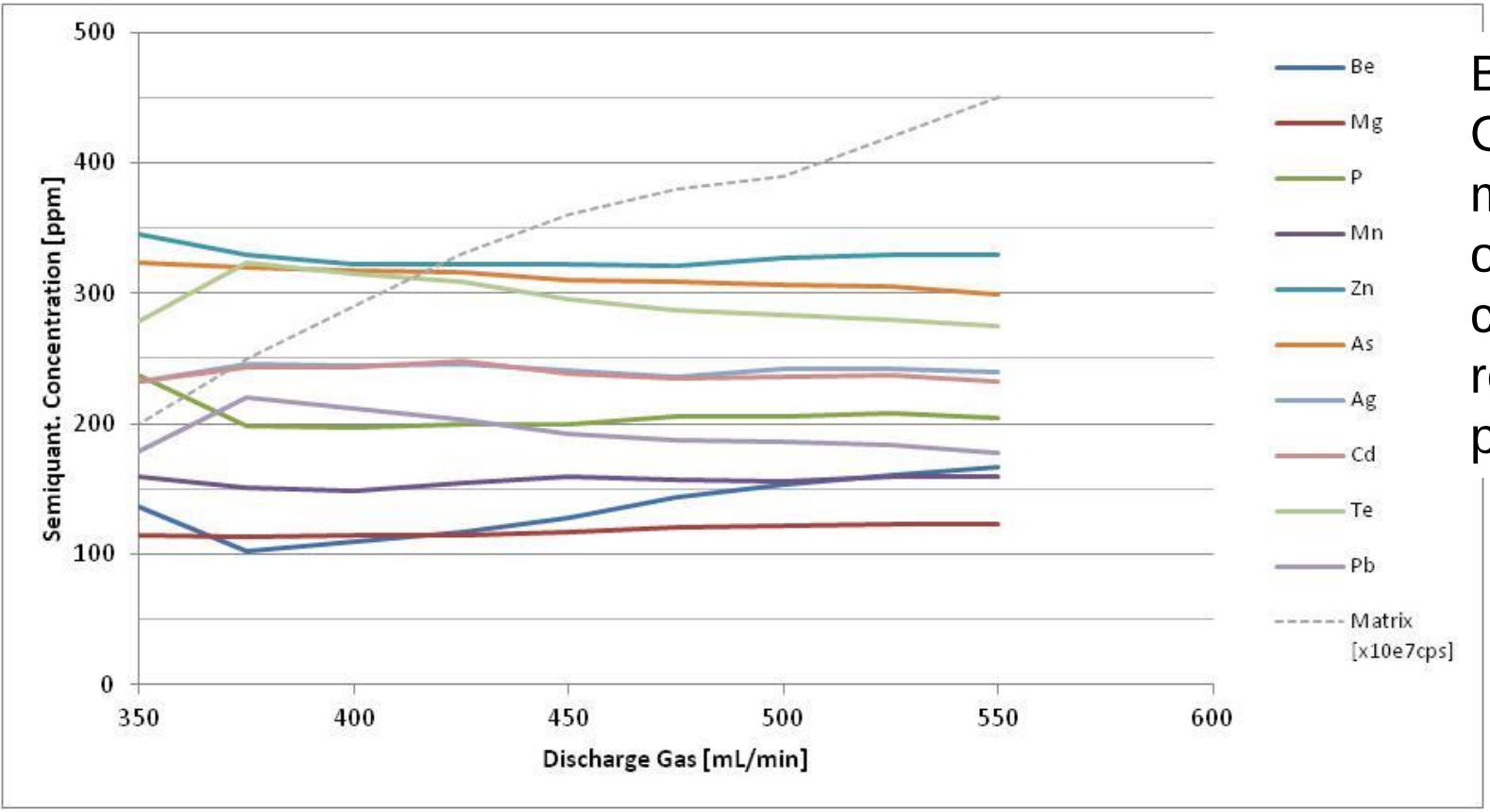
Scope for Pulsed Mode Fast Flow GD-MS

- DC-Pulsed mode is getting more and more used in FF-GD-MS
- Rather low duty cycles, but efficient ionization yielding plenty of signal
- Switching yields ns flanks, requiring EMC shielding. In practice noise < 0.2 cps
- Strongly reduced diffusion from sputter region into transported aerosol = close to behaviour of VG9000 static discharge
- Proposals: semi-static discharge / equilibrated discharge



Typically 50µs on, 450 µs off = 10% duty cycle at 2kHz repetition rate

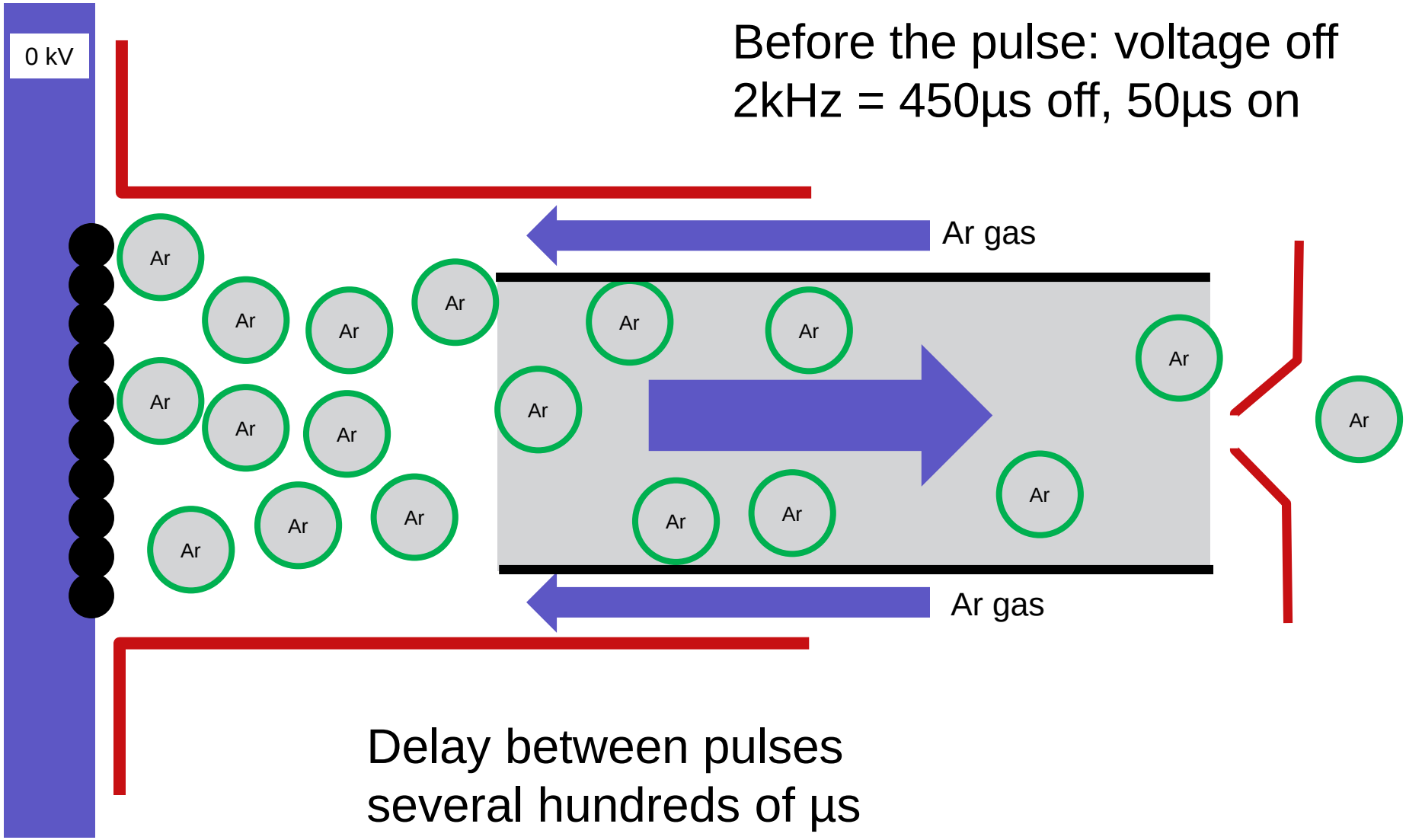
Effect of equilibrated discharge: IBR versus discharge gas flow



BAM376: Gas flow has minor effect on IBR/ concentration results in pulsed mode.

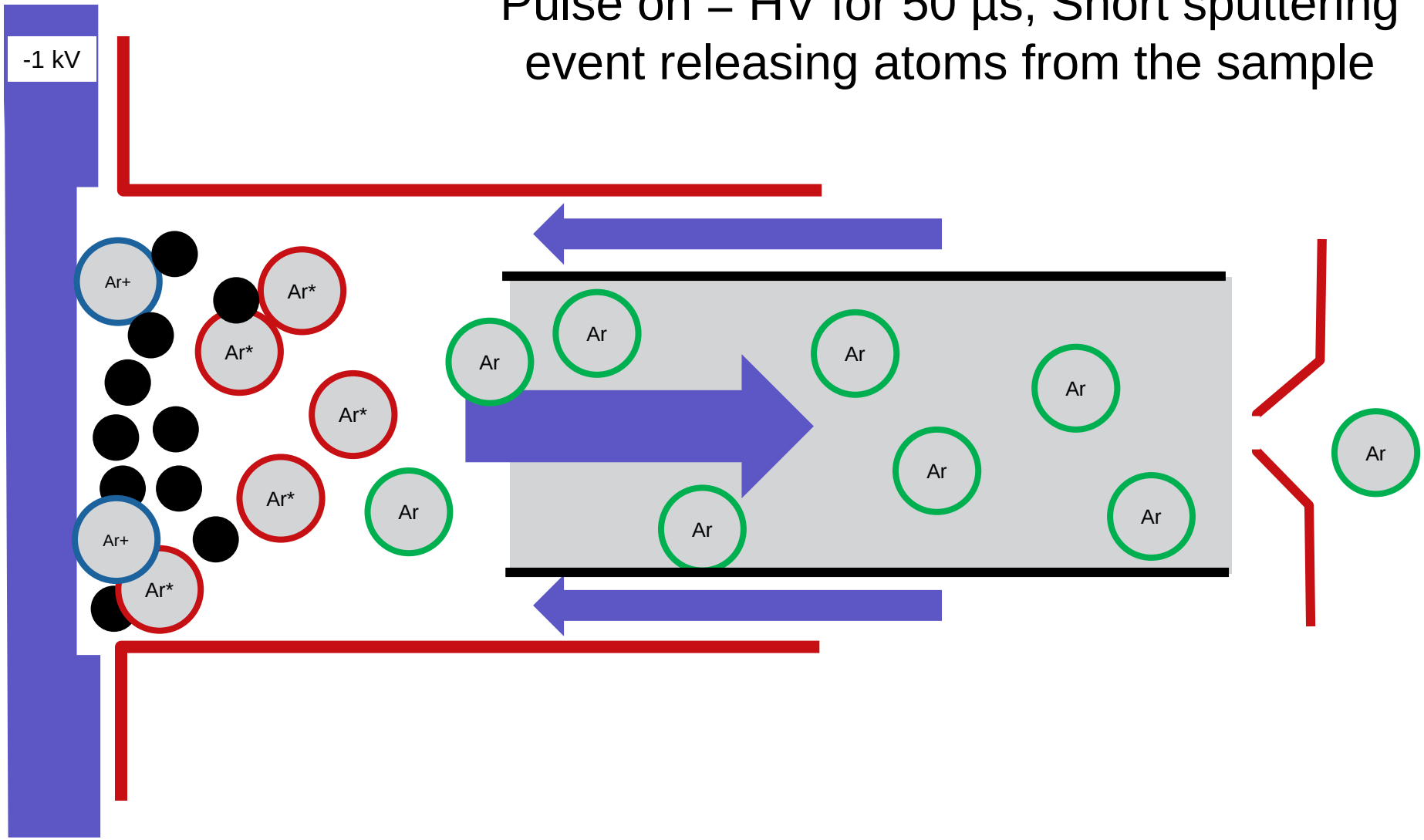
Probably the robustness of results is an effect of the short sputter time, followed by the long idle time allowing for equilibration of the ionization process.

Explanation trial for robustness…pulsing at 2kHz



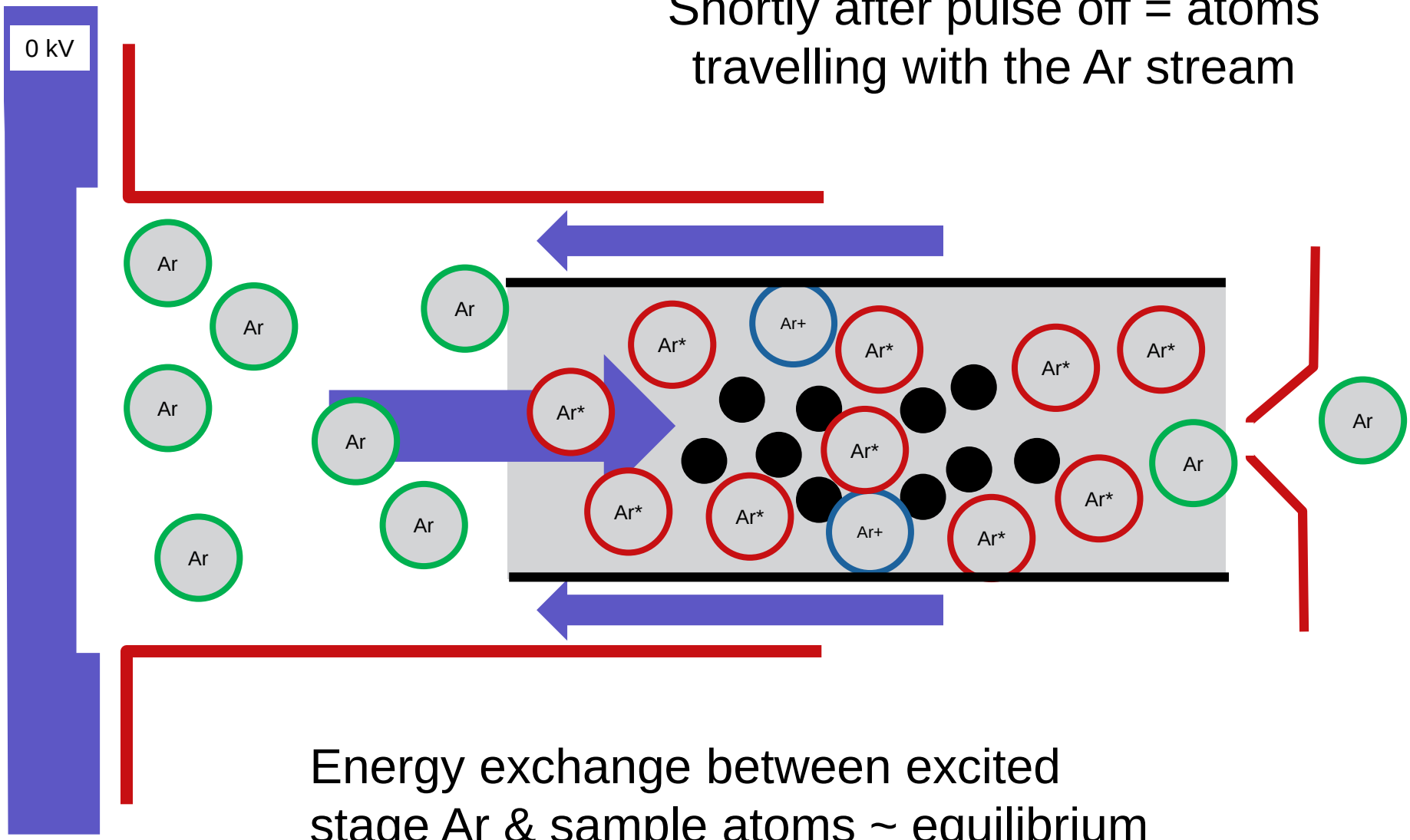
Schematics

Pulse on = HV for 50 µs; Short sputtering event releasing atoms from the sample



Schematics

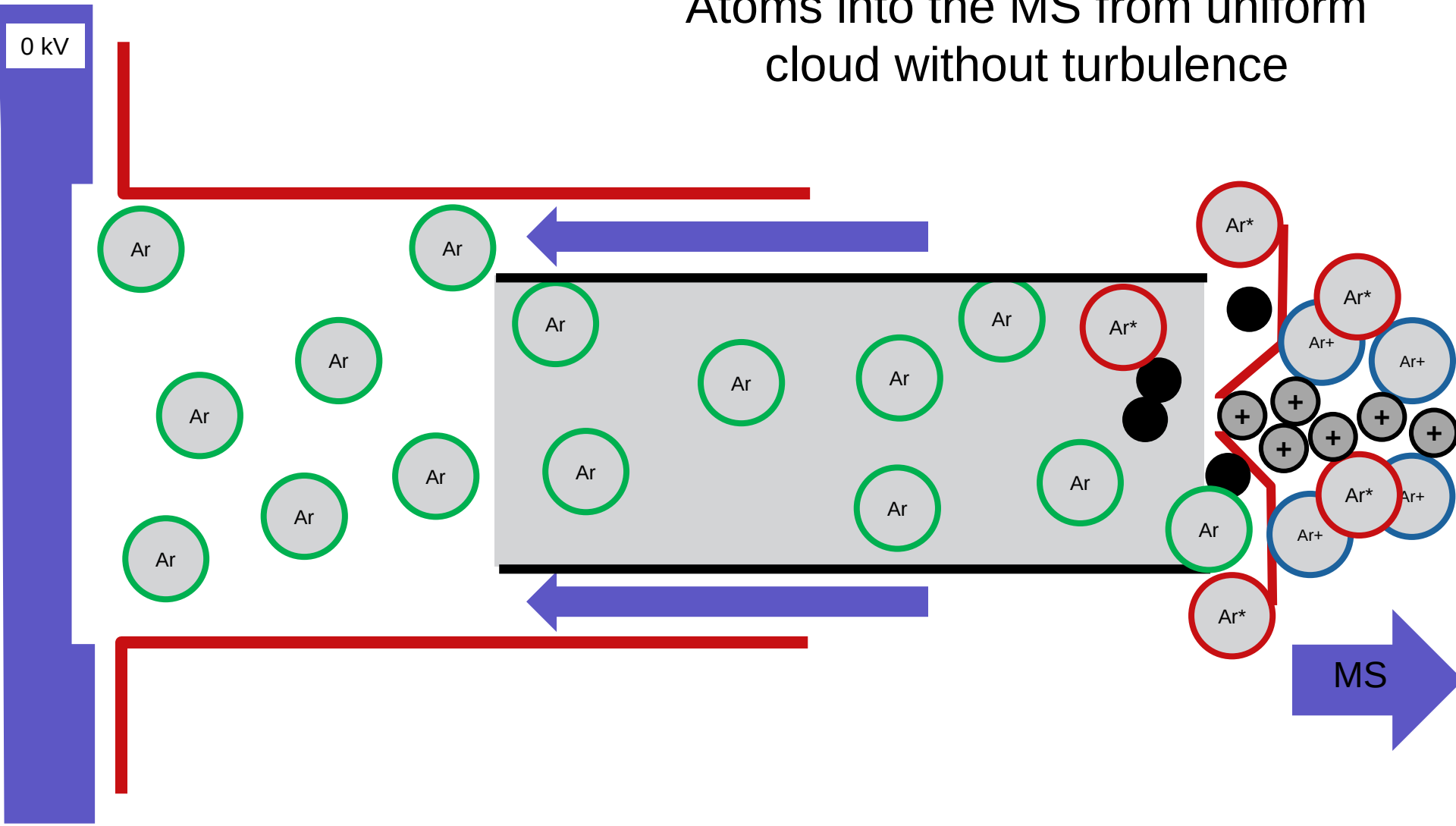
Shortly after pulse off = atoms travelling with the Ar stream



Energy exchange between excited stage Ar & sample atoms ~ equilibrium

Schematics

Atoms into the MS from uniform cloud without turbulence

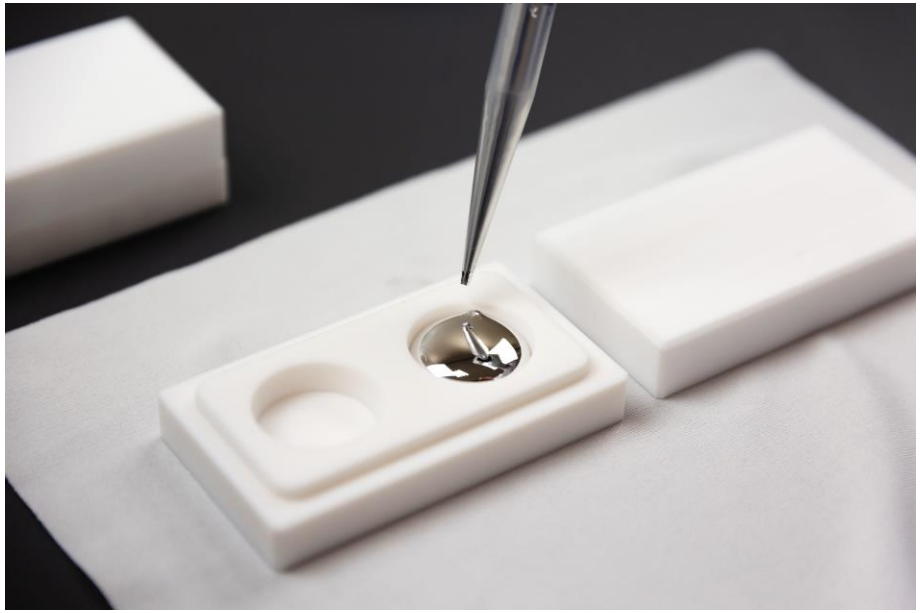


Gallium Kit Workflow (1)

Prepare sample: melt on hotplate, and take sample aliquot with pipette

Workflow (2)

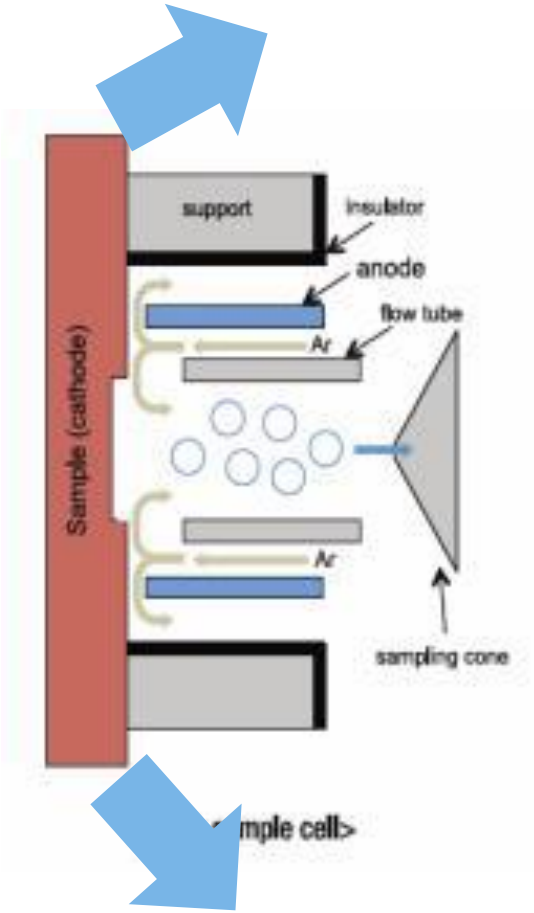
Prepare sample button: transfer liquid sample in pre-cleaned PTFE mould

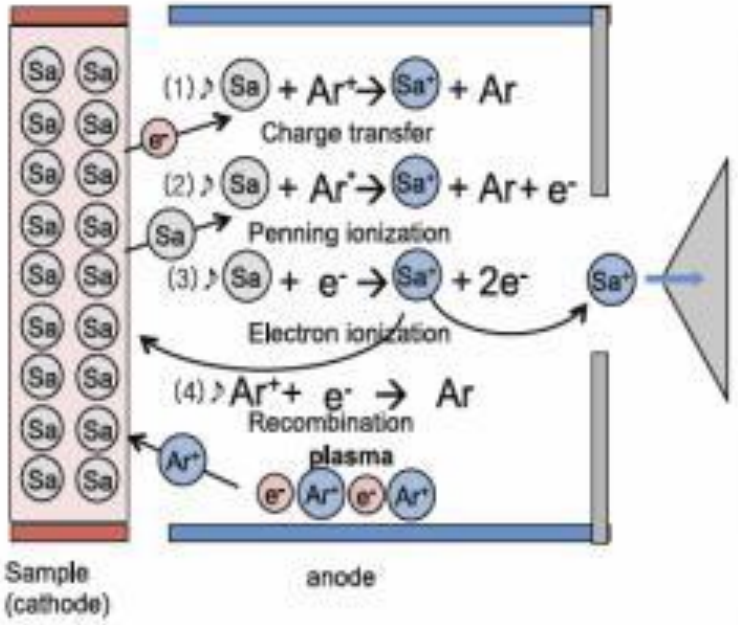


…solidify in deep-freezer @ -50ºC - ready for analysis

Workflow (3)

Analysis:
Cooling needs to be done as close as possible to heat generation from GD plasma running at ~10 to 15W





Workflow (4)

Analytical conditions:
Close to default pulsed mode conditions, just shorter pulse duration to reduce heat input into the GD plasma

Table 1. Instrument parameters used for gallium analysis.

Parameter	Value
Discharge voltage	1000 V (set value)
Discharge current	~10 mA
Discharge gas	500 mL/min
GD Source pressure	1.0 mbar
Extraction	-2000 V
Focus	-1000 V
Pulse duration	20 µs
Pulse frequency	2 kHz
Source temperature	~ -30 °C
Matrix sensitivity $^{69}Ga+^{71}Ga$ (MR)	1 x 10^{10} cps

Workflow (5)

Figures of merit: comparison to VG9000 cryo cooled source

Parameter	Mass	VG9000	Element GD Plus GD-MS	Improvement Factor Element GD Plus vs. VG9000
		Ratio of interference relative to ^{69}Ga [ppm]		
Abundance sensitivity	70	0.8	0.02	35
$^{38}Ar^{36}Ar$	74	1.0	0.04	28
$^{69}Ga^{38}Ar$	107	25	3.5	7
$^{69}Ga^{40}Ar$	109	1.0%	0.13%	8
$^{69}Ga^{40}Ar^{12}C$	121	0.068	0.0001	~700
$^{71}Ga^{40}Ar^{12}C$	123	0.058	0.0001	~600

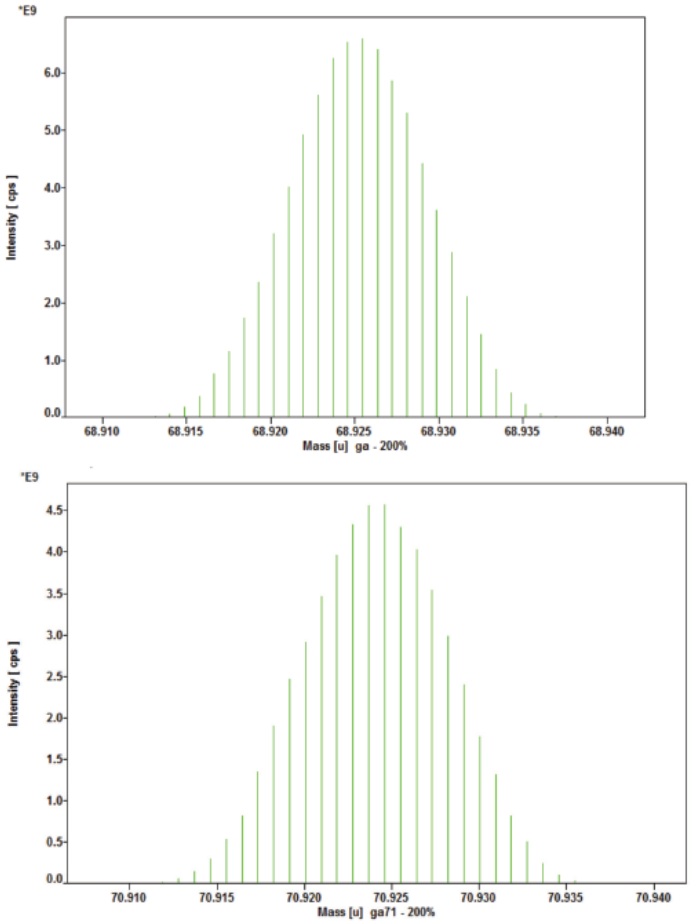


Figure 3. Matrix signals for both Ga isotopes in Medium Resolution on the Element GD Plus GD-MS.

Thanks to Esther Liessmann (PPM Langelsheim) for providing the VG9000 spectra

Workflow (6)

Figures of merit: High Resolution for Ga based interferences

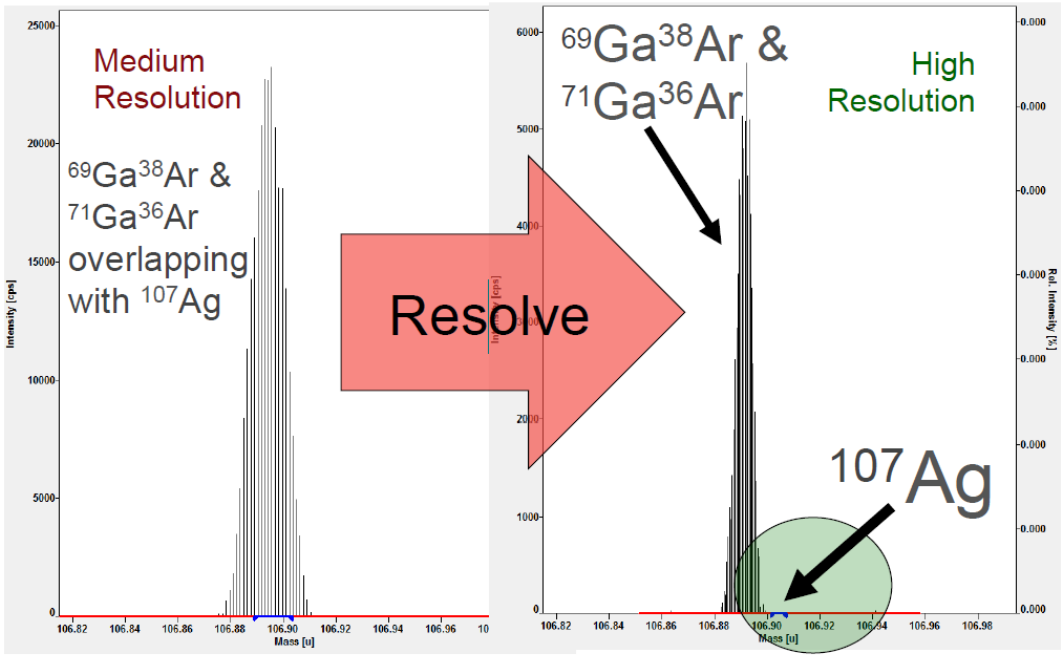
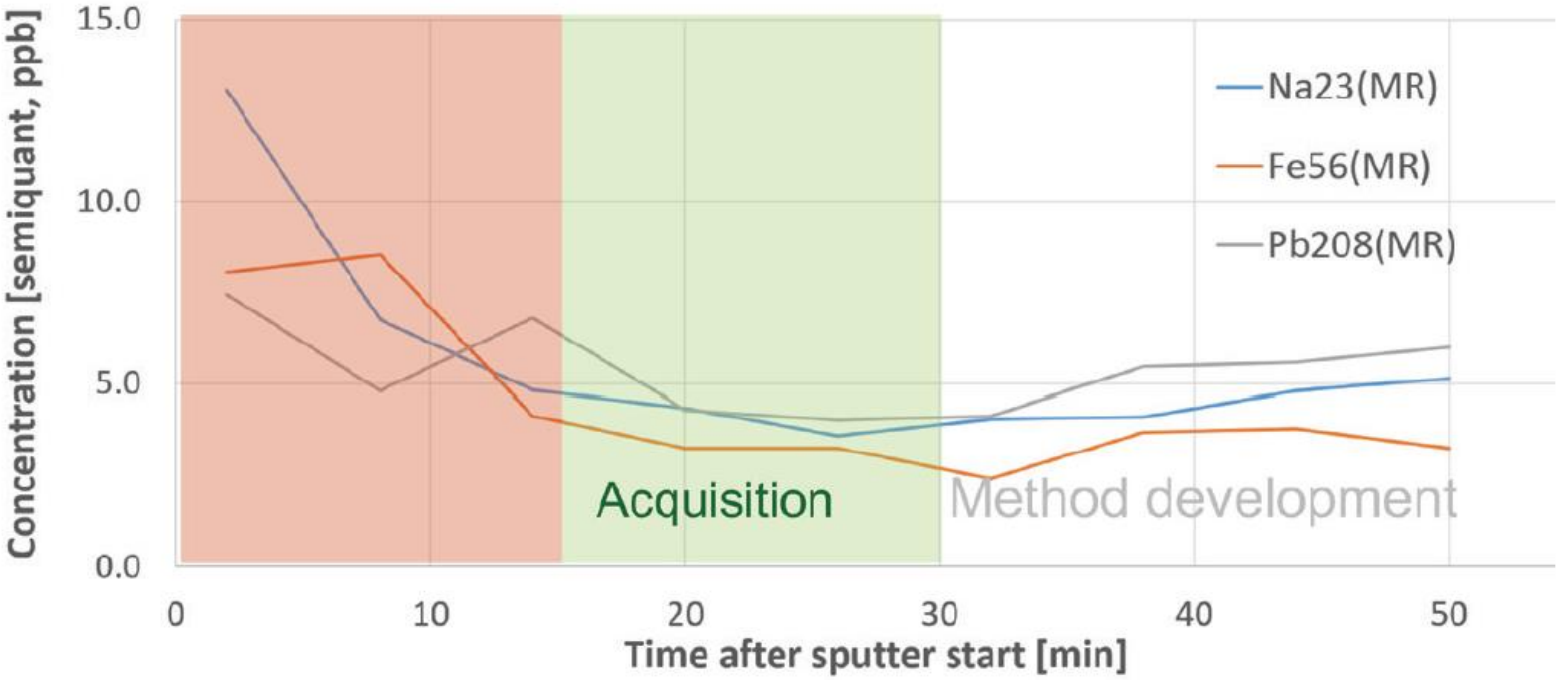


Figure 4. Spectra showing the main interference in Medium Resolution (R=4000) (left) and fully resolved using High Resolution (R=10000, right)

Methods templates for Ga analysis are available from Bremen Application lab

Workflow (7)

Presputter example: Presputter at ultra-trace level

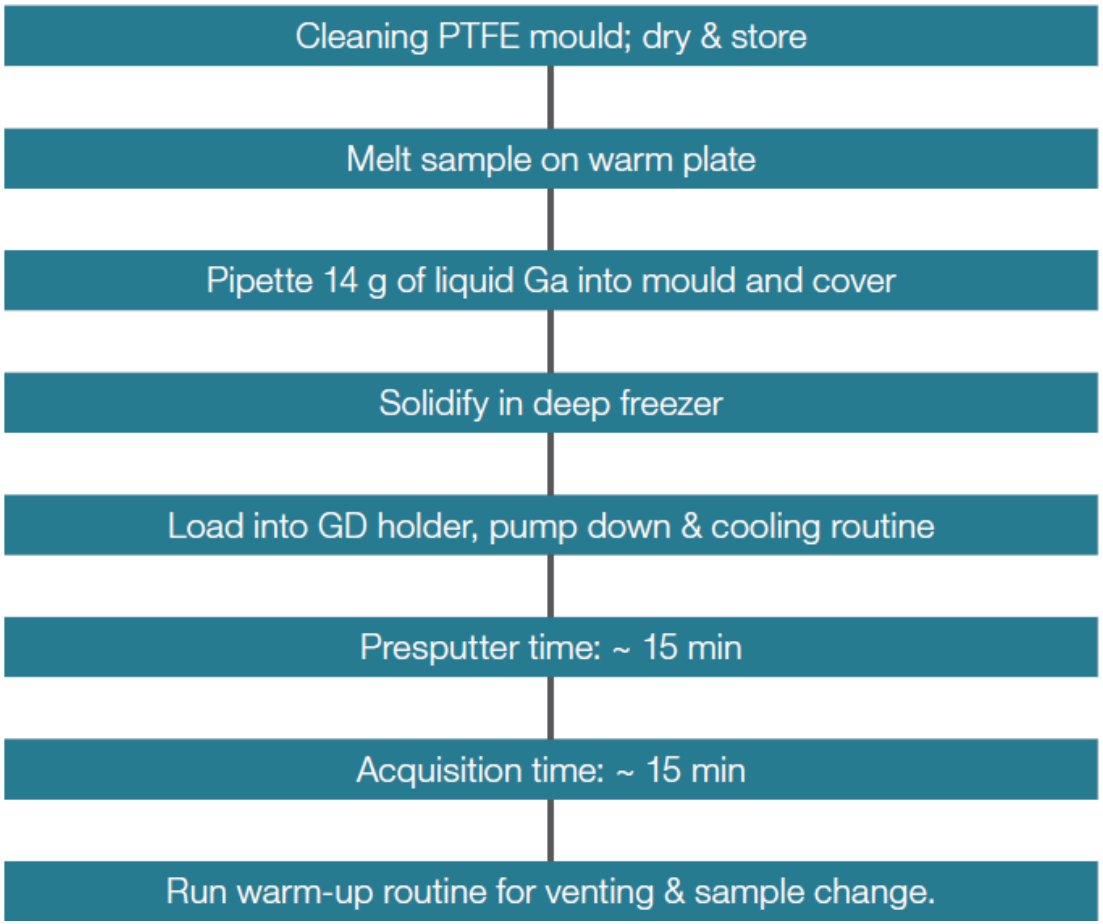


Each data point is the average of 3 scans with ~ 5min duration.
Stable low ppb-level values for evaluation after ~15min sputter time

Workflow (8)

Total Workflow proposed:

Table 2. Workflow proposed for sample preparation and analysis.



Parts overview

Hardware

- re-designed Peltier cooling electronics
- Recirculating chiller for precooling source Peltier elements to 10ºC
- Software control v. 3.1.8
- Source and source cover insulation

Workflow

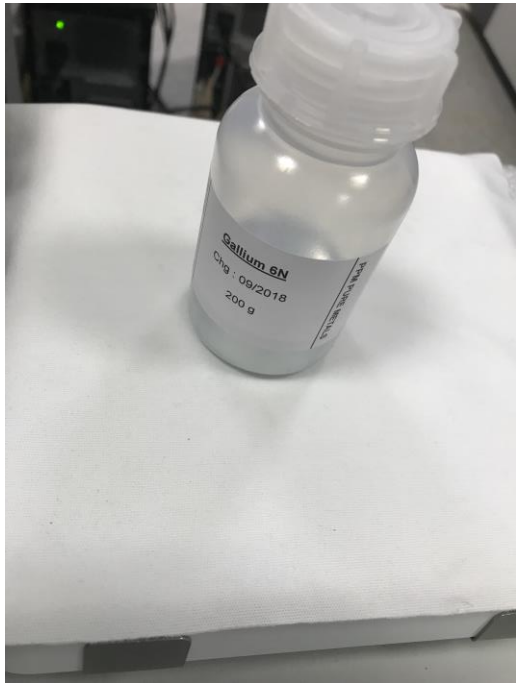
- Hot plate for melting sample
- PTFE moulds for preparation of buttons
- Deep freezer box for solidification of sample buttons @ -50ºC
- Accessories e.g. pipette, tips, storage, gloves, tweezer, beakers

Gallium kit & Element GD Plus: Value Proposition

- **Ease of use:**
  a) Complete lab workflow including sample preparation.
  b) Integrated cooling Peltier cooling – no liquid nitrogen required.
- **Productivity:** 45min per smp vs. 1.5h on traditional cryo-cooled GD ion sources.
- **Analytical:** higher sensitivity leading to better detection limits.
- **Routine:** worldwide coverage of service through Thermo Fisher service organization.



Thank you for your attention!



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