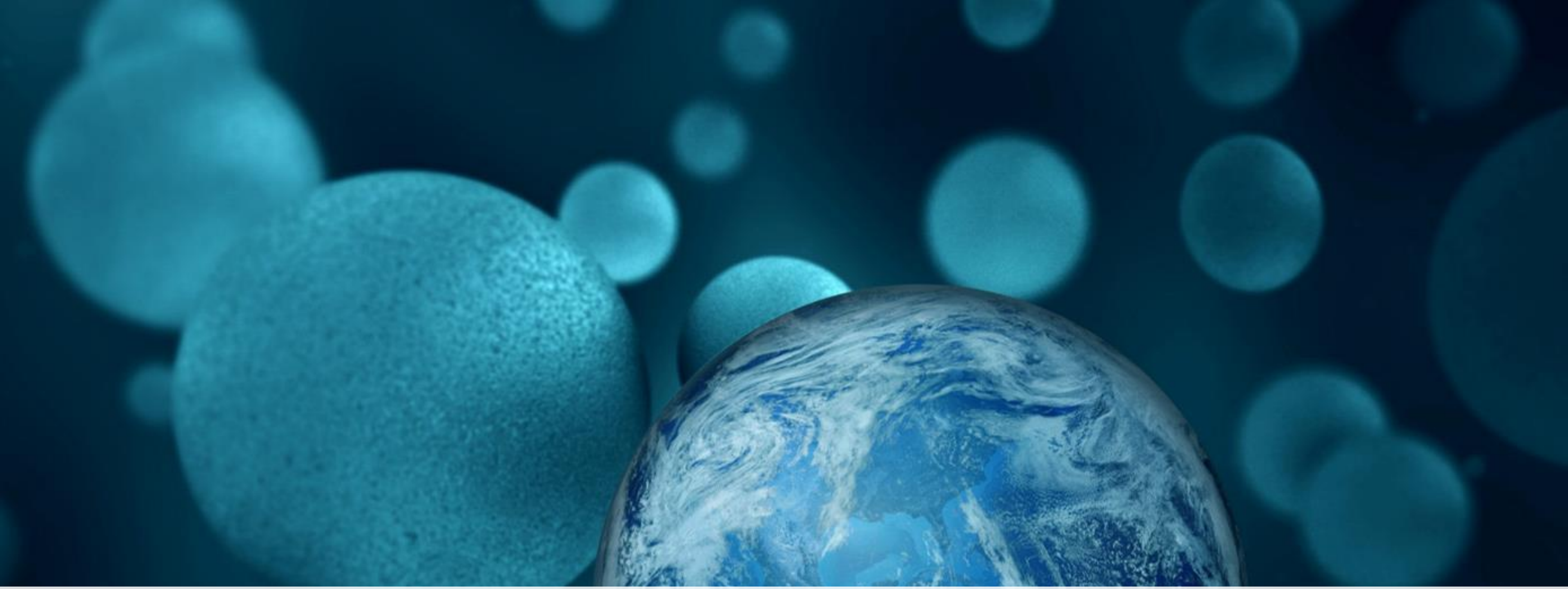

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Calibration factors in Fast Flow Glow Discharge Mass Spectrometry (FF-GD-MS): continuous versus pulsed mode

Joachim Hinrichs
17. GDS-Anwendertreffen, Bremen, May 2017
Thermo Fisher Scientific, Bremen, Germany

Scope

- Many GD-MS analyses rely on semiquantitative analyes
- Based on a general table of
  Relative
  Sensitivity
  Factors
- Universally applied to all matrices = Standard RSF
- Results of some elements tend to be low – mostly Ti and V
- Can pulse mode use the same RSF factors than continuous DC mode?

- Note: for many materials, CRM can be used. This yields accuracies close to solution based calibration by e.g. ICP-MS.

Poster at the Plasma Winter Conference 2017

thermo scientific

Calibration factors in Fast Flow Glow Discharge Mass Spectrometry (FF-GD-MS): continuous versus pulsed mode

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ABSTRACT

Purpose: To compare and revise calibration factors for the Thermo Scientific™ Element GD™ Plus GD-MS in continuous mode and pulsed mode operation.

Methods: The Element GD Plus GD-MS was used to measure a set of 23 Iron and Nickel based certified reference materials, selected to cover a wide range of elemental concentrations.

Results: Calibration factors for 33 elements were obtained from the set of reference materials analyzed.
In continuous mode operation, the calibration factors confirm those previously used for semiquantitative analyses. Significantly improved accuracy can be expected for Ti, V, Cr, and Zr with the data obtained during this study. For pulsed mode, the linearity at high concentrations is improved. Most elements are analyzed within the accuracy range of ±30% considered typical for semiquantitative GD-MS analyses. For improved accuracy, the use of a dedicated set of calibration factors is advisable.

INTRODUCTION

Sector field glow discharge mass spectrometry is applied for the analysis of high purity bulk metals and alloys, semiconductors and ceramics, especially by the aerospace, electronics and photovoltaic industries.
The Element GD Plus GD-MS features a fast flow glow discharge source that can be operated in continuous or pulsed mode. Continuous mode operation offers the advantage of high sputter rates to remove contaminated

Figure 1. Analytical procedure.

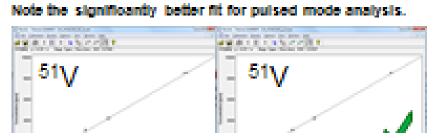
Wet grinding (SiC paper grit 180)
↓
Rinse: DI water, iso-Propanole, drying in N_2 stream
↓
Load sample and pump down
↓
Presputter: 5 minutes. Remove surface contaminations

Table 2. Instrumental parameters (standard conditions).

Parameter	Continuous DC mode	Pulsed DC mode
GD Source Pressure [mbar]	2.8	2.8
Discharge Voltage [V]	~700	1000 (set value)
Discharge Current [mA]	25 (set value)	~11
Discharge Gas [mL/min]	~340	~340
Extraction [V]	-2000	-2000
Focus [V]	-1200	-1200
Pulse Duration [µSec]	n.a.	50
Pulse Mode	no	yes
Pulse Frequency [kHz]	n.a.	2

Figure 3 shows the calibrations for V and Cr, available at higher levels, with Cr reaching ~ 20% in a few materials. At such high concentrations, matrix effects can occur, and a distinct difference between the measurement modes can be observed.
In continuous mode, V and especially Cr show a significant offset from the regression line in the low percent concentration range, while pulsed mode shows a much better fit. Since pulsed mode gives the same RSF over the entire range, this is therefore the preferable option for general survey analyses.

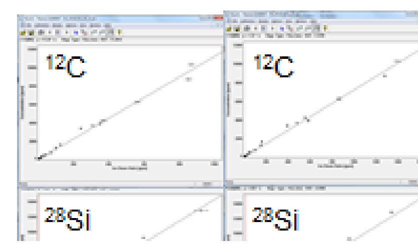
Figure 3. Calibration curves for V and Cr at the percent level. Left: continuous mode, right: pulsed mode. Note the significantly better fit for pulsed mode analysis.



For pulsed mode analysis, only a small data base was so far available [2]. Table 2 shows that the pulsed mode RSF overlap for many elements with continuous mode. In detail though, a number of elements show significantly lower RSF values, especially Mg, Ca, Mn, Zn, Se, Ag, Sn, Te, Pb and Bi. Others, e.g. Si, Ni, As and Sb, yield higher RSF. With these differences, the use of an RSF table derived from continuous mode operation may result in larger errors. Therefore, a dedicated RSF table for pulsed mode is recommended to support accurate routine operation for semiquantitative analyses.

The standard instrumental parameters used for pulsed mode cover the vast majority of applications. Still, further studies to investigate the influence of other pulse parameters, e.g. pulse duration and frequency, need to be carried out. Initial results (not shown) indicate a stable instrumental response for pulse durations ≥ 40 µs and pulse frequencies in the range 1 to 4 kHz.

Figure 4. Calibration curves for selected non-metallic elements. Left: continuous mode, right: pulsed mode.



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Quantification by GD-MS

Quantification by GD-MS

- Main application is concentration determination
- Concentration = mass fraction
- Isotopes are measured, concentrations are calculated and reported
- Abundance correction for isotopes is automatically applied
- No blanks, GD considered as blank free
- IBR = Ion Beam Ratio. This **means normalizing all signals to matrix signals**. Acts like an Internal Standard in ICP. IBR used for RSF quantification
- RSF concept = Relative Sensitivity Factor. Evaluation for semiquant = **recalculating calibration factors based on measured matrix composition**
- A **general RSF** table is commonly used for semiquantitative analysis by GD-MS. This is not absolutely accurate, but at least consistent. This is of major importance for quality control in industrial labs.
- **Calibrated RSF** give a matrix specific calibration = best accuracy

Evaluation Glow Discharge

Basic Assumption

$$\sum_{Elements} c_y = 1$$

$$IBR_x = \frac{I_x}{\sum_{Elements} I_y}$$

$$\sum_{Elements} IBR_y = 1$$

$$RSF_x = \frac{c_x}{IBR_x}$$

where

I	= intensity measured [cps]
c	= concentration
IBR	= ion beam ratio
RSF	= relative sensitivity factor.

(IBR_x all intensities known)

$$\boxed{c_x = RSF_x \cdot IBR_x}$$

$$\boxed{c_x = \frac{RSF_x \cdot IBR_x}{\sum_{Elements} RSF_y \cdot IBR_y}}$$

Quantification by GD-MS

The RSF concept works because in GD-MS…

- …the ionization is mostly occurring when the cloud of atoms is travelling in the Argon gas to the mass
- The GD plasma is mostly Argon with sample atoms, causing a very similar ionization regime even for different materials = similar environment for different materials
- The key is to consider the ionization efficiencies relative to each other, and maintain the same ionization process, which means similar Glow Discharge conditions
- For FF-GD-MS, the **pulsed** discharge generates a better equilibrated aerosol with uniform ionization. This is reflected by low influence of source parameters onto the IBR and Concentrations measured

Quantification by GD-MS

- Standard RSF are not fixed, but are instrument dependent: Source, Mass response of the MS, Tuning.
- In **continuous DC** mode, RSF were dependent on gas flow – needs to be strongly controlled
- In **pulsed** mode, there is just a small dependency on gas flow

- Semiquant = STD RSF typically in a range of ±30% accuracy.
- E.g. 10 ppm as a semiquant result should be regarded as "between 7 and 13 ppm"
- For high purity materials, usually semiquant results are sufficient, e.g. for "<0.01 ppm"

Standard RSF

The existing Standard RSF file lists sensitivity factors measured from steel and Iron matrix, normalized to 100% Fe:

Results - Thermo ELEMENT - [Standard RSF.rsf]

RSF

Element	LR	MR	HR
H	1.0000	1.0000	1.0000
He	1.0000	1.0000	1.0000
Li	3.1000	3.1000	3.1000
Be	5.0400	5.0400	5.0400
B	6.4900	6.4900	6.4900
C	9.2700	9.2700	9.2700
N	1.0000	1.0000	1.0000
O	1.0000	1.0000	1.0000
F	1.0000	1.0000	1.0000
Ne	1.0000	1.0000	1.0000
Na	0.9500	0.9500	0.9500
Mg	1.5100	1.5100	1.5100
Al	1.2700	1.2700	1.2700
Si	3.0400	3.0400	3.0400
P	3.6600	3.6600	3.6600
S	3.4300	3.4300	3.4300
Cl	1.0000	1.0000	1.0000
Ar	1.0000	1.0000	1.0000
K	0.5900	0.5900	0.5900
Ca	0.4500	0.4500	0.4500
Sc	0.5900	0.5900	0.5900
Ti	0.4100	0.4100	0.4100
V	0.5400	0.5400	0.5400
Cr	1.2800	1.2800	1.2800
Mn	1.0100	1.0100	1.0100
Fe	1.0000	1.0000	1.0000
Co	1.0400	1.0400	1.0400
Ni	1.5100	1.5100	1.5100
Cu	2.4400	2.4400	2.4400
Zn	3.8300	3.8300	3.8300
Ga	2.3400	2.3400	2.3400
Ge	1.3300	1.3300	1.3300
As	5.1300	5.1300	5.1300
Se	3.7700	3.7700	3.7700
Br	1.0000	1.0000	1.0000
Kr	1.0000	1.0000	1.0000
Rb	1.0000	1.0000	1.0000
Sr	0.5200	0.5200	0.5200
Y	0.5400	0.5400	0.5400
Zr	0.5600	0.5600	0.5600
Nb	0.6600	0.6600	0.6600
Mo	0.9200	0.9200	0.9200
Tc	1.0000	1.0000	1.0000
Ru	0.7600	0.7600	0.7600
Rh	1.3600	1.3600	1.3600
Pd	1.8100	1.8100	1.8100
Ag	3.8500	3.8500	3.8500
Cd	3.4100	3.4100	3.4100
In	1.4500	1.4500	1.4500
Sn	1.2900	1.2900	1.2900
Sb	4.8900	4.8900	4.8900
Te	4.4300	4.4300	4.4300
I	1.0000	1.0000	1.0000
Xe	1.0000	1.0000	1.0000
Cs	1.0000	1.0000	1.0000
Ba	0.5600	0.5600	0.5600
La	0.6400	0.6400	0.6400
Ce	0.7500	0.7500	0.7500
Pr	0.8100	0.8100	0.8100
Nd	0.8800	0.8800	0.8800
Pm	1.0000	1.0000	1.0000
Sm	0.7400	0.7400	0.7400
Eu	0.6500	0.6500	0.6500
Gd	0.6800	0.6800	0.6800
Tb	0.8300	0.8300	0.8300
Dy	0.7800	0.7800	0.7800
Ho	0.8100	0.8100	0.8100
Er	0.7600	0.7600	0.7600
Tm	0.7500	0.7500	0.7500
Yb	0.8000	0.8000	0.8000
Lu	0.6700	0.6700	0.6700
Hf	0.7900	0.7900	0.7900
Ta	1.2400	1.2400	1.2400
W	1.6100	1.6100	1.6100
Re	0.9700	0.9700	0.9700
Os	1.8200	1.8200	1.8200
Ir	1.3800	1.3800	1.3800
Pt	2.4300	2.4300	2.4300
Au	2.3700	2.3700	2.3700

- Continuous DC mode
- Discharge current 40 - 45 mA
- NIST and BAM standards
- Full procedure was not published

Standard RSF - revisions

Why revisiting the Standard RSF?

- Reports on problematic elements. Liverpool EW-GDS meeting 2016
- Gas flow dependency – difficult to define best conditions
- What is the effect of the pulsed mode on RSF?

Revisions:

2004 original version based on BAM doped pellets plus some steel CRM NIST 176x series

2008 update for Carbon: RSF for C in steel ~ 9.3

Standard RSF file

Anal Bioanal Chem
DOI 10.1007/s00216-006-0645-5

SPECIAL ISSUE PAPER

Ralf Matschat · Joachim Hinrichs ·
Heinrich Kipphardt

Application of glow discharge mass spectrometry to multielement ultra-trace determination in ultrahigh-purity copper and iron: a calibration approach achieving quantification and traceability

Example:

	BAM_Dot 3-6	BAM_Dot 7-9	Fe CRM	Average
Ti		0.44	0.39	0.415
V		0.59	0.49	0.540
Cr	1.49	1.09	1.26	1.280
Fe	1.00	1.00	1.00	1.00
Zr		0.57	0.56	0.565
Sn		1.19	1.4	1.295
Sb		4.88	4.9	4.890

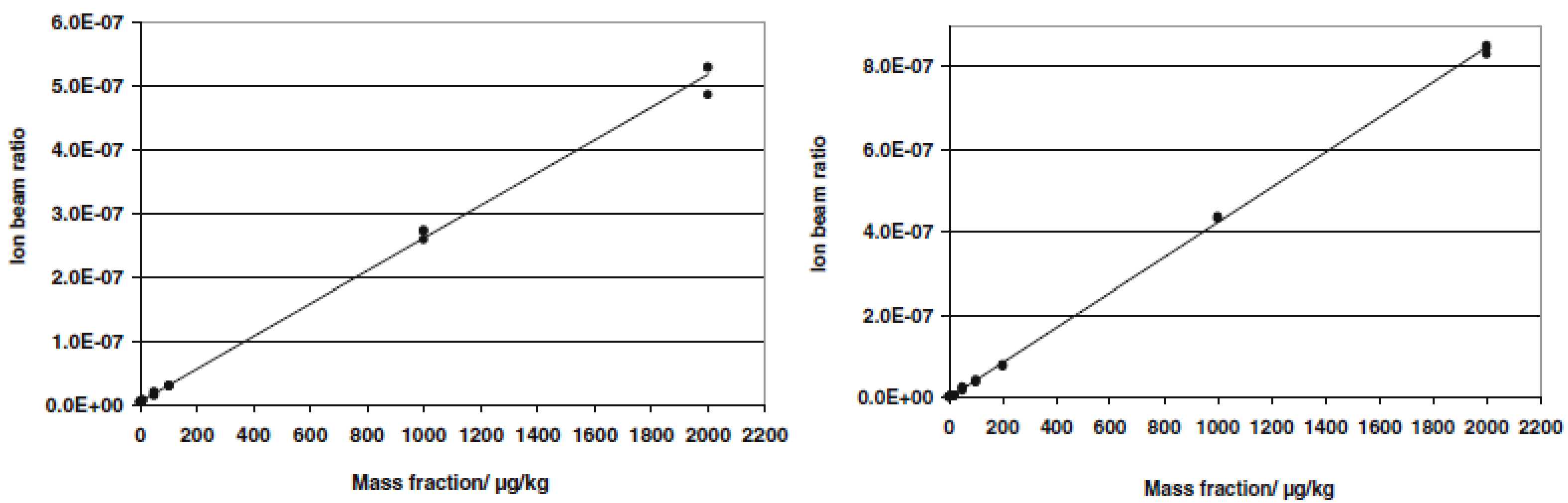


Fig. 10 Iron matrix: calibration curves of silver (^{109}Ag) *left graphs* (**a**) and of gallium (^{69}Ga) *right graphs* (**b**)

Standard RSF re-visited

	Type
ECRM098-1	High purity iron
ECRM270-1	High alloy steel 1.4835
ECRM271-1	Tool steel 1.2344
ECRM289-1	High temperature steel
ECRM295-1	Highly alloyed steel
ECRM298-1	Duplex stainless steel
ECRM297-1	Radionox steel 1.4696
ECRM379-1	Highly alloyed steel
NIST1261	AISI 4340 steel
NIST1262	AISI 94B17 steel
NIST1263	Cr-V steel
NIST1264	High carbon steel
NIST1265	Electrolytic iron
NIST1761	Low alloy steel
NIST1762	Low alloy steel
NIST1766	Low alloy steel
NIST1767	Low alloy steel
NIST1173	Ni-Cr-Mo-V steel
MBH12X353	Low alloy steel (wrought)
BS2205	Duplex alloy 2205
NIST1249	Nickel superalloy 718
IARM59C	Nickel alloy 825
BAS346A	Nickel alloy IN 100

Procedure:

Wet grinding:
(SiC paper grit 180)

Rinse:
DI water, iso-Propanole, drying in N_2 stream

Load sample and pump down

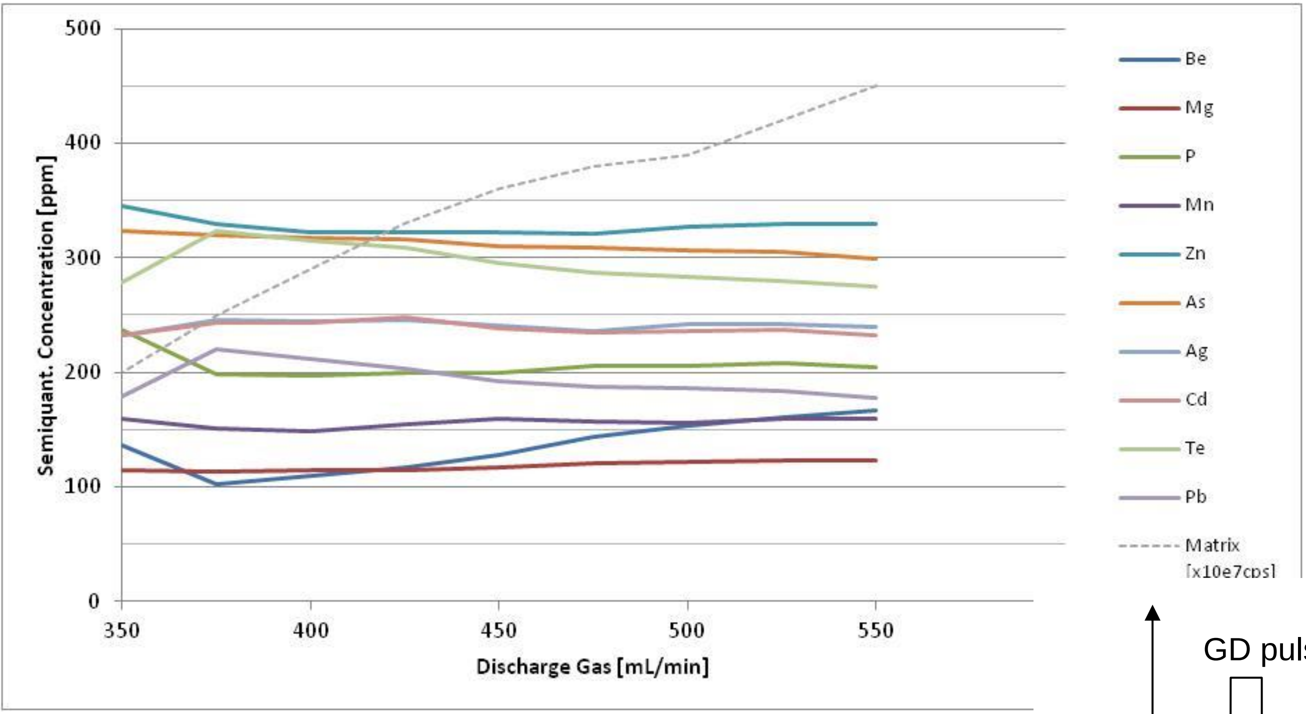
Presputter: 8 minutes. Remove surface contaminations

Continuous mode acquisition (35mA discharge current): 4 minutes

Stabilization time: 1 minute

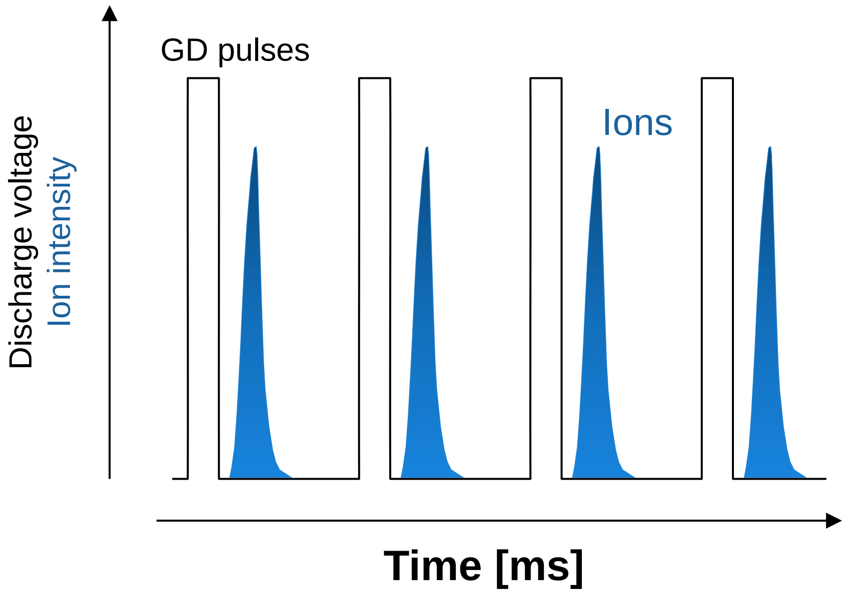
Pulsed mode acquisition: 4 minutes
(same sample spot)

Pulsed mode



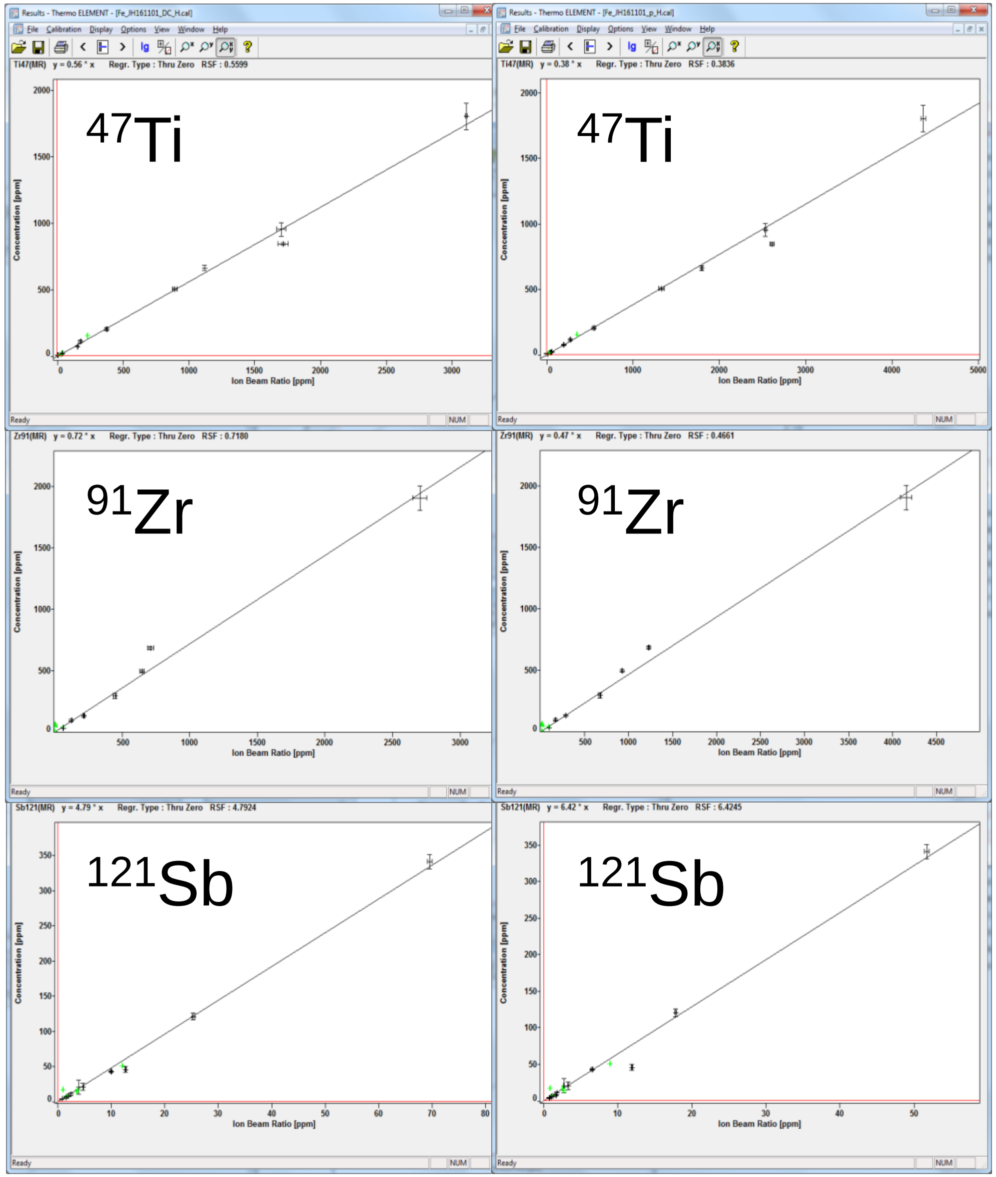
Gas flow dependency has minor effect in pulsed mode.

Propably an effect of the short sputter time, followed by the long idle time allowing for equilibration of the ionization process.



Example calibrations @ trace level

Left graphs:
Continuous DC



Right graphs:
Pulsed Mode

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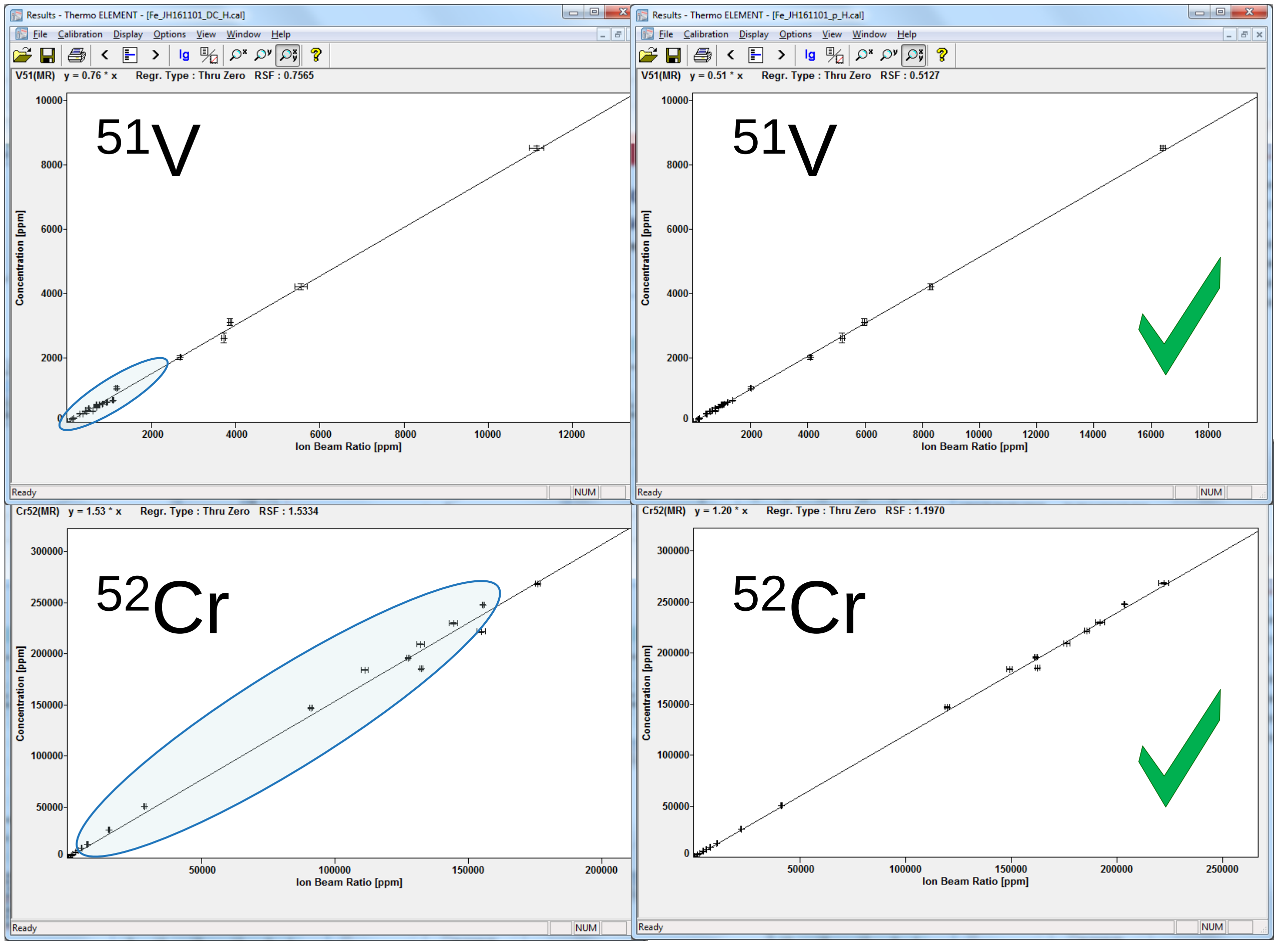
Continuous DC

Pulsed Mode



Less variation, better fit on a linear curve for especially Cr and V at higher level in pulsed mode.

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Results: Selection of RSF

	Standard RSF	Continuous Mode RSF	Pulsed Mode RSF	# Cert. values	# Info values
B	6.49	8.66	6.40	16	-
C	9.27	11.2	7.22	22	-
Mg	1.51	1.49	0.80	11	5
Si	3.04	4.06	4.96	21	-
P	3.66	4.69	4.15	20	-
Ti	0.41	0.56	0.38	16	3
V	0.54	0.76	0.51	21	-
Cr	1.28	1.53	1.20	22	-
Mn	1.01	0.96	0.57	22	-
Zr	0.56	0.72	0.47	11	4
Mo	0.92	0.89	0.75	22	-
Ag	3.85	3.25	2.00	6	3
Sn	1.29	1.24	0.71	18	3
Sb	4.89	4.79	6.42	16	5
Pb	1.36	1.28	0.86	13	5
Bi	2.94	2.59	2.00	7	2

Conclusion

- Step 1 – Ti, V, Cr, Zr give higher Standard RSF values during these experiments.

- Step 2 – verify at several instruments.
- Step 3 – generate new revision of STD RSF table.

- Further steps:
- Step 4 – pulsed mode with separate RSF table. First steps done for 33 elements.
- Step 5 – Round Robin study to create new, averaged STD RSF table in the future. Materials e.g. Ni alloys.
- Step 6 – rename STD RSF into e.g. “Generic RSF”.

Vielen Dank für die Aufmerksamkeit!

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