thermoscientific

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

Joachim Hinrichs, Shona McSheehy Ducos, Thermo Fisher Scientific, Bremen, Germany.
joachim.hinrichs@thermofisher.com

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 surface layers quickly. Also, the widely applied set of calibration factors (Standard RSF = general Relative Sensitivity Factors) is based on continuous mode operation. The pulsed mode of the glow discharge source results in enhanced overall stability. In terms of accuracy, it has been shown earlier that semiquantitative results obtained in pulsed mode typically yield accuracies within a range of ±30%, even though using the general calibration table based on continuous mode results. With the wider use of pulsed mode operation, a more detailed investigation on calibration factors is necessary.
In order to facilitate the use of both modes in routine analytical laboratories, the calibration factors have been re-visited to further evaluate the accuracies and the overlap between continuous and pulsed mode operation.

MATERIALS AND METHODS

Table 2 lists the set of 23 certified reference materials analyzed. The materials were chosen to provide a wide range of concentrations and elements certified. In part, also provisional or informational values were considered, in case they were in accordance with other certified values.

Table 2. Materials.

	Type	Source
ECRM098-1	High purity iron	1)
ECRM270-1	High alloy steel 1.4835	1)
ECRM271-1	Tool steel 1.2344	1)
ECRM289-1	High temperature steel	1)
ECRM295-1	Highly alloyed steel	1)
ECRM298-1	Duplex stainless steel	1)
ECRM297-1	Radionox steel 1.4696	1)
ECRM379-1	Highly alloyed steel	1)
NIST1261	AISI 4340 steel	2)
NIST1262	AISI 94B17 steel	2)
NIST1263	Cr-V steel	2)
NIST1264	High carbon steel	2)
NIST1265	Electrolytic iron	2)
NIST1761	Low alloy steel	2)
NIST1762	Low alloy steel	2)
NIST1766	Low alloy steel	2)
NIST1767	Low alloy steel	2)
NIST1173	Ni-Cr-Mo-V steel	2)
MBH12X353	Low alloy steel (wrought)	3)
BS2205	Duplex alloy 2205	4)
NIST1249	Nickel superalloy 718	2)
IARM59C	Nickel alloy 825	5)
BAS346A	Nickel alloy IN 100	6)

Sources:
1) European Committee for Iron and steel standardization
2) National Institute of Standards & Technology, Gaithersburg, MD 20899, USA
3) MBH Analytical Ltd., Holland House, Queens Road, Barnet EN5 4DJ, England, UK
4) Brammer Standard Company Inc., 14603 Benfer Road, Houston, TX 77069-2895, USA
5) Analytical Reference Materials International, 700 Corporate Cr., Suite A, Golden, Colorado 80401, USA
6) Bureau of Analysed Samples Ltd., Newham Hall, Middlesbrough, England, UK

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: 8 minutes. Remove surface contaminations

Continuous mode acquisition: 4 minutes

Stabilization time: 1 minute

Pulsed mode acquisition: 4 minutes
(same sample spot)

RESULTS

The large spread of elemental concentrations analyzed enables the revision of the general table of calibration factors. Several user-reports indicated that the elements Mg, Ti, V, Cr, Zr and Sb were generally at less accuracy in semiquant mode than the majority of other elements.
In GD-MS, the calibration is performed by plotting certified concentration vs. the measured Ion Beam Ratio (IBR), i.e. the raw elemental ratio relative to the matrix element. The slope of the regression curve is representing the Relative Sensitivity Factor (RSF) used for general semiquantitative analysis in various matrices. Since commonly the calibration is forced through zero as no intercept is expected, R^2 values for this regression type are not available.

Figure 2. Calibration curves for Ti, Zr, and Sb at the ppm level. Left: continuous mode, right: pulsed mode.

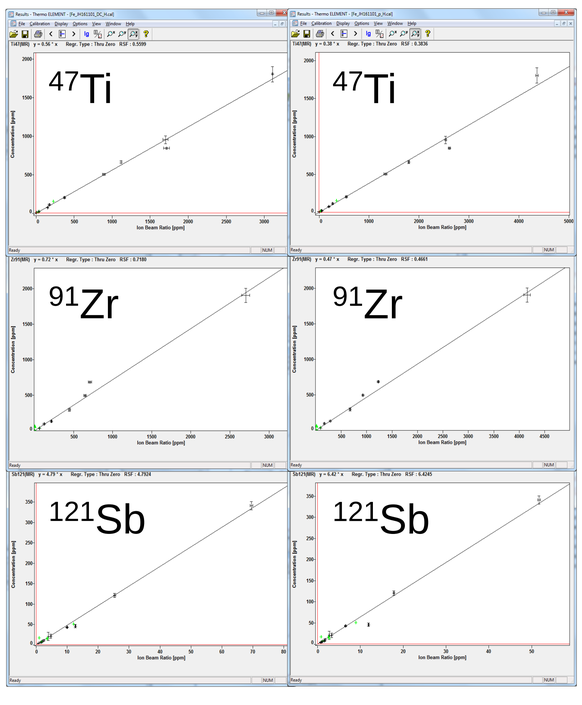


Figure 2 shows the calibrations at high ppm level for Ti, Zr, and Sb. The regression lines show a good linear fit, giving a high degree of confidence into the newly derived RSF.

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]	35 (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.

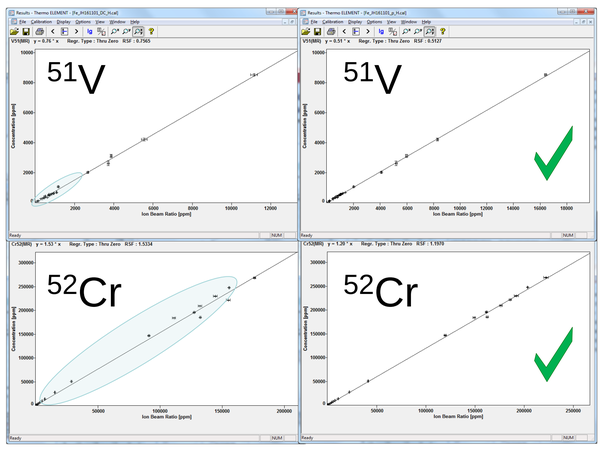


Table 3. Overview of Relative Sensitivity Factors: existing general Standard RSF, continuous mode RSF (this study), pulsed mode RSF (this study).

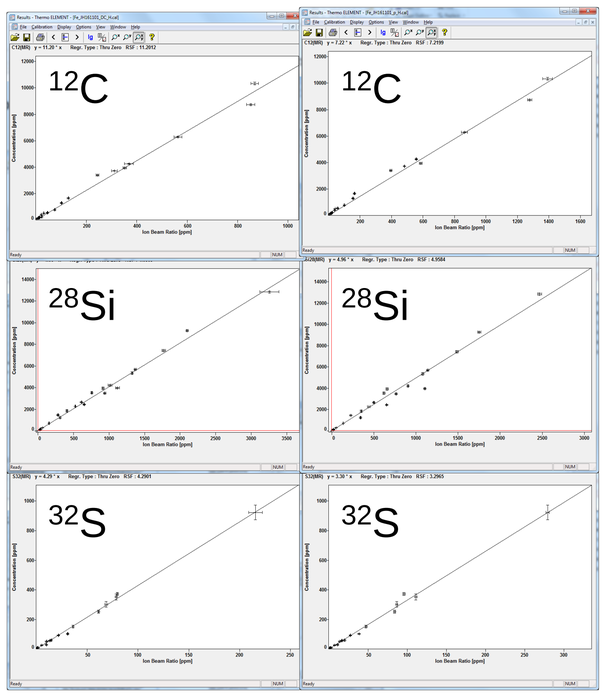
	Standard RSF	Continuous Mode RSF	Pulsed Mode RSF	# Cert. values	# Info values
B	6.49	8.66	6.40	16	-
C	9.27	11.2	7.22	22	-
Mg	1.51	1.49	0.80	11	5
Al	1.27	1.89	1.00	19	4
Si	3.04	4.06	4.96	21	-
P	3.66	4.69	4.15	20	-
S	3.43	4.29	3.30	22	-
Ca	0.45	0.56	0.27	8	1
Ti	0.41	0.56	0.38	16	3
V	0.54	0.76	0.51	21	-
Cr	1.28	1.53	1.20	22	-
Mn	1.01	0.96	0.57	22	-
Co	1.04	1.22	1.42	19	2
Ni	1.51	1.67	2.02	12	-
Cu	2.44	3.51	2.87	17	-
Zn	3.83	3.33	2.24	8	6
As	5.13	4.73	6.40	17	4
Se	3.77	3.38	2.52	6	4
Zr	0.56	0.72	0.47	11	4
Nb	0.66	0.79	0.75	13	2
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
Te	4.43	3.21	2.91	7	2
La	0.64	0.63	0.48	5	-
Ce	0.75	0.69	0.65	5	-
Pr	0.81	0.85	0.68	5	5
Ta	1.24	1.40	1.13	10	6
W	1.61	1.58	1.47	13	5
Au	2.37	2.10	2.30	2	-
Pb	1.36	1.28	0.86	13	5
Bi	2.94	2.59	2.00	7	2

Table 3 summarizes the RSF values obtained from the 23 reference materials analyzed. For comparison, also the values of the existing Standard RSF are shown. This table had originally been setup by combining the NIST 1761 – 1767 low alloy steel series with a range of doped Fe pellets at the low ppm level [1]. As expected, the newly measured RSF in continuous mode generally show a good overlap with the Standard RSF, which was also obtained in continuous mode. Proposed by the GD-MS community is to update the existing Standard RSF table for the elements shown in Figures 2 and 3.
The new RSF for Ti, V, Cr, and Zr confirm that the original values underestimated concentrations obtained in semiquant analyses, while Mg and Sb did not show a significant deviation and are not updated.

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.



GD-MS is typically applied for full scan analyses of all available trace elements. This routinely includes the direct analysis of the non-metallic elements C, Si, P and S, which are difficult to assess by many other analytical techniques. Figure 4 shows that both modes provide excellent capabilities, using the high mass resolution of the GD-MS instrument to completely eliminate interfering species.

CONCLUSIONS

A high quality calibration set for the Element GD Plus GD-MS has been obtained for continuous and pulsed mode analysis. Based on a wide variety of Fe and Ni reference materials, the calibration factors for Ti, V, Cr, and Zr are significantly improved for the continuous mode.
For pulsed mode, it is confirmed that the calibration is generally similar to continuous mode. For high levels of alloying matrices, pulsed mode offers the advantage of more linear calibrations. Therefore, pulsed mode combined with the dedicated set of calibration factors developed in this study is the preferred analytical method for obtaining best GD-MS data.

REFERENCES

1) Matschat, R., Hinrichs, J., Kipphardt, H., Application of glow discharge mass spectrometry to multi-element ultra-trace determination in ultrahigh-purity copper and iron: a calibration approach achieving quantification and traceability. J. Anal. Bioanal. Chem. 2006.
2) Hinrichs, J., Churchill, G., Putyera, K., Rottmann, L., Hamester, M., Development of a Pulsed DC-GD-MS Instrument. Poster contribution at the Winter Conference on Plasma Spectrochemistry 2011.

ACKNOWLEDGEMENTS

We thank Volker Hoffmann (IfW, Dresden, Germany) and Hans Heck (Cronimet GmbH, Karlsruhe, Germany) for providing materials. We acknowledge the many fruitful discussions with GD-MS users.

ThermoFisher SCIENTIFIC