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

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Abstract

The Thermo Scientific™ Element GD Plus™ GD-MS was used to measure a set of 13 iron based certified reference materials. Calibration factors for 29 elements were obtained in continuous and pulsed mode.

In continuous mode operation, the calibration factors obtained confirm most of those factors previously used for semiquantitative analyses. However, significantly improved accuracy can be expected for Ti, V, Cr, and Zr with the data obtained during this study.

In pulsed mode operation, the calibration factors for many elements are similar to the ones in continuous mode. In detail though, some elements show lower calibration factors. Therefore, a dedicated RSF table for pulsed mode is recommended to support accurate routine operation for semiquantitative analyses.

Most elements are analyzed within the accuracy range of ±30 %, considered to be 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%, despite using the general calibration table based on continuous mode results.

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Materials and methods

An Element GD Plus GD-MS was used to measure the calibration factors in continuous and pulsed mode. The instrumental parameters (standard conditions) are summarized in table 1, and the analytical procedure is shown in figure 1.

Table 1. Instrumental parameters

Parameter	Continuous DC mode	Pulsed DC mode
Pulse mode	No	Yes
Pulse duration	n.a.	50 µs
Pulse frequency	n.a.	2 kHz
GD source pressure	0.94 mbar	0.94 mbar
Discharge voltage	600 - 700 V	1000 V (set value)
Discharge current	35 mA (set value)	10 - 11 mA
Extraction voltage	-2000 V	-2000 V
Focus lens voltage	-1000 V	-1000 V

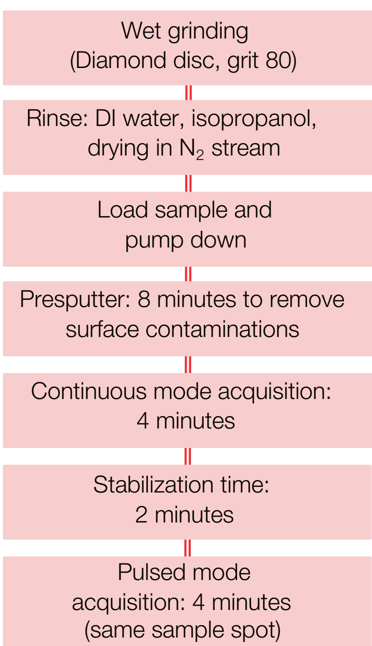

Figure 1. Analytical procedure

Following certified reference materials were analyzed: ECRM090-1, ECRM096-1, ECRM097-1 and ECRM098-1 (European Committee for Iron and Steel Standardization) and NIST SRM 1261, 1262, 1263, 1264, 1265, 1761, 1762, 1766 and 1767 (National Institute of Standards & Technology, Gaithersburg, MD 20899, USA).

In part, not only certified, but also informational and reference values were considered, in case they were in accordance with other certified values.

Results

The large spread of elemental concentrations analyzed enables the revision of the general table of calibration factors. Some user-reports indicated that the elements 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 the 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. Calibration lines for a selection of elements are shown in figure 2.

Table 2 summarizes the RSF values obtained from the 13 reference materials analyzed both in continuous and pulsed mode. For comparison, existing Standard RSF values are shown. These Standard RSF values were obtained in continuous mode. 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.

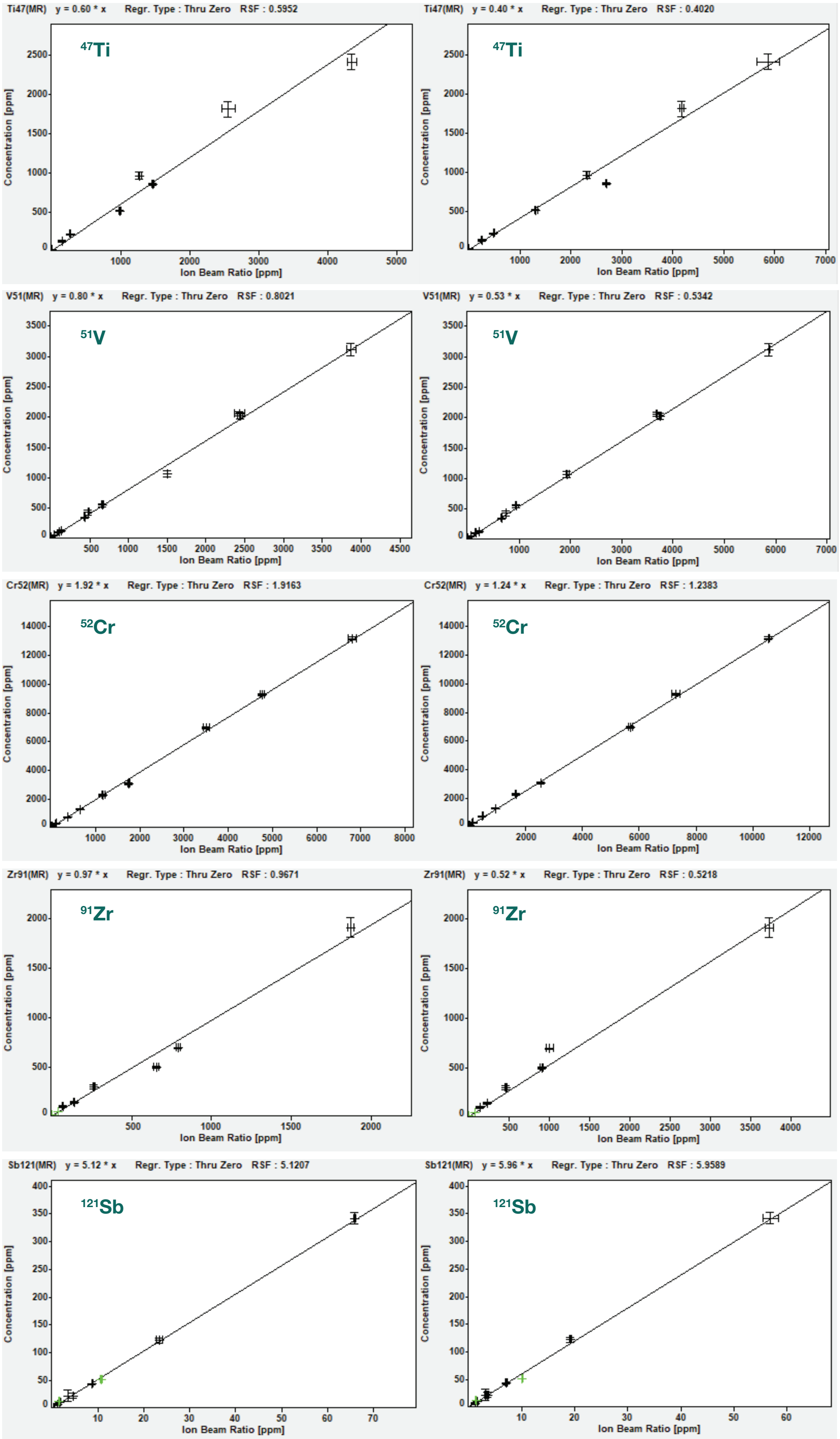

Figure 2. Calibration lines. Left: continuous mode, right: pulsed mode.

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Table 2. 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	5.65	5.47	10	-
C	9.27	7.55	6.06	12	-
Mg	1.51	2.23	1.70	4	-
Al	1.27	1.90	1.11	8	2
Si	3.04	3.30	3.87	12	-
P	3.66	3.75	3.37	12	-
S	3.43	3.56	3.06	13	
Ti	0.41	0.60	0.40	9	-
V	0.54	0.80	0.53	11	-
Cr	1.28	1.92	1.24	13	-
Mn	1.01	1.28	0.76	13	-
Co	1.04	1.01	1.23	9	2
Ni	1.51	1.44	1.81	12	-
Cu	2.44	3.26	2.73	11	-
Zn	3.83	3.42	2.42	1	2
Ga	2.34	2.70	1.32	1	-
As	5.13	5.54	6.74	9	2
Se	3.77	4.18	2.92	1	3
Zr	0.56	0.97	0.52	6	2
Nb	0.66	1.06	0.74	10	-
Mo	0.92	1.09	0.81	12	-
Ag	3.85	3.79	2.40	5	2
Sn	1.29	1.58	0.88	7	2
Sb	4.89	5.12	5.96	7	2
Te	4.43	4.64	3.09	4	2
Ta	1.24	1.58	1.22	4	4
W	1.61	1.74	1.70	4	1
Au	2.37	2.71	2.49	2	-
Pb	1.36	1.40	0.93	7	1

Proposed by the GD-MS community is to update the existing Standard RSF table for Ti, V, Cr, Zr, and Sb. The new RSF for Ti, V, Cr, and Zr confirm that the original values underestimated concentrations obtained in semiquant analyses, while Sb did not show a significant deviation and does not need to be updated.

For pulsed mode analysis, only a small data base was so far available[2]. Table 3 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 C, Zn, Ga, Ag, Sn, Te, and Pb. Others, e.g. Si, yield higher RSF. With these differences, the use of an RSF table derived from pulsed mode operation would result in better accuracy. Therefore, a dedicated RSF table for pulsed mode is recommended to support accurate routine operation for semiquantitative analyses.

Conclusions

A high quality calibration set for the Element GD Plus GD-MS has been obtained for continuous and pulsed mode analysis. Calibration factors for Ti, V, Cr, and Zr are significantly improved for continuous mode.

For pulsed mode, it is confirmed that the calibration is generally similar to continuous mode.

Acknowledgements

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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.
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