



New Oxide-Specific Relative Sensitivity Factors to Improve Nonconductive Oxide Materials Analysis by Glow Discharge Mass Spectrometry

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Abstract

Glow discharge mass spectrometry (GDMS) relies on relative sensitivity factors (RSFs) in order to convert ion beam ratios of elements into mass fractions. GDMS has been used to analyze metals, alloys, and semiconductors for the past 50 years which resulted in the development of a universal RSF set for conductive samples, dubbed the “Standard RSF” set. GDMS is considered to be matrix independent, with RSF values generally varying between matrices up to a factor of 2. With the increase in analysis of nonconductive oxide samples using holding electrodes, a new RSF set needs to be created in order to reduce the analytical uncertainty of concentrations obtained from oxide samples. We analyzed four oxide standards – two aluminum oxide, an aluminum-rich silicon oxide, and a basalt rock powder standard – and developed an oxide RSF set. This new RSF set will reduce the uncertainty of oxide materials analysis.

Introduction

Glow discharge source mass spectrometry (GDMS) is a powerful analytical tool and has been used for direct solid sampling analyses of metals, alloys, and semiconductors for the past 50 years (Hoffman et al., 2005). GDMS combines a glow discharge source to a high-resolution magnetic sector mass spectrometer, providing excellent sensitivity and mass resolution. It remains among the most sensitive analytical techniques for full survey elemental analysis of homogeneous samples and is also highly effective for depth specific distribution evaluations of analytes in films and coatings in the micrometer range.

The sample to be analyzed by direct current GDMS is introduced into the glow discharge cell and used as the cathode of the glow discharge. During discharge the cathode/sample surface is bombarded with positive ions from the plasma. Consequently, the cathode not only releases secondary electrons, but also atoms from the cathode. These atomized species from the sample surface diffuse into the argon plasma and are ionized. Subsequently, ions are extracted from the plasma and accelerated into the high mass resolution magnetic sector analyzer. Ion beam intensities of all analyte elements are then measured using a combination of analog and digital detectors and evaluated in reference to a matrix element or normalized to multiple matrix elements. These are called ion beam ratios. To convert the measured ion beam ratios of elements to mass fractions, relative sensitivity factors (RSFs) are needed. RSFs are defined as:

$$RSF_X = \frac{C_X}{C_M} \times \frac{I_M}{I_X} \times \frac{f_X}{f_M} \quad \text{Eq(1)}$$

Where C_X and C_M are the concentrations, I_X and I_M are the measured signal intensities, and f_X and f_M are the isotopic abundances of the analyte of interest and matrix element, respectively. Thus, the RSF in GDMS is defined as the multiplication factor that must be applied to the measured ion beam ratios to evaluate mass fractions of analytes in the sample.

The quantification of all measurable elements across a diverse range of sample matrices by GDMS requires a large number of reference

materials to obtain the RSFs. To overcome this limitation, a generalized set of RSFs was developed using combinations of reference materials starting with steel alloys and expanding to other alloys such as aluminum, titanium, nickel, copper, and platinum (Harrison, 1988; Vieth and Huneke, 1991). These “generalized” RSF values were standardized to iron (Fe = 1.00) and were later referred to as the “Standard RSF” by manufacturers of commercial GDMS instruments. Owing to the stability of the GDMS method, it is possible to analyze samples in a semi-quantitative way (without matrix-matched standards) using the Standard RSF set to a reasonable degree of accuracy – generally within a factor of 2 (Hoffman et al., 2005). However, if possible, creating matrix-specific RSF sets will result in more accurate results (Vieth and Huneke, 1991; Milton and Hutton, 1993).

Starting in the early 1990s, methods using secondary electrodes to analyze non-conductive samples, such as oxides, were developed (Milton and Hutton, 1993). Oxide matrices sputter differently than conductive metals due to the different bond strengths and mechanism of atomizing elements. Oxide materials generally have much stronger bond strengths than metal alloys and require back deposition of a secondary conductive electrode material, such as tantalum (Ta), in order to create a thin conductive surface film on the oxide sample that will co-sputter the sample into the plasma (Milton and Hutton, 1993). Owing to the stronger bonds and different sputtering mechanisms, it is important to create an oxide-specific RSF set to reduce the uncertainty of the quantifications.

Methods

Four different reference powders were used in this study to create the oxide RSF sets – NMIJ CRM 8006a, NMIJ CRM 8007a, NIST SRM 1413, and USGS BCR-2. NMIJ CRM 8006a and 8007a are aluminum oxide (Al_2O_3) powders, NIST SRM 1413 is an aluminum-rich silicon oxide (SiO_2) sand, and USGS BCR-2 is a basalt rock powder standard (54-wt% SiO_2). All certificates are readily available online. Analyses were performed using three different Ametek Nu Instruments Astrum ES glow discharge mass spectrometers at Eurofins EAG Laboratories (EAG).

The reference powders were dried for at least one hour at 110°C in graphite crucibles prior to analysis. The samples were packed onto acid cleaned Ta sample holding electrodes in order to reduce possible cross contamination. The reference samples were analyzed using glow conditions of 3.0 mA fixed current and a voltage of 1.0 kV, with the argon flow adjusted to achieve the desired voltage. Specific isotopes were selected based on matrix composition to avoid or mitigate the impact of isobaric interferences.

Results and Discussion

Oxide RSF

Table 1 shows the calculated RSF values for the oxide matrices and Table 2 compares the new oxide RSF values with the existing Standard RSF set. Most of the oxide RSF values are within a factor of 2 the existing Standard RSF. Eight elements – lithium (Li), boron (B), fluorine (F), sodium (Na), germanium (Ge), antimony (Sb), tungsten (W), and rhenium (Re) – have RSF values that vary by more than a factor of 2 from the values in the Standard RSF set. It should be noted here that the Standard RSF set contains experimentally measured as well as calculated RSF values that were evaluated based on semi-empirical models (Vieth and Huneke, 1991), as opposed to our oxide RSF set which is fully experimentally measured.

Tantalum electrode background on W

The Ta electrode has low levels of phosphorous (P), niobium (Nb), molybdenum (Mo), and tungsten (W). The typical concentration of these analytes are P = 0.03 ppm, Nb = 0.18 ppm, Mo = 0.24 ppm, and W = 0.03 ppm. The expected signal interferences were calculated using the existing Standard RSF and the analyzed ^{181}Ta signal. W has a low certified value in BCR-2 (0.456 ppm), with total signal in the 10^{-17} amps range, the Ta correction is the same order of magnitude, making it harder to calculate the true W value, and therefore its RSF. Even with such a high interference, the new oxide RSF for tungsten is just slightly higher than a factor of 2 from the Standard RSF.

Fluorine RSF

Fluorine exhibits the largest difference between the Standard RSF and oxide RSF sets. There are a couple of reasons for this large discrepancy. First, fluorine has one of the highest ionization potentials (17.423 eV) of all elements, notably higher than that of argon (15.760 eV) which forms the plasma in GDMS. This results in very low ion yields for F analysis in argon plasmas; requiring, in turn, very high F concentrations in order to analyze its concentrations well. Secondly, the RSF values for F were only semi-empirically calculated, as opposed to experimentally measured due to the lack of reference materials with certified F values in the samples that were used to generate the universal Standard RSF set (Vieth and Huneke, 1991). In contrast, BCR-2 has a relatively high F concentration (470 ppm; consensus value from Jochum et al., 2005), which permitted its detection and mass fraction evaluation, enabling us to calculate its RSF value.

Oxide RSF versus Standard RSF

As the range of nonconductive oxide materials analyzed by GDMS using a conductive sample holding electrode continues to grow, it is increasingly important to have a comprehensive oxide-specific RSF set in order to reduce the uncertainty of quantifications. Creating this oxide RSF set achieves three goals. First, it enables us to analyze oxide materials more accurately than the Standard RSF. This is achieved by accounting for ion yields affected by bond strength differences between metal alloys and oxide materials, plasma conditions due to the high oxygen content, and co-sputtering effects caused by the conductive sample holding electrode – for example, sodium creates a solid solution with Ta during the sputtering process, which results in preferential sputtering and over-estimation of Na concentrations. Secondly, the oxide RSF also establishes experimentally measured RSF values for elements that were not present or did not have certified values in the reference samples that were used for developing the Standard RSF set. Finally, we were able to reaffirm the assertion that GDMS is generally matrix independent with RSF values for most elements lying within a factor of two of the existing Standard RSF.

References

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Table 1. Oxide RSF calculations and pre-existing Standard RSFs

	Oxide RSF	Standard RSF	n ^a		Oxide RSF	Standard RSF	n ^a
Li	0.20	1.67	6	Zr	0.44	0.60	12
Be	2.44	1.53	3	Nb	0.41	0.78	4
B	0.67	1.74	3	Mo	0.72	1.12	7
O	86	50	7	Cd	4.15	5.71	2
F^b	148	2	4	Sn	1.51	2.00	4
Na	0.46	2.03	7	Sb	2.34	5.26	4
Mg	0.89	1.54	11	Cs	2.23	1.30	2
Al	0.68	1.05	8	Ba	0.93	1.17	12
Si	2.52	1.85	11	La	0.81	0.74	4
P	5.28	3.16	4	Ce	0.76	0.74	4
S^b	5.20	3.00	4	Pr	0.72	0.81	4
Cl	1.16	1.00	4	Nd	0.72	0.72	3
K	0.63	1.21	9	Sm	0.69	0.73	6
Ca	0.34	0.55	14	Eu	0.72	0.81	7
Sc	0.37	0.39	4	Gd	0.73	0.70	4
Ti	0.27	0.35	11	Tb	0.67	0.70	4
V	0.34	0.56	6	Dy	0.68	0.75	4
Cr	1.13	2.21	9	Ho	0.70	0.80	4
Mn	0.89	1.46	6	Er	0.64	0.76	5
Fe	1.00	1.00	8	Tm	0.80	0.85	4
Co	0.84	1.10	3	Yb	0.75	0.96	5
Ni	1.40	1.51	6	Lu	0.66	0.81	3
Cu	3.51	5.14	12	Hf	0.66	0.80	6
Zn	5.55	5.77	10	W	3.46	1.60	6
Ga	1.55	2.70	11	Re^b	0.20	1.40	4
Ge^b	1.67	5.72	7	Tl	3.12	2.50	6
As^b	3.46	5.00	3	Pb	2.05	2.00	11
Rb	1.68	1.30	4	Bi	3.38	4.05	2
Sr	0.56	0.42	6	Th	0.97	0.60	4
Y	0.53	0.55	6	U	0.89	0.80	7

^a n calculated based on number of analyses and isotopes of the same element

^b Concentration not originally certified by USGS, but is the consensus value in the widely used GeoReM database (Jochum et al., 2005)

Table 2. Oxide RSF values relative to the pre-existing Standard RSF values

	Oxide/Standard		Oxide/Standard
Li	12%	Zr	73%
Be	159%	Nb	107%
B	38%	Mo	67%
O	171%	Cd	73%
F^a	7379%	Sn	75%
Na	23%	Sb	44%
Mg	58%	Cs	172%
Al	65%	Ba	79%
Si	136%	La	109%
P	167%	Ce	102%
Sa	173%	Pr	89%
Cl	116%	Nd	101%
K	52%	Sm	95%
Ca	61%	Eu	89%
Sc	94%	Gd	104%
Ti	78%	Tb	95%
V	61%	Dy	90%
Cr	51%	Ho	88%
Mn	61%	Er	84%
Fe	100%	Tm	94%
Co	77%	Yb	78%
Ni	93%	Lu	81%
Cu	68%	Hf	82%
Zn	96%	W	216%
Ga	57%	Re^a	14%
Ge^a	29%	Tl	125%
As^a	69%	Pb	102%
Rb	129%	Bi	84%
Sr	132%	Th	161%
Y	97%	U	111%

^a Concentration not originally certified by USGS, but is the consensus value in the widely used GeoReM database (Jochum et al., 2005)