

Theoretical Calculations of Relative Ion Yields for Glow Discharge Mass Spectrometry

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Quantitative determination of the elemental composition of metals and other solids by glow discharge mass spectrometry requires a calibration factor for each element. In past work, these factors, called relative ion yields (RIYs), have been determined experimentally from the mass spectra of standards of certified composition. The RIYs of some elements were found to be over 10 times larger than the RIYs of other elements. In this study a simple calculation of the RIYs of the elements within the same sample is derived from a theoretical framework which takes into account the combined effects of sputtering and ionization. The ionization function involves the electron affinity and the first ionization potential of each element, plus two unknown parameters. By favorable selection of a temperature parameter and a chemical-potential parameter, the RIYs calculated by this method were found to agree satisfactorily with the experimental RIYs of former work. The temperature of 16,000 K (used in this work) corresponds to an average electron energy of ~ 2 eV. (*J Am Soc Mass Spectrom* 1992, 3, 79-84)

Glow discharge mass spectrometry (GDMS) has become an increasingly popular analytical tool for the elemental analyses of metals and other solids. A glow discharge [1-3] is easily obtained by applying a negative potential of ~ 1000 V dc to a metallic sample surrounded by argon gas at a pressure of ~ 1 torr. Under these or similar conditions, a visible glow surrounds the sample. Argon ions, accelerated into the sample by the applied voltage, cause atoms to be sputtered off the surface of the sample. These atoms subsequently become ionized within the glowing argon by one of several mechanisms.

A major advantage of the GDMS method is its dynamic range capability for measuring elements from the 99 + wt% level down to the 100-wt-ppb level by using a quadrupole mass spectrometer or to the sub-weight-parts per billion level using a double-focusing magnetic-sector mass spectrometer. A survey analysis of all elements present down to a level of 1 wt ppm can be completed in < 1 h.

The calibration factors required for this analytical method are called relative ion yields (RIYs). RIYs are measured by acquiring the mass spectrum of a standard material and measuring the ion beam ratio (IBR) for each of the elements certified with respect to composition. To determine the IBR (and subsequently the RIY), a ratio is taken between the peak height of an isotope of an element of the sample (denoted by subscript "s" in the subsequent equations) and the

peak height of an isotope of a matrix element, such as iron (denoted as subscript "Fe" in the subsequent equations) for a sample of steel. Each of the measured peak heights (intensities) is corrected for the isotopic abundance of the corresponding element:

$$IBR_s = \frac{(\text{isotope intensity})_s / (\text{isotope abundance})_s}{(\text{isotope intensity})_{Fe} / (\text{isotope abundance})_{Fe}} \quad (1)$$

$$RIY_s = \frac{IBR_s}{(\text{certified wt}\%)_s / (\text{certified wt}\%)_{Fe}} \quad (2)$$

The RIYs are defined on a per-weight basis rather than on a per-atom basis. After having established the RIY for a certified element within a standard, one can determine composition by measuring IBR_s for that element in a similar sample and then by using the following equation:

$$(\text{Wt}\%)_s = (\text{wt}\%)_{Fe} IBR_s / RIY_s \quad (3)$$

If the weight percent iron (in this example) is not known precisely, an assumed value can be tested and subsequently scaled to achieve 100 wt% for the sum total of the elements. Relative sensitivity factors (RSFs) are also commonly reported. RSFs are (mostly) the reciprocals of the RIYs making them factors to be multiplied in eq 3 rather than to be divided.

The analytical power of the GDMS method depends upon reliably knowing the RIYs for all of the

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elements present within samples of unknown composition. Experimental RIYs, often plotted on logarithmic scales, have been described as being fairly constant among the elements. However, within the same steel standard, the RIYs of different elements have been measured [4] and found to vary from 0.15 to 2.0 among the certified elements (relative to iron).

In a recent article by Vieth and Huneke [5], RIYs have been calculated by applying the Saha-Eggert equation which uses the ionization potentials of the elements, an electron temperature in the range of 2-3 eV, and the partition functions of both atoms and positive ions at the electron temperature. The correlation between experimental RIYs and calculated RIYs was favorable even though the units for the equation (in relative intensity per mole) did not match the units for the RIYs (in relative intensity per gram).

The purpose of the present work is to describe an alternative calculation for the RIYs of elements in a given sample by means of a theoretical framework with a temperature parameter and a chemical-potential parameter. By assigning values to these unknown parameters, useful agreement can be obtained between calculated and experimental [4] values of the RIYs for the certified elements of two standards of the National Institute of Standards and Technology (NIST).

Method of Calculation

For the purpose of calculating the RIYs of the elements, the formation of sample ions is separated into two phenomena, described analytically by a sputtering factor and an ionization factor. The following equation describes this approach for any element in the sample (denoted as subscript "s" in the equation) relative to the matrix element iron (denoted as subscript "Fe" in the equation):

RIY_sCALC

$$\frac{(\text{sputter factor})_s(\text{ionization factor})_s(\text{atomic weight})_{\text{Fe}}}{(\text{sputter factor})_{\text{Fe}}(\text{ionization factor})_{\text{Fe}}(\text{atomic weight})_s} \quad (4)$$

Because the RIYs are relative to iron (or another element), the factors required in eq 4 are those that account for differences among elements such as ionization potentials and atomic weights. Factors that do not change from element to element can be assumed to be unity because they cancel in the ratio with iron. The atomic weight factors in eq 4 are necessary to convert theoretical RIYs calculated on an ions per mole basis to an ions per gram basis. Eq 4 is evaluated for each element.

The sputtering factor, needed in eq 4, is given [6, 7] by:

$$(\text{Sputter factor})_s = \frac{3.56 \alpha_s Z_i Z_s W_i s(E)}{(Z_i^{2/3} + Z_s^{2/3})^{1/2} (W_i + W_s) U_0} \quad (5)$$

In eq 5 (misprinted in ref 1), Z_i and W_i are the atomic number and atomic weight of the incident (argon) ions, whereas Z_s and W_s correspond to the atomic number and atomic weight of an element in the sample. For the sake of simplicity, the interatomic potential in the sputtering model was chosen to have a reciprocal-distance-squared form corresponding to $m = 1/2$ in the notation of ref 6. For this interatomic potential, the reduced stopping power $s(E)$ is equal to the constant 0.327 [6]. In this work the term $[3.56 Z_i W_i s(E)/U_0]$ is set to unity because it cancels in the ratio with iron. The value of the mass-dependent factor α_s , shown in Figure 6 of ref 6, is applicable for $m = 1/2$ (or for $m = 1/3$). In the present work α_s (required in eq 5) has been approximated by the following simple expression:

$$\alpha_s = 0.160 + 0.125(W_s / W_i) \quad (6)$$

The ionization factor used in the present work is a statistical mechanical concept [8] called an occupation number. For the equilibrium process, $M \rightleftharpoons M^+ + 2e^-$, the occupation number gives the fraction of the total particles (atoms plus ions) of an element which are positive ions. As a function of energy and temperature, the occupation number for each element gives the probability (between 0 and 1) of achieving the ionization state, which resides (above the anionic reference state) at an energy equal to the sum of the electron affinity and the first ionization potential. The following equation corresponds to Fermi-Dirac statistics for an ideal gas [8, 9]:

$$(\text{Ionization factor})_s = \frac{1}{1 + e^{+11600(EA_s + IP_s - \mu)/T}} \quad (7)$$

The factor, 11600, in eq 7 is the reciprocal of the Boltzmann constant and has units of reciprocal electron volts. IP_s is the first ionization potential and EA_s is the electron affinity for a given element. The positive electron affinity of most elements corresponds to the energetically favored attachment of an electron to form a negative ion. The anion Au^- from a sputtered sample of gold has been observed by GDMS [10]. Eq 7 is also used for the few elements, including manganese, which have a negative electron affinity. Values for the ionization potentials were taken from ref 11. Values of the electron affinities were taken from Table V of ref 12 with the exception of elements of atomic numbers 58-71, which were either found in the text or set to zero. It was stated [12] that the reported values of the electron affinities, which are typically accurate to $\sim \pm 0.3$ eV, may be accurate only to ± 0.6 eV for some elements.

If the total number of electrons, protons, and neutrons in an atom, ion, or molecule is an even number, then the atom, ion, or molecule will obey Bose-Einstein statistics; whereas if the total number is an odd number, then this particle will obey Fermi-Dirac statistics [8, 9]. By these criteria, the neutral atoms of most of the naturally occurring isotopes are bosons (^6Li , ^9Be , ^{10}B , and ^{14}N are common exceptions); whereas both the anions and the cations of most isotopes are fermions. Electrons are also fermions. In eq 7, the temperature, T , and the chemical potential, μ , are each assumed to be constant at a single location within a given plasma. Degeneracy factors have been ignored. The chemical potential is referenced to the lowest energy state both of the anions for each element and of the unbound electrons of the plasma. For a local equilibrium within the plasma, the electron temperature would equal the ion temperatures. It can be seen from eq 7 that an element would be 50% ionized if $\text{EA} + \text{IP} = \mu$, > 50% ionized if $\text{EA} + \text{IP} < \mu$, and < 50% ionized if $\text{EA} + \text{IP} > \mu$. Eq 5.21 in Chapter 14 of ref 9 is a potentially useful equation which employs only one unknown parameter to predict how μ decreases with increasing temperature in the case of an ideal Fermi-Dirac gas having a fixed composition.

Eq 7 can also be derived by writing the equilibrium constant K for the process, $\text{M}^- \rightleftharpoons \text{M}^+ + 2e^-$, in terms of partition functions: $K = [\text{M}^+][e^-]^2/[\text{M}^-] = Q_{\text{M}^+}Q_e^2/Q_{\text{M}^-}e^{-11600(\text{EA} + \text{IP}_e)/T}$. The ratio $[\text{M}^+]/[\text{M}^-]$ equals $X/(1-X)$ and equals $K/[e^-]^2$. Eq 7 is obtained by (1) assuming that $Q_{\text{M}^+}/Q_{\text{M}^-}$ has a constant ratio among the different elements, (2) letting $e^{11600\mu/T} = Q_{\text{M}^+}Q_e^2/Q_{\text{M}^-}[e^-]^{-2}$, and (3) by solving for X , which is the fraction of the total particles of an element that are positive ions. By this derivation, the term μ , previously called the chemical potential, depends upon the partition function of the electrons, the partition functions of the positive and negative ions of the elements, and $[e^-]$, the total electron concentration in the plasma (at the location that the ions are extracted into the mass spectrometer).

Eq 7 has been derived by two thermodynamic models. In each of these models, the glow discharge plasma can be described as a partially ionized gas mixture in local equilibrium at a single temperature.

Comparison of Calculated RIYs to Experimental RIYs

RIYs calculated for the first 84 elements by the method described by eqs 4-7 are shown in Table 1. Also shown in Table 1 are 17 experimental RIYs previously determined [4] for NIST 1263a Cr-V steel which was analyzed on an EXT-1000 (Extrel Corp.) quadrupole GDMS. (Experimental RIYs were calculated from data in ref 4 to the nearest 0.01.) A temperature parameter of $T = 16,000$ K was chosen to correspond to an average electron energy of ~ 2 eV [1] within the

argon plasma. The chemical-potential parameter of $\mu = 8.3$ eV was chosen within 0.1 eV to give nearly complete agreement to the experimental RIY for aluminum (2.03). By definition, the RIY of iron is 1.00 relative to iron.

Figure 1 shows a strong correlation between calculated RIYs (vertical scale) from Table 1 and the 17 experimental RIYs [4] (horizontal scale) for NIST 1263a Cr-V steel. The element sulfur had the largest relative deviation, which was about a factor of 2 away from a slope of 1.00. The vertical error bars on the individual points of Figure 1 correspond to a reported, typical uncertainty of ± 0.3 eV in the electron affinities of the elements. This uncertainty appears to influence the calculations significantly. Taking into consideration the previously unexplained range from 0.15 to 2.0 among these experimental RIYs, the calculation of RIYs by this method looks promising for these 17 plotted elements. If complete mass-spectral data had been taken originally, it is imagined that fairly reliable concentrations could have been computed for up to 67 other elements within this standard using eq 3 with the calculated RIYs in Table 1.

The temperature parameter of 16,000 K, used in the present calculation, falls within a range of electron temperatures which have been previously reported. Electron temperatures of steel hollow cathodes in argon plasmas at a pressure of 1 torr have been measured [13] in the range of 10,000-25,000 K using a double-probe configuration. (Significantly lower electron temperatures have been obtained in recent work [14, 15] using a Langmuir probe, but at positive potentials even a tiny probe in a single-probe configuration begins to draw significant current [1] as it becomes an anode.) Although ion temperatures have been assigned values near 500 K [1] within a plasma having an average electron energy near 2 eV (corresponding to an electron temperature near 15,500 K), it would seem that, in order for most elements (neutrals and ions) to remain vaporized within a glow-discharge plasma, a temperature of several thousand degrees would be required.

In Table 1, the calculated RIY of oxygen is shown to be 0.02 (about 50 times smaller than the RIY of iron), and only 0.7% of the oxygen of this plasma was calculated to be positive ions. The ionization of oxygen from a europium-oxide sample has been interpreted [16] by the mechanism of Penning ionization whereby metastable neon atoms, but not metastable argon atoms, have sufficient energy to ionize oxygen by interatomic collision. Another explanation, also consistent with the observation of oxygen ion within the neon plasma (but not within the argon plasma), is that the neon plasma may have been higher in temperature than the argon plasma to the extent that a significant fraction of the oxygen was ionized. The calculated percentages of positive ions for all the elements, including oxygen, have reasonable values in Table 1.

Table 1. RIYs calculated for 84 elements using eqs 4-7 with $T = 16,000$ K and $\mu = 8.3$ eV

Element	IP	EA	Percent positive ion	RIY	RIY [4]	Element	IP	EA	Percent positive ion	RIY
H	13.60	0.77	1.21	0.08		Tc	7.28	0.99	50.54	0.83
He	24.48	-0.22	0.00	0.00		Ru	7.36	1.51	39.81	0.65
Li	5.39	0.62	84.03	2.31		Rh	7.46	1.68	35.23	0.58
Be	9.32	0.38	26.60	0.73		Pd	8.33	1.02	31.84	0.51
B	8.30	0.18	46.74	1.30	1.49	Ag	7.57	2.00	28.48	0.46
C	11.26	1.29	4.39	0.13	0.15	Cd	8.99	-0.27	42.45	0.67
N	14.53	-0.21	1.26	0.04		In	5.78	0.20	84.32	1.32
O	13.61	1.46	0.73	0.02		Sn	7.34	1.03	48.73	0.75
F	17.42	3.50	0.01	0.00		Sb	8.64	0.94	28.33	0.43
Ne	21.56	-0.30	0.01	0.00		Te	9.01	1.96	12.61	0.18
Na	5.14	0.54	86.98	2.19		I	10.45	3.06	2.24	0.03
Mg	7.65	-0.22	85.27	1.67		Xe	12.13	-0.45	7.94	0.12
Al	5.98	0.20	82.30	2.02	2.03	Cs	3.89	0.39	94.86	1.39
Si	8.15	1.36	29.37	0.74		Ba	5.21	-0.48	93.01	1.34
P	10.48	0.71	10.96	0.26	0.20	La	5.61	0.55	82.51	1.19
S	10.36	2.04	4.87	0.12	0.25	Ce	5.60	0.60	82.09	1.19
Cl	13.01	3.62	0.24	0.01		Pr	5.46	0.30	86.31	1.26
Ar	15.76	-0.37	0.58	0.01		Nd	5.51	0.10	87.55	1.26
K	4.34	0.47	92.62	2.11		Pm	5.50	0.00	88.39	1.28
Ca	6.11	-1.93	95.20	2.21		Sm	5.60	0.00	87.63	1.24
Sc	6.54	-0.73	85.88	1.84		Eu	5.67	0.00	87.07	1.23
Ti	6.82	-0.02	74.79	1.55	1.78	Gd	6.16	0.20	80.32	1.11
V	6.74	0.63	66.25	1.34	1.58	Tb	5.98	0.00	84.32	1.17
Cr	6.76	0.97	60.19	1.23	1.20	Dy	6.80	0.00	74.79	1.02
Mn	7.43	-0.97	79.15	1.58	1.27	Ho	6.00	0.00	84.12	1.15
Fe	7.87	0.46	49.46	1.00	1.00	Er	6.08	0.00	83.33	1.13
Co	7.86	1.06	38.95	0.77	0.77	Tm	5.81	0.00	85.88	1.17
Ni	7.63	1.62	33.43	0.68	0.68	Yb	6.20	0.00	82.09	1.10
Cu	7.72	1.80	29.22	0.56	0.57	Lu	6.00	0.00	84.12	1.13
Zn	9.39	0.09	29.83	0.57		Hf	7.00	-0.63	80.21	1.06
Ga	6.00	0.37	80.21	1.48		Ta	7.88	0.15	54.88	0.73
Ge	7.88	1.44	32.31	0.59		W	7.98	1.23	34.08	0.45
As	9.81	1.07	13.35	0.24	0.21	Re	7.87	0.38	50.91	0.67
Se	9.75	2.12	6.99	0.12		Os	8.50	1.44	23.34	0.30
Br	11.84	3.36	0.67	0.01		Ir	9.00	1.97	12.61	0.16
Kr	14.00	-0.42	2.13	0.04		Pt	9.00	2.56	8.60	0.11
Rb	4.18	0.42	93.60	1.60		Au	9.22	2.80	6.32	0.08
Sr	5.69	-1.51	95.20	1.62		Hg	10.43	-0.19	19.68	0.25
Y	6.38	-0.40	84.32	1.44		Tl	6.11	0.32	79.51	1.00
Zr	6.84	0.45	67.53	1.15	0.94	Pb	7.42	1.03	47.28	0.59
Nb	6.88	1.13	55.24	0.94	1.17	Bi	7.29	0.95	51.09	0.64
Mo	7.10	1.18	50.36	0.84	1.14	Po	8.43	1.32	25.90	0.33

The RIYs, which were calculated by Vieth and Huneke [5] using the Saha-Eggert equation, correlated within a factor of about 2 to each of the 26 experimental RIYs, which are labeled "a" in ref 17 and which have a range of 0.13-1.89. When the calculated RIYs in Table 1 of the present work are compared to RIYs of [17], 23 of the 26 experimental RIYs agree within a factor of 2.5 with the calculated RIYs in Table 1. This correlation to these experimental RIYs is only slightly more favorable than assigning a value of one to all "calculated" RIYs. Basically, differences exist between the experimental RIYs of refs 4 and 17,

regardless of subsequent theoretical calculations. For example, the experimental RIYs [17] of boron and aluminum, which gave the poorest agreement to calculated RIYs in Table 1, were each lower by a factor of about 6 compared to the experimental RIYs reported in ref 4. Data from these two references were obtained by using different prototype instruments, each based on a quadrupole mass spectrometer.

Figure 2 shows the correlation between 12 calculated and experimental values of RIYs [4] for NIST 495 unalloyed copper. Elements other than copper are present at significantly lower levels in this standard

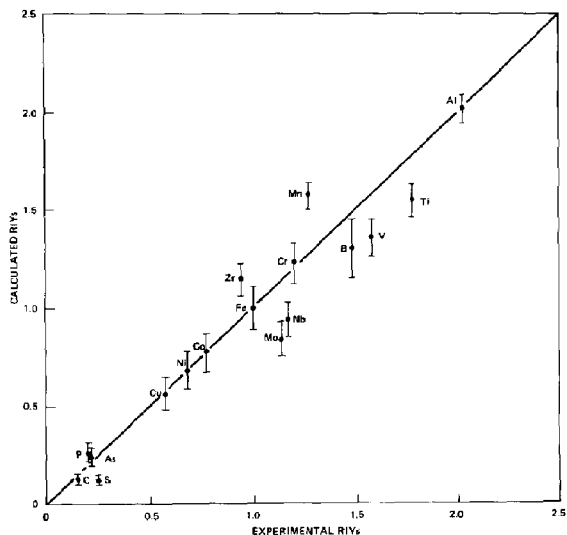


Figure 1. Plot of RIYs determined [4] experimentally for elements certified in NIST 1263a Cr-V steel versus RIYs calculated using eqs 4-7 with $T = 16,000$ K and $\mu = 8.3$ eV. The vertical error bars correspond to the typical uncertainty of ± 0.3 eV in the electron affinities.

than those for which RIYs had been determined in the previous standard. The RIYs for this standard have been measured and calculated relative to the matrix-element copper rather than iron. The correlation shown in Figure 2 is weaker than the correlation in Figure 1. The temperature parameter of 16,000 K was also used to calculate these RIYs. The value of the

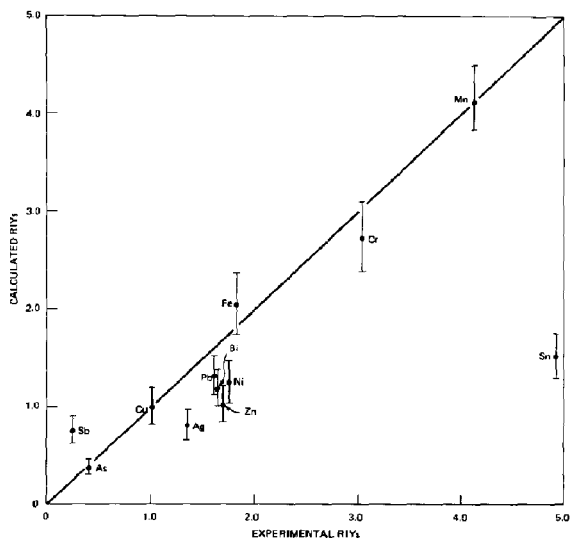


Figure 2. Plot of RIYs determined [4] experimentally for elements certified in NIST 495 unalloyed copper versus RIYs calculated using eqs 4-7 with $T = 16,000$ K and $\mu = 7.2$ eV. The vertical error bars correspond to the typical uncertainty of ± 0.3 eV in the electron affinities.

chemical potential ($\mu = 7.2$ eV) was chosen within 0.1 eV to give nearly complete agreement with the experimental RIY for manganese (4.17). The plotted point for the element tin (Sn), present in the NIST 495 copper at 1.5 wt ppm, is about a factor of 3 away from the line. (In the same ref [4], the experimental RIY of tin, present at 0.88 wt % in NIST 1103 brass, can be calculated to be ~ 2.0 relative to copper. If plotted, this RIY of tin would be favorably close to the line of Figure 2.) The plotted point for the element antimony (Sb), present in the NIST 495 copper at 8.0 wt ppm, is also about a factor of 3 away from the line. Because the correlation in Figure 2 is relatively weak, a fairly wide range of other combinations of temperature and chemical-potential parameters could also have given a correlation comparable to that shown in Figure 2.

Additional work will be required to determine whether further correlations can be found that are strong enough to help determine how the chemical potential and the temperature parameters vary with the plasma compositions derived from different samples. Calculations performed with either a lower temperature parameter or a lower chemical-potential parameter correspond to a plasma in which all elements undergo less ionization. A lowering of either or both of these parameters has the tendency to increase the RIYs which are greater than one and to decrease the RIYs which are less than one. For example, the decrease in the chemical potential from 8.3 to 7.2 eV at 16,000 K (corresponding to Figures 1 and 2) had the effect of increasing RIYs which were larger than one by factors between ~ 1.0 and 1.5 and of decreasing RIYs which were < 1 by factors between about 1.0 and 1.5.

Several experimental requirements are associated with the physical model used for calculating RIYs. The sample should be homogeneous. Both the temperature and the pressure of the plasma should be constant. The plasma should be free of electric arcs and should be sampled by the mass spectrometer at a single location during the measurement. Finally, the peaks in the mass spectrum should be correct both in assignment (with no interferences from ions of similar mass) and in intensity (with no carryover from past samples).

Summary

RIYs have been calculated by using a simple model that takes into account the combined effects of sputtering and ionization. The model requires a temperature parameter and a chemical-potential parameter. Novel features of this model are (1) the reference state of the chemical potential is the electronic ground state of the anion of each element, (2) the chemical potential is assumed to be a constant at a given location within a plasma, and (3) the fraction of the positive ions present in the plasma at a given temperature depends upon the electron affinity and the first ionization potential of the corresponding element.

RIYs calculated from the proposed model correlate favorably with the RIYs previously measured by using two NIST standards. By adjustment of the two parameters of the model, it is hoped that useful, future correlations will be found to the RIYs determined for other samples and for other glow discharge mass spectrometers. Although the establishment of such a correlation could easily improve the semiquantitative elemental analyses from a given instrument, the ultimate analytical goal of this work is to apply RIYs, calculated from theoretical principles, to samples of unknown composition for complete, quantitative elemental analyses by GDMS.

Acknowledgments

The Oak Ridge Y-12 Plant is managed for the U.S. Department of Energy by Martin Marietta Energy Systems, Inc., under Contract DE-AC05-84OR21400. The author thanks Dr. Bill (W. S.) Taylor in the Department of Chemistry at the University of Central Arkansas for his helpful comments regarding this paper.

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