Application of Internal Standard Method for Several 3d-Transition Metallic Elements in Flame Atomic Absorption Spectrometry Using a Multi-wavelength High-resolution Spectrometer

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We investigated a simultaneous internal standard method in flame atomic absorption spectrometry (FAAS), in order to better the analytical precision of 3d-transition metals contained in steel materials. For this purpose, a new spectrometer system for FAAS, comprising a bright xenon lamp as the primary radiation source and a high-resolution Echelle monochromator, was employed to measure several absorption lines at a wavelength width of ca. 0.3 nm at the same time, which enables the absorbances of an analytical line and also an internal standard line to be estimated. In considering several criteria for selecting an internal standard element and the absorption line, it could be suggested that platinum-group elements: ruthenium, rhodium, or palladium, were suitable for an internal standard element to determine the 3d-transition metal elements, such as titanium, iron, and nickel, by measuring an appropriate pair of these absorption lines simultaneously. Several variances of the absorption signal, such as a variation in aspirated amounts of sample solution and a short-period drift of the primary light source, would be corrected and thus reduced, when the absorbance ratio of the analytical line to the internal standard line was measured. In Ti-Pd, Ni-Rh, and Fe-Ru systems chosen as typical test samples, the repeatability of the signal responses was investigated with/without the internal standard method, resulting in better precision when the internal standard method was applied in the FAAS with a nitrous oxide-acetylene flame rather than an air-acetylene flame.

Keywords Flame atomic absorption spectrometry, internal standard method, continuum radiation source spectrometer, 3d-transition metals, palladium-group elements

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the repeatability of absorption signals is investigated for Ti, Fe and Ni, when appropriate line pairs of the analyte and internal standard elements are measured due to the selection criteria for the internal standard method.

**Experimental**

**Apparatus and the operating conditions**

Figure 1 illustrates a block diagram representing the flow of the measurement. A multi-wavelength atomic absorption measurement system (contr AA-700, Analytik Jena Corp., Japan) was employed with a chemical flame atomizer. This apparatus comprised a high-bright xenon lamp as the continuum primary radiation source, covering the wavelength range of 190 – 900 nm, and a high-resolution Echelle-type monochromator equipped with a CCD detector having 200 pixels. A wavelength width of 0.2 – 0.5 nm, which is dependent on the wavelength range, can be simultaneously recorded at an effective spectral resolution of ca. 0.01 nm (full-width at the half maximum of an absorption peak). The chemical flame was generated with gas mixtures of air-acetylene or nitrous oxide-acetylene, where a length of the burner slot was 100 mm for the former and 50 mm for the latter. The mixing ratio of these gas mixtures was varied as an experimental parameter, as will be described later. A conventional pre-mixing-type spray chamber was employed to introduce the sample solution into the burner. A background correction was conducted in each spectrum through the measurement program by using a continuum light source. The beam from the primary radiation source passed above the burner slot at a height of 4 – 16 mm. The absorption values for each spectral line were recorded and analyzed statistically on a personal computer through repeated measurements.

**Reagents and sample preparation**

The following procedures were used to prepare stock solutions of analytes or internal standard elements.

A stock solution of ruthenium was prepared by dissolving 1 g of anhydrous ruthenium chloride(III) (Strem Chemicals Corp.) with a 2.4 M-hydrochloric acid solution, heated on a hot plate. After cooling, the residue was removed with a 5C filter and the solution was heated on a hot plate completely; it was then diluted with 0.5 dm³ with 1 M-hydrochloric acid solution. The concentration of rhodium was determined by ICP atomic emission spectrometry with a standard solution of rhodium. A stock solution of 0.594 gdm⁻³ was obtained.

A stock solution of 1.0-gdm⁻³ palladium was prepared by dissolving pure palladium plate (Nilaco Corp., 99.95 % purity) with a 0.04-dm³ mixture of 4.0 M-hydrochloric acid and 4.7 M-nitric acid on a hot plate completely, and it was then diluted with 0.05-dm³ nitric acid and deionized water to a concentration of 1.0 gdm⁻³ palladium.

A stock solution of 5.0-gdm⁻³ iron was prepared by dissolving 1 g of high-purity iron (Toho Zinc Corp.; more than 99.99%) with a 0.025-dm³ mixture of 2.4 M-hydrochloric acid and 5.6 M-nitric acid on a hot plate completely. After cooling, it was further diluted with 0.7 M-nitric acid to a volume of 0.2 dm³.

A stock solution of 5.0-gdm⁻³ nickel was prepared by dissolving 1 g of pure nickel plate (Nilaco Corp.; 99.95% purity) with 0.03 dm³ of 9.3 M-nitric acid on a hot plate completely, and it was then diluted with deionized water to a volume of 0.2 dm³.

A stock solution of 1.0-gdm⁻³ titanium was prepared by dissolving 0.25 g of pure titanium lump (Mitsuwa Chemicals Corp.; 99.9999% purity) with 0.05 dm³ of 6.0 M-hydrochloric acid on a hot plate completely; it was then diluted with 6.0 M-hydrochloric acid to a volume of 0.25 dm³.

Working solutions for various concentrations of each element were prepared by diluting with deionized water or a hydrochloric acid solution, just before the measurement. Hydrochloric acid and nitric acid were purchased from Nacalai Tesque Corp. (Special-grade reagent).

**Results and Discussion**

**Criterion for selection of internal standard element**

The most important role of an internal standard element is to work as a common standard in the atomization efficiency of an analyte element, which is also affected by the excitation and ionization processes, between the sample solution and the solutions for calibration. Therefore, it is desirable that the chemical and spectrochemical properties of the internal standard element are similar to those of the analyte element. If this condition is fulfilled, several experimental factors; for instance, variations in the aspiration amount of sample solution, fluctuation of the flame, and a long-term drift of the spectrometer, can be corrected by estimating the absorbance ratio between the
analyte and internal standard elements
Furthermore, all of the test solutions should include the internal standard element at exactly the same concentration; therefore, it is required that the internal standard element is not found in the specimen originally but can be later added to the test solutions. In steel materials, not only iron as the matrix, but most of the other 3d-transition metals, are included as the alloyed elements, implying that they are not suitable for the internal standard element. On the other hand, platinum-group elements are not generally alloyed in iron-based materials, meaning that they may be candidates for the internal standard element, also because their oxides, which are generally produced in a chemical flame, are easy to be decomposed and are thus atomized easily. Refractory metals are not suitable for the internal standard element due to their high evaporation temperatures and low vapor pressures, and elements forming stable oxides cannot be selected, due to difficulty concerning their thermal decomposition in a flame. Another criterion for selecting the internal standard element is that it should have many atomic resonance lines related to optical transitions from the ground state of the neutral atom, because larger parts of the atom is in the ground state at the gas temperature of a typical chemical flame (ca. 3000 K) and thus only the resonance atomic lines can give the absorption signal, whereas no absorption response of non-resonance lines appears in the spectrum. Several of palatinum-group elements have high spin multiplicity in the ground-state electron configuration, and thus lead to an absorption spectrum consisting of many atomic resonance lines. Due to a limitation of the spectrometer system regarding the wavelength width, an absorption line of the internal standard element must be located in the neighborhood of that of the analyte element.

When considering these criteria, we can suggest three platinum-group elements: ruthenium, rhodium, and palladium, as the internal standard element. Table 1 lists possible pairs of absorption lines for various 3d-transition metallic elements, indicating that there are several combinations with the atomic resonance lines of ruthenium, rhodium, or palladium. A typical example is a line pair in titanium-palladium, in which the wavelength difference is 0.076 nm and of which the lower energy level is the 3d4s2 F4 (0.0480 eV) for titanium and the 4d5s D3 (0.8138 eV) for palladium. The next step is to validate the effect of the internal standard measurements. In this paper, titanium-palladium, iron-ruthenium, and nickel-rhodium systems are described in the following sections.

### Titanium-palladium system

The atomic absorption of the Ti I 363.546-nm line was measured when the Pd I 363.470-nm line was selected as the internal standard. A nitrous oxide-acetylene flame, which has a higher temperature and reducing atmospheres due to nitrogen radicals such as CN and NH, is recommended to determine titanium in inorganic sample solutions, because thermally-stable titanium oxide may cause a low atomization efficiency of the titanium atom in an air atmosphere. In this case, the flame was burned with a gas mixture of acetylene (fuel) of 190 dm³ h⁻¹ and nitrous-oxide gas of 352 dm³ h⁻¹ (oxidant), and the observation height was fixed at 5 mm above the burner head. These operating conditions were optimized by the absorption signals of titanium as well as palladium.

Each dynamic range for these absorption lines was first estimated by aspirating working solutions of titanium or palladium at a concentration range from 0.04 to 0.4 gdm⁻³. It was defined as the concentration when the slope of a calibration curve at higher concentrations became reduced by a factor of 70% compared to that at the lower concentration. Figure 2 shows calibration curves in the titanium-palladium system, indicating that the dynamic range of Ti I 363.546 nm and Pd I 363.470 nm looks to have a similar value of about 0.4 gdm⁻³. Therefore, a test solution including titanium of 0.1 gdm⁻³ and palladium of 0.1 gdm⁻³, which were within the dynamic range, was prepared.

The absorbances of Ti I 363.546 nm and Pd I 363.470 nm and their ratio were measured repeatedly, and then the standard

| Analyte | Wavelength/nm | Internal standard | Wavelength/nm |
|---------|---------------|-------------------|---------------|
| Sc      | 228.083       | Ru                | 227.957       |
| Ti      | 372.981       | Ru                | 372.803       |
| V       | 363.546       | Pd                | 363.470       |
| Cr      | 359.349       | Ru                | 359.302       |
| Mn      | 209.216       | Ru                | 209.089       |
| Fe      | 273.731       | Ru                | 273.572       |
| Co      | 340.511       | Pd                | 340.458       |
| Ni      | 324.306       | Pd                | 324.270       |
|         | 343.356       | Rh                | 343.489       |

Fig. 2 Relationship between the atomic absorbance of Ti I 363.546 nm (a) and Pd I 363.470 nm (b) and the concentration in several working solution samples.
deviations of them were calculated. Figure 3 shows variations in the absorbance of the absorption lines (the left-hand axis) and the absorbance ratio (the right-hand axis) in ten measurements. Each plot of the absorbance was obtained at an integration time of 3 s. As indicated in Fig. 3, the absorbance ratio was obtained with smaller variations than the absorbances, themselves; the average value of the relative standard deviation was 3.00% for Ti I 363.546 nm and 3.28% for Pd I 363.470 nm, whereas that of the absorbance ratio became lower down to 1.38%. This result is probably because the variances in the absorption signals due to any physical phenomena, such as a temporal variation in the aspirated amount of sample solution or a drift of the flame, could be well corrected, also because the chemical and thermodynamic behaviors of these elements would not be so different in the nitrous oxide-acetylene flame. On the other hand, an air-acetylene flame was not recommended for titanium determination in FAAS, because the absorption signal became very weak due to the poor atomization of titanium. This effect would be attributed to a large difference in the thermodynamic stability of their oxides at higher temperatures. Figure 4 indicates changes in the Gibbs free energy of formation for titanium oxide and palladium oxide, cited from a thermodynamic data collection. The free energy of the titanium oxide becomes more negative at higher temperatures above 600 K in air atmosphere, meaning that it cannot be decomposed under the thermo-dynamic equilibrium condition, and thus becomes more stable at higher temperature, whereas that of the palladium oxide is positive and is thus decomposed spontaneously. Therefore, titanium would be atomized with the aid of any reducing agent; the nitrous oxide flame includes reducing radicals, such as CN and NH, which can contribute to the reduction of titanium oxide. As an effect that oxidation against titanium atom can be overcome in the nitrous oxide flame, the atomization of titanium as well as palladium would occur in a similar manner, contributing to an analytical benefit, such that the internal standard method can work effectively in FAAS, as shown in Fig. 3.

Nickel-rhodium and iron-ruthenium systems

According to a similar procedure to that of the titanium-palladium system, the absorbance ratios of the Ni I 343.356-nm line to the Rh I 343.489-nm line as the internal standard, and of the Fe I 273.731-nm line to the Ru I 273.572-nm line as the internal standard, were measured when an air-acetylene flame was employed instead of the nitrous oxide-acetylene flame. The assignment of these lines is the 3d^4s^2 3F_5/2 (0.0000 eV) for Ni I 343.356 nm, the 4d^75s^2 4F_9/2 (0.0177 eV) for Ru I 273.572 nm, and the 4d^5s^2 4F_7/2 (0.0000 eV) for Ru I 273.572 nm. The air flame is generally employed in the FAAS analysis of iron and nickel, because their oxide species are considered to be reduced into the metallic state, even in the air flame. The measurements were conducted with a gas mixture of acetylene of 50 dm^3 h^-1 and air gas of 440 dm^3 h^-1 in the nickel-rhodium system, and acetylene of 60 dm^3 h^-1 and air gas of 440 dm^3 h^-1 in the iron-ruthenium system. The observation height was set to be 7 and 6 mm above the burner head, respectively. These experimental conditions were optimized so that the absorbance of the analyze element can be maximized. The dynamic ranges of the analyze lines as well as the internal standard lines were estimated by a similar procedure to that of the titanium-palladium system, of which the estimated values were ca. 0.15 gdm^-3 for Fe I 273.731 nm, 0.20 gdm^-3 for Ru I 273.572 nm, 0.10 gdm^-3 for Ni I 343.356 nm, and 0.03 gdm^-3 for Rh I 343.489 nm. Therefore, two test solutions including nickel of 0.04 gdm^-3 and rhodium of 0.0117 gdm^-3 or including iron of 0.1 gdm^-3 and ruthenium of 0.0742 gdm^-3, which were within their dynamic ranges, were prepared for subsequent measurements.

Figure 5 shows plots of the absorbances of Ni I 343.356 nm and Rh I 343.489 nm, as well as their ratio for ten replicates, where each plot of the absorbance was obtained at an integration time of 3 s. Their standard deviations were calculated to be 1.98% for Ni I 343.356 nm, 2.44% for Rh I 343.489 nm, and 1.57% for their ratio, indicating that the data precision was improved to a lesser extent. Also in the nickel-rhodium system, a similar measurement was carried out to investigate the effect of the internal standard method; as a result, the standard deviation of the absorbance was obtained to be 2.76% for Fe I 273.731 nm, 3.89% for Ru I 273.572 nm, and 3.01% for their ratio; therefore, the data precision was almost not improved. It was found in the air-acetylene flame that the internal standard elements, in the nickel-rhodium and the iron-ruthenium systems, could work less effectively than palladium in the titanium-

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**Fig. 3** Repeatability of the absorbance of Ti I 363.546 nm (triangle) and Pd I 363.470 nm (cross-mark), and in their absorbance ratio (square) in ten-replicate measurements, when using a nitrous oxide-acetylene flame.

**Fig. 4** Temperature dependence of the Gibbs free energy of formation for titanium oxide (triangle) and palladium oxide (square).
efficiency, resulting from decomposition of salt and oxide species, is different between standard effect in a different manner. If the atomization oxidant gas, air or nitrous oxide, would contribute to the internal element could work effectively. This effect occurring in the deviations for the variations in the ratio. Also in the iron-ruthenium system, the relative standard deviations were calculated to be 2.18% for Ni I 343.356 nm, 1.77% for Rh I 343.489 nm, and 1.14% for their absorbance were calculated to reduce the variance to be reduced. Their relative standard deviations were calculated to be 2.18% for Ni 343.356 nm, 1.77% for Rh I 343.489 nm, and 1.14% for their ratio. Also in the iron-ruthenium system, the relative standard deviations for the variations in the absorbance were calculated to be 2.90% for Fe I 273.731 nm, 2.65% for Ru I 273.572 nm, and 0.70% for their ratio, indicating that the data precision could be improved to a great extent. Therefore, the nitrous oxide flame would be a key factor so that the internal standard method cannot work effectively in the nickel-rhodium and the iron-ruthenium systems, especially when using the air-acetylene flame.

In the nickel-rhodium and the iron-ruthenium systems, variations in the absorbance signals were also investigated when a nitrous oxide-acetylene flame was employed instead of air-acetylene gas. In this case, the measurements were commonly conducted with a gas mixture of acetylene of 532 dm$^3$ h$^{-1}$ and nitrous oxide gas of 170 dm$^3$ h$^{-1}$, and the observation height was set to be 5 mm above the burner head for the nickel-rhodium system and 6 mm for the iron-ruthenium system. These experimental conditions were optimized so that the absorbance of the analyte elements could be the most intense. Figure 6 shows variations in the absorbances of Ni I 343.356 nm and Rh I 343.489 nm, and their ratio for ten replicates, in the case of the nitrous oxide-acetylene flame, which clearly demonstrates that the absorbance ratio enabled the variance to be reduced. Their relative standard deviations were calculated to be 2.18% for Ni I 343.356 nm, 1.77% for Rh I 343.489 nm, and 1.14% for their ratio. Also in the iron-ruthenium system, the relative standard deviations for the variations in the absorbance were calculated to be 2.90% for Fe I 273.731 nm, 2.65% for Ru I 273.572 nm, and 0.70% for their ratio, indicating that the data precision could be improved to a great extent. Therefore, the nitrous oxide flame would be a key factor so that the internal standard method would be less effective; in this case, the Gibbs free energy of formation for the corresponding oxides should be noted, as summarized in Table 2. It indicates that ruthenium and rhodium oxide can be decomposed much more easily than iron and nickel oxide at a typical flame temperature of 2600 K, leading to different behaviors of their atomization and eventually different responses of the absorption signal. Figure 7 indicates the temperature dependence of the Gibbs free energy of formation for nickel oxide and rhodium oxide. The Gibbs free energy of the nickel oxide is expected to decrease down towards zero at a temperature of more than 3000 K (the oxide becomes more stable at higher temperatures), whereas that of the rhodium oxide is always positive at higher temperatures (the oxide is intrinsically unstable and is decomposed spontaneously). This data implies that there remains a different behavior concerning the decomposition of these oxide species due to their chemical stability in a high-temperature flame. The nitrous oxide-acetylene flame could reduce this effect compared to the air-acetylene flame, because the former flame has a higher gas temperature as well as includes active reducing radicals, such as CN and NH, which can contribute to the reduction of nickel oxide.

**Actual application on internal standard method**

The internal standard method was applied to the determination of nickel in steel materials. The specimens were two standard reference materials for steel analysis (a series of low-alloyed steel), numbered JIS 151-18 and JIS 152-16, which contained 2.96 and 1.98 mass% of nickel, respectively. The samples of 1.0 g were dissolved with a mixed acid solution of 0.01-dm$^3$ hydrochloric acid, 0.01-dm$^3$ nitric acid, and 0.01-dm$^3$ deionized water on a hot plate. After cooling, the residue was removed with a 5B filter, and then 0.05 dm$^3$ of the rhodium standard solution (Rd 0.594 gdm$^{-3}$) was added, and finally sample solutions of 10 gdm$^{-3}$ were prepared by diluting.
duplicate measurements. The internal standard method gives samples with/without the internal standard of rhodium in lower RSDs compared with the normal calibration method, enabling the analytical precision to be improved. It is thus prepared at a nickel concentration range of 0.1 – 0.5 gdm$^{-3}$ by for selecting an internal standard element was investigated, high-resolution spectrometer was employed for an internal water together with 0.05 dm$^3$ of the rhodium standard solution, diluting the stock solution of nickel (5.0 gdm$^{-3}$) with deionized standard method to improve the analytical precision. A/uni00A0criterion difference in the thermodynamic stability of oxide between the standard method to improve the analytical precision under adequate measuring conditions, therefore, the nitrous oxide flame could suppress oxidation of the 3d-transition metallic elements generally. Our work concludes that the nitrous oxide-acetylene flame is recommended for the internal standard method. This technique was applied to analysis of an actual steel material, confirming the better analytical precision in FAAS.

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References

1. J. A. Broekaert, “Analytical Atomic Spectrometry with Flames and Plasmas”, 2002, Chap. 4, Wiley-VCH Verlag, Weinheim.

2. C. R. T. Tarley and M. A. Z. Arruda, Anal. Sci., 2004, 20, 961.

3. M. A. Farajzadeh and M. R. Fallahi, Anal. Sci., 2006, 22, 635.

4. P. Liang, E. Zhao, Q. Ding, and D. Du, Spectrochim. Acta, Part B, 2008, 63, 714.

5. M. T. Naseri, P. Hemmatkhah, M. R. M. Hosseini, and Y. Assadi, Anal. Chim. Acta, 2008, 610, 135.

6. R. Saxena, N. Sharma, and S. Tiwari, Anal. Sci., 2015, 31, 1303.

7. K. E. Thelning, “Steel and Its Heat Treatment”, 2000, Chap. 3, Butterworth-Heinemann, Oxford.

8. H. E. Townsend, Corr. Sci., 2001, 57, 497.

9. JIS G. 1257-0-9, “Atomic Absorption Spectrometric Method of Iron and Steel”, 2013, Japanese Standards Association, Tokyo.

10. T. Ashino, K. Takada, and K. Hirokawa, Anal. Chim. Acta., 1994, 297, 443.

11. T. Ashino and K. Takada, J. Anal. At. Spectrom., 1996, 11, 577.

12. M. B. O. Giacomelli, J. B. B. da Silva, and A. J. Curtius, Analyst, 1999, 124, 1249.

13. J. B. B. da Silva, M. B. O. Giacomelli, and A. J. Curtius, Mikrochim. Acta, 1999, 132, 25.

14. T. Itagaki, T. Ashino, and K. Takada, Fresenius J. Anal. Chem., 2000, 368, 344.

15. K. Yasuda and T. Hasegawa, “Atomic Absorption Analysis”, 1972, Kodansha Scientific, Tokyo.

16. Analytik Jena Corp., “Operation Manual for contr AA-700”, 2013, Analytik Jena Japan, Tokyo.

17. ISO5725, “Accuracy (Trueness and Precision) of Measurement Methods and Results”, 1994 and 1998.

18. T. Itagaki, T. Ashino, K. Takada, and K. Wagatsuma, Bunseki Kagaku, 2015, 64, 117.

19. C. E. Moore, “Atomic Energy Levels”, 1958, Vols. 1 - 3, NBS Circular 467, Washington.

20. I. Barin, “Thermochemical Data of Pure Substances”, 1995, VCH-Verlag, Weinheim.

21. G. F. Kirkbright, M. K. Peters, and T. S. West, Talanta, 1967, 14, 789.

are decomposed much more easily than those of the 3d-transition metals in a high-temperature flame. The nitrous oxide-acetylene flame would work more effectively for reducing these oxide species because of reducing radicals, such as CN and NH in the flame; therefore, the nitrous oxide flame could suppress oxidation of the 3d-transition metallic elements generally. Our work concludes that the nitrous oxide-acetylene flame is recommended for the internal standard method. This technique was applied to analysis of an actual steel material, confirming the better analytical precision in FAAS.

Conclusions

In flame atomic absorption spectrometry, a multi-wavelength high-resolution spectrometer was employed for an internal standard method to improve the analytical precision. A criterion for selecting an internal standard element was investigated, suggesting that 3d-transition metals could be quantized with palatinum-group elements of Ru, Rh, or Pd as the internal standard element. The internal standard method improved the analytical precision under adequate measuring conditions, especially by selecting a nitrous oxide-acetylene flame rather than an air-acetylene flame. The reason for this is that a difference in the thermodynamic stability of oxide between the analyte elements: Ti, Fe, and Ni, and the internal standard element: Pd, Ru, and Rh; oxides of the platinum-group elements

with deionized water. Working solutions for calibration were prepared at a nickel concentration range of 0.1 – 0.5 gdm$^{-3}$ by diluting the stock solution of nickel (5.0 gdm$^{-3}$) with deionized water together with 0.05 dm$^3$ of the rhodium standard solution, while hydrochloric acid and nitric acid were added so that the acid concentration could be maintained to be the same as that in the sample solution.

Table 3 summarizes the analytical result of nickel in the samples with/without the internal standard method in duplicate measurements. The internal standard method gives lower RSDs compared with the normal calibration method, enabling the analytical precision to be improved. It is thus confirmed that the internal standard method can be effective for obtaining the quantification of FAAS with better precision.

| Sample  | Internal standard method | Non-internal standard method |
|---------|--------------------------|------------------------------|
|         | Ni/mass% | RSD, % | Ni/mass% | RSD, % |
| 151-18  | 3.00     | 0.3    | 2.98     | 1.7    |
|         | 3.02     | 0.3    | 2.95     | 1.0    |
| 152-16  | 2.04     | 1.0    | 2.00     | 2.0    |
|         | 2.00     | 1.0    | 2.04     | 1.5    |

Fig. 7 Change of the Gibbs free energy of formation for nickel oxide (triangle) and rhodium oxide (square).