

Determination of Residual Carbon and Nitrogen in Glow Discharge Lamp for Optical Emission Spectrometry

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Since a glow discharge (GD) was developed as a light source by Grimm in 1967,¹ many atomic spectrochemical analysts have been interested in the GD lamp because of its versatility, stability, matrix independence, and depth profile capability. Therefore, GD lamp became an efficient light and ionization source of atomic and inorganic mass spectrometry for the determination of most elements up to sub-ppb levels.²⁻⁴ At present, vacuum pumped and nitrogen purged spectrometers are used in GD-OES so that the determination of gaseous elements as well as metallic elements became possible even if the spectral radiation is emitted in a vacuum ultraviolet region.^{5,6} But the accuracy of analytical result for carbon and nitrogen is hampered by much higher intensity of background than expected. It is known that a part of the high background is caused by the existence of residual gases, which comes from walls in the vacuum system or sample surface by the de-sorption, penetration of atmospheric air through tiny leakage of sealing parts, the oil in the vacuum pump, and the impurities in the plasma gas.⁷

In this work, residual carbon and nitrogen in a GD lamp were determined by using steel standards with known concentrations of carbon and nitrogen.

Experimental Section. The instrument used was LECO 750A glow discharge optical emission spectrometer, which has a dispersion system of two gratings of 3,600 and 1,800 grooves/mm and multi-channel detector. The spectrometer could be evacuated by oil pump and the spectral lines even in the region of vacuum ultraviolet could be measured with a good sensitivity. Following spectral lines were used for the intensity measurements: C 156.143 nm; N 174.272 nm; Fe 371.994 nm. The measuring conditions were 800 to 1200 V and 8 torr Ar for the lamp and 900 V for PM tube. The resulting current was slightly changed depending on the type of specimen, a gas pressure in the lamp and the applied voltage. The lamp of 4 mm dia. anode was used.

The standards of BR 89 (C 6 $\mu\text{g/g}$), NBS 1265 (C 67 $\mu\text{g/g}$), and BAM 191-1 (C 130 $\mu\text{g/g}$) were used for the determination of carbon. But the concentration of carbon in BAM 191-1 was not homogeneous depending on the depth and location so that the values varied within a relative range of $\pm 20\%$. NBS 1265 (N ~ 11 $\mu\text{g/g}$, uncertified), a laboratory made standard P-900 (N 0.57%) and Coronite JK-1N (N

6.7%) for the calibration of nitrogen.

The intensity of each line was measured by a bulk analysis mode, a depth profile mode, and the diagnostics mode. Average intensities were measured by a bulk analysis mode with a specified integration time and then used to calculate average concentrations of elements in a sample. In this work, the intensity of the bulk mode was measured with the integration time of 10 seconds after the pre-sputtering of 3 minutes. The intensity as a function of time was measured by the depth profile mode. And the peak of analytical line was scanned by the diagnostics mode. The scanning of peak was used to characterize the shape of peaks, backgrounds and so on. The background intensity was obtained at the wavelength of peak maximum from the interpolation of measured intensities at the proper both sides of the analytical line. The calibration curves were prepared by plotting the background-corrected peak intensity versus the analyte concentrations in the standards. The concentrations of residual carbon and nitrogen were calculated with the slope and the intercept of calibration curve.

Determination of Carbon. A calibration curve of carbon by the bulk analysis mode showed a larger background than expected. Tusset and Willem⁸ reported that such large background was shown as a large intercept in the calibration curve, which was plotted with 18 steel standards of several Japanese organizations. This is caused by electronic and spectral backgrounds. Stray light, interfering lines and so on were included in the spectral background. Of course, the residual carbon also contributed in the intercept.

For the determination of the residual carbon, the electronic and spectral backgrounds should be eliminated from the total intensity completely as possible. The real background due to the residual carbon was obtained by the interpolation of measured intensities at left and right sides of the analytical line to the wavelength of the peak maximum (see Figure 1). For it, the peak was scanned with the diagnostics mode after the pre-sputtering of 3 minutes. And then the corrected intensity was obtained by subtracting such an instrumental background from the total intensity at the peak. These intensities were plotted versus the carbon concentrations to make the calibration curve (Figure 2).

As shown in Figure 2, the curve also did not pass through

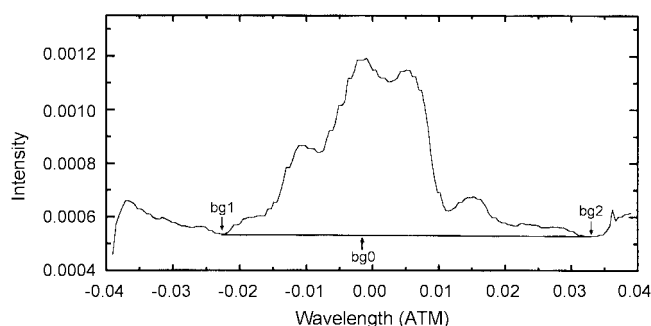


Figure 1. The scanned peak of carbon in a steel standard, BAM 191-1 by a diagnostic mode. Conditions: 800 V and 8 torr for GD lamp; 900 V for PMT. bg1: left background; bg2: right background; bg0: interpolated background.

the origin and the intercept of a significant size exists. This intercept is most probably due to the residual carbon in the lamp. Therefore, the concentration of the residual carbon was calculated from the slope and intercept of the curve. It was $24 \mu\text{g/g}$ at 800 V. Because the conditions for the presence of carbon in the lamp were not constant depending on the time, deviations of about $\pm 10 \mu\text{g/g}$ occur in the concentration of carbon when several measurements of this background equivalent concentration (BEC) are performed during one day. The BEC is significantly dependent on the contamination of the lamp. Therefore, the cleaning of the lamp should be done during the working time and a so called warming-up procedure is recommended. But it was not possible to decrease the deviation to less than $10 \mu\text{g/g}$ in this case because the carbon was not fixed in a specimen, but floated in a space of the lamp. The possibility of such variation was supported by the results of 9 to $61 \mu\text{g/g}$, which were obtained in the round robin test⁹ for the determination of carbon in a low alloy steel sample by the GD-OES. Nine laboratories in European countries participated in the test.

In fact, the determined value was not a real carbon concentration in the GD lamp. It represents only an equivalent value to the carbon in the steel matrix because it was calculated on the base of the carbon concentration in steel standards. If other types of standards were used for this,

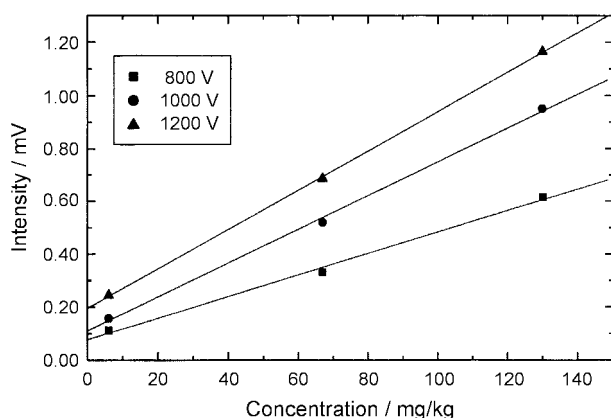


Figure 2. Calibration curves to determine residual carbon in GD lamp and to show applied voltage dependence on intensity of carbon.

different values could be obtained even in the lamp at the same discharge conditions because of the different sputtering rate by the different matrix. Regardless of the type of standards, it could be provided as the absolute mass of carbon per time in the lamp volume if the sputtering rate was included in the calculation. Because only iron matrix standards were used with the same erosion rate, the above value was given in this case.

On the other hand, the slope of calibration curve was known to be dependent upon the applied voltage to GD lamp. In addition to 800 V, the other curves were plotted with the emission intensities at the applied voltages of 1,000 and 1200 V (see Figure 2). The slope of the curve increased with the increase of applied voltage. Such tendency can be explained by the introduction of more sample material at the higher voltage.

Nitrogen. It is considered that the contamination route of nitrogen is different to carbon in GD lamp. That is, most of carbon comes from the pump oil, but nitrogen comes from argon plasma gas as an impurity and from an atmospheric air through the leakage of a lamp by the incomplete sealing.

The size of background could be estimated from the calibration curve of original intensity data, which were obtained by a depth profile mode. Weiss¹⁰ showed such large backgrounds in several calibration curves. As in the case of carbon, the intercept value of the curve was high because there really is nitrogen in the GD lamp existing, which is not caused by the sample. For this, the peak of nitrogen also was scanned by a diagnostics mode and the intensity was corrected by subtracting the electronic and spectral background from the peak intensity. But there were only two kinds of steel standards for nitrogen in this laboratory and their matrixes are much different each other. Therefore, the calibration curve was made by plotting the intensity ratio of nitrogen to iron versus their concentration ratio (Figure 3). The residual concentration of nitrogen was also calculated. The concentration was 0.051%. This value also is not a real concentration in GD lamp, but only an equivalent value in steel as in a case of carbon.

Nitrogen intensity was also observed by using high pure

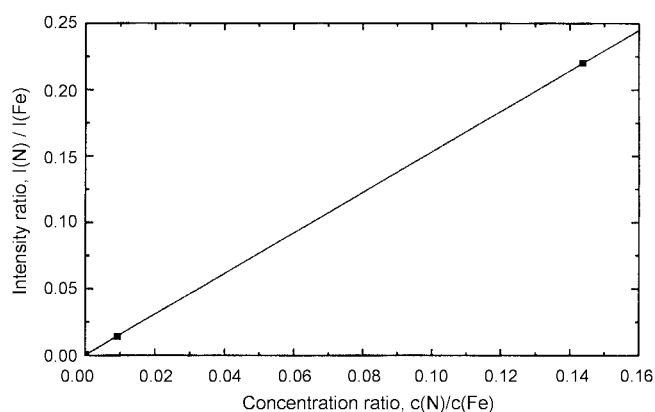


Figure 3. Calibration curve for the residual nitrogen in a GD lamp. Measured at 800 V and 8 torr for lamp, 900 V for PMT.

argon to see the contribution of the impure nitrogen in argon gas to the residual concentration. But the intensity was scarcely decreased by the use of high pure argon. Therefore, the introduction of atmospheric nitrogen through leakages could be considered to be a main source for the residual nitrogen in our case.

In a Summary. residual concentrations of carbon and nitrogen in a GD lamp were determined by using the calibration curves, in which the background-corrected intensity and its ratio were plotted versus the concentration and the ratio for carbon and nitrogen, respectively. The concentrations were 24 $\mu\text{g/g}$ for carbon and 51 $\mu\text{g/g}$ for nitrogen as equivalent values in a steel matrix. The main source of carbon in the GD lamp was considered to be the oil from the vacuum pump and nitrogen was the atmospheric gas through the leakage. Such residual gases can significantly interfere with the accuracy of analytical results. Therefore, the vacuum system must be improved (*e.g.* the oil pump could be replaced with an oil free pump) for carbon and the leakage must be completely sealed, which means the

realization of a high vacuum system for nitrogen.

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