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# Comparative study on the emission spectrometric determination of manganese using nitrogen-oxygen Okamoto-cavity microwave induced plasma and argon radio-frequency inductively-coupled plasma

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ABSTRACT

Microwave-induced plasma optical emission spectrometry (MIP-OES) using Okamoto-cavity was investigated in the determination of manganese, in comparison with argon radio-frequency inductively-coupled plasma (ICP)-OES. An important point of this study is that, in the Okamoto-cavity MIP, the emission intensity of particular atomic emission lines is much elevated by adding oxygen of ca. 10% to the nitrogen matrix plasma gas. Intensity variations in emission lines of manganese atom as well as the ion and in a band head of nitrogen molecule were observed, when oxygen was added to the nitrogen plasma, indicating that the emission intensity of the atomic lines was drastically elevated while the intensities of the ionic lines and the nitrogen band head decreased in a similar manner. This observation can be explained by the fact that the nitrogen excited species, contributing to the transition of the band head, are consumed through collisions with oxygen molecules to cause their dissociation, and eventually manganese atoms in the nitrogen–oxygen plasma would be less ionized than in the pure nitrogen plasma, because the ionization of manganese is also caused by collisions with the nitrogen excited species. Optimization of the measuring parameters in the Okamoto-cavity MIP-OES was conducted for the determination of manganese; as a result, the Mn I 403.076-nm line was recommended as the analytical line in the nitrogen-oxygen mixed gas MIP, while the most intense ionic line, Mn II 257.065 nm, should be employed in the argon ICP. Their detection limits were of the same order, implying that the Okamoto-cavity MIP had as good analytical performance as the conventional ICP.



## 1. Introduction

A 27.12-MHz or 40.68-MHz inductively-coupled plasma (ICP) now becomes the most common excitation source for optical emission spectrometry (OES), which is extensively employed in determination of metallic and metalloid elements in various industrial materials, in spite of several drawbacks of the ICP; for instance, a large amount of argon gas to be introduced. On the other hand, a 2.45-GHz microwave-induced plasma (MIP) has been partly applied for the excitation source in OES. The major reason for this would be some difficulty in loading of aqueous aerosol solution to conventional MIPs excited with a Beenaker cavity [1] or a Surfatron [2], because they cannot be maintained at high microwave powers enough to evaporate water solvent due to overheating of the plasma tube. Furthermore, they cannot produce an annular-shaped plasma like the ICP having a central channel where sample aerosol can be easily introduced with the carrier gas. This weak point has hindered extensive applications of MIP-OES, in spite of a benefit from low consumption of the plasma gas.

The mode transformer of microwave for making the introducing gas to be a plasma state, developed by Okamoto (Okamoto-cavity) [3], excites a surface-wave along the cylindrical conductors under no resonant conditions to concentrate the electric field of microwave at the surrounding portion of the plasma. As a result, the plasma has a doughnut-like structure so that sample aerosols can be easily introduced through a central tube of the plasma torch [3,4], similar to ICP. It has a unique feature beyond the conventional MIPs. The Okamoto-cavity can work at high powers up to 1.5 kW, to make this plasma source highly tolerant to loading of wet aerosols not only in an excitation source in OES [4] but also in an ionization source in mass spectrometry [5]. The MIP-OES with an Okamoto-cavity also has several features beyond a conventional ICP-OES. The Okamoto-cavity MIP can be maintained with various gases, such as nitrogen, nitrogen–oxygen, and helium [6,7], each of which can be available for OES, and, in some cases, it can be operated by using an air compressor without any cylinder gas [8]. As a useful application, organic solvents can be introduced directly when using nitrogen–oxygen mixed gas [7–11]. It was reported that the analytical procedure in a solvent extraction method could be simplified by direct loading of the organic solvent, such as 4-methyl-2-pentanone (methyl isobutyl ketone, MIBK) [11,12]. Furthermore, Okamoto-cavity MIP using pure nitrogen gas is also suitable

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**Table 1**
Apparatus and the operating conditions.

| Components and operating parameters | Description |
|---|---|
| (1) MIP system | |
| Microwave generator | MKN-153-LR-OSC (Nippon Koushuha Corp.) |
| Driving frequency | 2.45 GHz |
| Power supply | KN-153-3T-LR-PS (Nippon Koushuha Corp.) |
| Forward power | 2.0 kW (max) |
| Microwave cavity | Okamoto-type (Hitachi Ltd.) |
| Plasma torch | Duplex quartz tube (No. 300-8352, Hitachi Ltd.) |
| Nebulizer | Pneumatic concentric type (No.306-1582, Hitachi Ltd.) |
| (2) ICP system | |
| RF generator and power supply | Model P-5200 (Hitachi Ltd.) |
| Driving frequency | 27.12 MHZ |
| Forward power | 2.0 kW (max) |
| Load coil | 3 turns |
| Plasma torch | Fassel-type (No.306-1418, Hitachi Ltd.) |
| Neburizer | Pneumatic concentric type (No.306-1582, Hitachi Ltd.) |
| (3) Scanning spectrometer | |
| Monochromator | Modified Czerny-Turner mounting (Hitachi Ltd.) |
| Focal length | 0.75 m |
| Grating | 3600 grooves/mm |
| Blaze wavelength | 200 nm |
| Width of entrance and exit slits | 0.03 mm |
| Photomultiplier | Model R-955 (Hamamatsu Photonics Corp.) |
| (4) Two-dimensional spectrograph | |
| Monochromator | Model 12580 (BunkoKeiki Corp.) |
| Focal length | 0.25 m |
| Grating | 2400 grooves/mm |
| Blaze wavelength | 300 nm |
| Width of entrance and exit slits | 0.5–1.0 mm |
| CCD detector | SensiCam QE Model (PCO Imaging Corp.) |
| Pixels | 1024 × 1024 |

for an ionization source in mass spectrometry due to its low mass interferences [5].

The emission characteristics and the analytical performance of the Okamoto-cavity MIP have been found in several scientific papers [6,8,13,14]. We were interested in the behavior of the Okamoto-cavity MIP using nitrogen–oxygen mixed gas, where the intensities of particular emission lines increased largely when oxygen of up to 20% was added to the nitrogen plasma [9]. It was predicted that emission lines of analyte neutral atoms could be generally enhanced by the oxygen addition, if they had relatively low excitation energies. The reason for this is that a depopulation in higher excited states of nitrogen molecule would be caused by collisions with oxygen molecule, thus suppressing the ionization of the analyte atoms through collisions with these excited species of nitrogen molecule. Our previous study has reported that several emission lines of chromium, having excitation energies of 3.0–3.1 eV, can be employed for the analytical application in the mixed gas MIP-OES, whose detection limits are superior to the result in conventional ICP-OES [15]. Manganese, as well as chromium, is one of the important elements for alloying in steel materials, and thus needs to be frequently analyzed in atomic emission spectrometry. Furthermore, manganese also has sensitive emission lines of the neutral atom having low excitation energies. This paper focuses on the signal-to-background ratio as well as the detection limit in manganese determination in the Okamoto-cavity MIP-OES, in comparison with the corresponding results in ICP-OES, in order to discuss on the applicability of the mixed gas plasma to various metallic elements.

## 2. Experimental

Okamoto's papers have described the structure of the plasma cavity and the principle of operation in detail [3–5]. Also, our previous papers have already denoted the experimental system employed here, where a block diagram of the measuring system is illustrated [15,16]. Table 1 lists the apparatus for the Okamoto-cavity MIP. In this study, nitrogen–oxygen mixed gas was employed as the plasma gas under the conditions that a flow rate of nitrogen was fixed at 14.0 $dm^3$/min and that of the oxygen was varied in the range of 0–1.8 $dm^3$/min, and pure argon of 0.5 $dm^3$/min was introduced as the carrier gas. The forward power of the microwave was adjusted to be 0.8–0.9 kW. The other plasma and measuring conditions were optimized for each analytical line as described later. The emission signal was observed using two spectrometer systems: one was a scanning spectrometer consisting of a Czerny-Turner-mounting monochromator and the other was a two-dimensionally imaging spectrograph [17]. The former spectrometer was employed for measuring the emission intensity at a particular wavelength with high spectral resolution, and the latter provided the spatial distribution of the emission intensity to optimize the measuring conditions [18]. The details for these spectrometers are included in Table 1. For comparison, the emission signal from an argon ICP was also measured on the same scanning spectrometer system and by using the same sample solutions as in the MIP. The details for the ICP system are also summarized in Table 1. Argon flow rates of the plasma, the intermediate, and the carrier gas were fixed at 11.5, 0.50, and 0.55 $dm^3$/min, respectively. An incident power was selected to be 1.0 kW. Two observation heights were employed for each analytical line as described later.

A stock solution of manganese (10 g/$dm^3$) was prepared by dissolving a high-purity manganese metal (99.9%) with 4-M/$dm^3$ hydrochloric acid. Test solutions for estimating the emission characteristics, having the manganese concentration of 200 mg/$dm^3$ or 1000 mg/$dm^3$, and sample solutions for obtaining calibration curves containing 0–30 mg/$dm^3$ were each prepared by diluting the stock solution with de-ionized water.

## 3. Results and discussion

### 3.1. Analytical emission lines

Six neutral atomic lines and three singly-ionized atomic lines of manganese were selected as the analytical lines. The atomic lines have the excitation energies of 4.4 eV and 3.1 eV and the ionic lines have the excitation energy of 4.8 eV. Table 2 summarizes their assignments

**Table 2**
Emission lines of manganese employed in this study.

| Wavelength/nm | Energy levels [19] | | Transition Probability |
|---|---|---|---|
| | Upper (eV) | Lower (eV) | |
| MnII 257.610 | $3d^5 4p\ ^7\mathbf{P}_4$ (4.8114) | $3d^5 4s\ ^7\mathbf{S}_3$ (0.000) | 80 |
| MnII 259.373 | $3d^5 4p\ ^7\mathbf{P}_3$ (4.7786) | $3d^5 4s\ ^7\mathbf{S}_3$ (0.000) | 50 |
| MnII 260.569 | $3d^5 4p\ ^7\mathbf{P}_2$ (4.7567) | $3d^5 4s\ ^7\mathbf{S}_3$ (0.000) | 33 |
| MnI 279.482 | $3d^5 4s4p\ ^6\mathbf{P}_{7/2}$ (4.4348) | $3d^5 4s^2\ ^6\mathbf{S}_{5/2}$ (0.000) | 8.3 |
| MnI 279.827 | $3d^5 4s4p\ ^6\mathbf{P}_{5/2}$ (4.4294) | $3d^5 4s^2\ ^6\mathbf{S}_{5/2}$ (0.000) | 6.7 |
| MnI 280.106 | $3d^5 4s4p\ ^6\mathbf{P}_{5/2}$ (4.4249) | $3d^5 4s^2\ ^6\mathbf{S}_{5/2}$ (0.000) | 4.9 |
| MnI 403.076 | $3d^5 4s4p\ ^6\mathbf{P}_{7/2}$ (3.0750) | $3d^5 4s^2\ ^6\mathbf{S}_{5/2}$ (0.000) | 1.4 |
| MnI 403.307 | $3d^5 4s4p\ ^6\mathbf{P}_{5/2}$ (3.0733) | $3d^5 4s^2\ ^6\mathbf{S}_{5/2}$ (0.000) | 0.95 |
| MnI 403.449 | $3d^5 4s4p\ ^6\mathbf{P}_{3/2}$ (3.0721) | $3d^5 4s^2\ ^6\mathbf{S}_{5/2}$ (0.000) | 0.54 |