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Magnesium nitrate as a chemical modifier to improve sensitivity in manganese determination in plant material by tungsten coil atomic emission spectrometry

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Abstract

In this work, magnesium nitrate is used for the first time as a chemical modifier in atomic emission spectrometry to improve sensitivity and minimize matrix effects in Mn determinations. Magnesium/Mn interactions in the condensed and the gas phases contribute to increasing the population of excited-state Mn atoms, which result in improved sensitivity, precision and accuracy in plant analysis by tungsten coil atomic emission spectrometry (WCAES). The limit of detection calculated for Mn determinations in the presence of 750 mg L^{-1} Mg was 0.05 mg L^{-1}, which is a 17-fold improvement when compared to determinations without using the chemical modifier. Repeatabilities also improved from 6.4 to 3.6 % (RSD, n = 10, Mn 2.5 mg L^{-1}) when Mg was used, and linear responses were observed in the 0.1–7.5 mg L^{-1} Mn range. Manganese concentrations in standard reference materials of plant were 2-fold higher than the certified values for determinations without the modifier. For determinations using $Mg(NO_3)_2$, no statistically significant difference was observed between determined and certified Mn values at the 95% confidence level.

Keywords: Charge-transfer reactions; Chemical modifier; Manganese; Tungsten coil atomizer; Atomic emission spectrometry; Magnesium.

Introduction

Devices that use tungsten coils as atomizers are characterized as open systems with pronounced temperature gradients between the coil surface and the gas phase.[1,2] Due to this inherent characteristic of open systems, some interference process and analyte atomization mechanisms may be affected during instrumental measurement.[3] One of the reasons for such interfering processes is associated to the formation of stable compounds between analyte and concomitant elements, such as mixed oxides, in the condensed phase.[4]

An alternative to minimize matrix effects in electrothermal atomization-based methods is the application of chemical modifiers.[2,5] Commonly used in high concentrations, chemical modifiers provide thermal and temporal separation between analytes and concomitants during the pyrolysis step.[5–13] Often, chemical modifiers thermally stabilize the analyte and allow the removal of matrix components by volatilization, which contributes to minimizing analyte-concomitant interactions and their consequent interfering effects.[10] Different chemical modifiers have been employed in GFAAS measurements, however the mixture Pd + Mg, also known as universal modifier, is used for most analytes.[14] In this case, the effect of Mg is related to thermal stabilization by imbedding analyte atoms in a matrix of MgO, which delays analyte vaporization.[15–17] There still are some controversy regarding the mechanisms involved in chemical modification with palladium. One hypothesis is that intermetallic compounds and stable phases are formed from the interaction between Pd and the analyte.[7] Some authors attribute the analyte thermal stability in presence of Pd to the formation of intercalation compounds, followed by their activation. Finally, the active metal forms strong covalent bonds with the volatile analyte.[18]

The first work employing a chemical modifier in a tungsten coil-based procedure was reported in 1994, for the determination of Ba in water samples.[19] In this work, the authors used EDTA as chemical modifier to eliminate interferences caused by Ca. Due to the high concentrations of EDTA used, the atomizer lifetime was significantly reduced, probably because of the formation of tungsten carbides. Other chemical modifiers were also evaluated for W-coil atomic absorption spectrometry (WCAAS), such as $NH_4H_2PO_4$,[20,21] ascorbic acid,[22] and even the mixture of Pd and Mg.[23] However, the use of Pd as well as the mixture Pd + Mg are usually avoided in WCAAS due to pitting effects on the coil surface observed after only a few runs.[23]

The use of chemical modifiers in tungsten coil-based devices has been mostly restricted to WCAAS. On the other hand, this strategy remains mainly unexplored for tungsten coil atomic emission spectrometry (WCAES), with only two studies published to date. Salido and Jones proposed a procedure using Al or K as chemical modifiers to improve sensitivity in Sr determinations.[24] In a recent work, Silva *et al.* described the use of Co as a chemical modifier to improve sensitivity and minimize matrix effects in Cr determinations by WCAES.[25] In this work, the presence of Co contributes to increasing the population of Cr^+ by charge-transfer reactions in the gas phase. In a second step, Cr^+/e^- recombination takes place, which results in a larger population of excited-state Cr atoms. The charge-transfer reactions are more effective for elements with ionization potential differences (ΔIE) of 2.0 eV or lower.[26–28] This same mechanism could be used to explain the emission signal enhancements observed by Salido and Jones, and Silva *et al.*[24,25] In addition to this two-step mechanism, the analytical signal enhancements observed in WCAES are also depend on similar boiling points (BP) for analyte and chemical modifier. Elements with large BP differences ($\Delta BP \geq \pm 600$ K) from the analyte cause no significant improvement in the analytical signal, probably because they have little interaction in the gas phase due to temporal separation of atomization processes.[25]

In the present work, magnesium nitrate is evaluated to improve sensitivity and minimize matrix effects in Mn determinations by WCAES. Considering Mg effects as chemical modifier,[15] and the gas-phase mechanisms proposed in a previously published work,[23] this strategy may significantly improve limits of detection and accuracy in WCAES determinations.

Experimental

Apparatus

The WCAES device employed in this work has been previously described in the literature.[29] The atomizer consists of a tungsten coil 15 V, 150 W (Osram, Pullach, Germany) housed in a customized glass cell equipped with 2 quartz windows. To control the output current in the filament, a solid state power supply (BatMod, Part Number VI-LU1-EU-BM, Vicor, Andover, MA, USA) was used. A digital-to-analog converter (Measurement Advantage MiniLab 1008, Measurement Computing, Norton, MA, USA), connected to a USB 2.0 port of a Pentium 4 microcomputer (Intel®), in combination with a lab-written Visual Basic 6.0 (Microsoft, Seattle, WA, USA) program, were used to control current and time. Atomic emission signals were collected by a fused silica lens and focused as a 1:1 image onto the entrance slit of a CCD-based spectrometer (Ocean Optics, USB 4000, Dunedin, FL, USA), powered by the same computer used to control the filament power supply.

For Mn (λ = 403.1 nm) determination, 25 µL of sample or reference solutions were directly deposited on the tungsten coil atomizer using an automatic micropipette (Eppendorf 10-100 µl, Brinkman, Westbury, NY, USA). The heating program presented in Table 1 was used in all experiments. The inverted ramp drying cycle was adopted to keep a constant temperature during and right after the complete vaporization of the solvent.[30,31] Vaporization takes place during steps 1-3. By the end of step 3, all solvent has been vaporized and the applied current is reduced further to prevent the atomizer from overheating, which would result in analyte losses. Sample pyrolysis takes place during steps 4 and 5, and a short step with no applied current allows the sample to cool down near room temperature, which can minimize atomization differences due to physical properties of the analytes. Finally, a high current, high temperature atomization step (step 7) is employed to atomize and excite the analytes. Ten consecutive spectra, each one with a 0.4 s integration time, were collected for each measurement during the atomization step. For background correction, the average between background signals recorded on each side of the Mn analytical peak was used.

Reagents and solutions

All solutions were prepared with analytical grade chemicals and distilled-deionized water (18.2 MΩ cm, Milli-Q®, Millipore, Bedford, MA, USA). Manganese reference solutions were prepared by diluting a single-element 1000 mg L^{-1} stock solution (SPEX CerPrep, Metuchen, NJ, USA). A 10 g L^{-1} Mg stock solution (SPEX CerPrep) was used as chemical modifier. For measurements employing chemical modification, the analytical blank consisted of a 750 mg L^{-1} Mg solution.

Trace metal grade concentrated nitric acid (Fischer, Pittsburgh, PA, USA) and hydrogen peroxide 30 % m m^{-1} (Acros, Morris Plains, NJ, USA) were employed for sample digestion. Peach Leaves (SRM 1547, National Institute of Standards and

Technology, NIST, Gaithersbugh, MD, USA) and Tomato Leaves (SRM 1573, NIST) were used to check the procedure's accuracy.

Sample preparation

Aliquots of approximately 250 mg of reference plant material were accurately weighted directly in plastic extraction containers. After this, a volume of 2 mL of concentrated HNO_3 was added to the sample and the mixture was left to react for 1 h. Then, 3 mL of H_2O_2 plus 2 mL of deionized water were added, and the mixtures were heated at 100 ^{o}C in an aluminum block for 2 h. The flasks were then allowed to cool down and reach room temperature before transferring blanks and sample digests to 15 mL polypropylene tubes. The volumes were then made up to 10 mL with distilled-deionized water. Finally, aliquots of chemical modifier were added to each solution to a final concentration of 750 mg L^{-1} Mg, and the volumes were made up to 15 mL with distilled-deionized water.

Results and Discussion

General Aspects

In preliminary studies, it was observed that the presence of Mg at high concentrations cause significant increase in Mn emission signals (λ = 403.1 nm). This effect may be related to charge-transfer and cation/electron recombination reactions in the gas-phase, which increase the population of Mn excited atoms, ultimately increasing atomic emission intensity.[28] A similar effect has been previously observed in both inductively coupled plasma mass and optical emission spectrometries (ICP-MS and ICP OES).[27,28;32–35] In this case, Mg has an ionization potential only 0.21 eV higher than Mn.

Such small difference may facilitate charge-transfer reactions involved in a two-step excitation mechanism (Eqns. 1-2),[36] as described previously for Cr.[25]

$$Mn_{(g)} + Mg^{+}_{(g)} \rightarrow Mn^{+}_{(g)} + Mg_{(g)} \qquad \Delta H = -\ 20.5\ kJ/mol \qquad \textbf{(1)}$$

$$Mn^{+}_{(g)} + e^{-} \rightarrow Mn^{*}_{(g)} \qquad \Delta H = -\ 420.5\ kJ/mol \qquad \textbf{(2)}$$

Magnesium nitrate has been widely used as chemical modifier to increase analytical signals in GF AAS.[5,37] Some authors attribute the thermal stabilization of analytes to their physical occlusion in the presence of high concentrations of Mg.[11,15] Slavin *et al.* evaluated the presence of Mg as a chemical modifier for the determination of Mn.[15] It was observed that Mn atomization is delayed to a higher temperature in the presence of Mg, which, in combination to the use of a L'vov platform, allows atomization to take place in a more thermally homogeneous environment, minimizing matrix effects.[15] In this case, Mg is present as an oxide even in the solid phase. Manganese atoms are then trapped in a matrix of MgO, which delays their atomization until the MgO matrix is vaporized.[15] This process, combined to the two-step mechanism described previously may explain the significant signal improvements observed for Mn when using $Mg(NO_3)_2$ as chemical modifier in WCAES determinations (Fig. 1). For the two-step mechanism to be effective, both analyte and chemical modifier atoms must be in contact in the gas-phase during the atomization step, which requires similar boiling points.[25] Although the BP difference between Mn and Mg is relatively large ($\Delta BP = 971$ K),[36] the fact that Mn atoms are trapped in a MgO matrix, and that they most likely atomize at the same time enables a better interaction between gas-phase species probably formed after the MgO vaporization.[15]

Muzgin *et al.*[38] evaluated some atomization mechanisms taking place on tungsten coil atomizers under an atmosphere of Ar/H_2 (such as the one used in the present work). According to the authors, free Mn atoms are mainly generated by thermal dissociation of MnO (Eqn. 3). On the other hand, Queiroz *et al.*[39] proposed a mechanism for Mg atomization in which mono-magnesium hydroxide is generated in the condensed phase, followed by reduction by hydrogen and generation of free Mg atoms (Eqns. 4-5). Considering these mechanisms, it is reasonable to assume that MnO and MgO/MgOH atomizing at the same time would both be reduced by H_2, and the resulting gas-phase species would participate in the two-step excitation mechanism represented in Eqns. 1-2.

$$\mathrm{MnO_{(s,l)}} + \mathrm{H_{2(g)}} \rightarrow \mathrm{Mn_{(g)}} + \mathrm{H_2O_{(g)}} \quad \mathbf{(3)}$$

$$\mathrm{MgO_{(s,l)}} + \frac{1}{2}\mathrm{H_{2(g)}} \rightarrow \mathrm{MgOH_{(s,l)}} \quad \mathbf{(4)}$$

$$\mathrm{MgOH_{(s,l,g)}} + \frac{1}{2}\mathrm{H_{2(g)}} \rightarrow \mathrm{Mg_{(g)}} + \mathrm{H_2O_{(g)}} \quad \mathbf{(5)}$$

Considering the signal improvement provided by the use of magnesium nitrate (Fig. 1), a procedure employing this chemical modifier to increase sensitivity and minimize matrix effects was developed and applied to Mn determination by WCAES in certified reference samples of plant materials.

Effect of chemical modifier concentration

The effect of modifier concentration on Mn emission signal was evaluated aiming to establish the minimum reagent concentration to yield maximum sensitivity. According to the results presented in Figure 2, the highest emission signals at 403.1 nm were obtained for Mg concentrations above 750 mg L^{-1}, which resulted in analytical signals 3.7-fold higher than the ones obtained without chemical modification. In these conditions, 19 μg of Mg were consumed per determination, which represents a minimal

Mg/Mn ratio of 170. Therefore, a 750 mg L^{-1} Mg solution was used as chemical modifier in all following studies.

Analytical figures of merit and application

The analytical features for Mn solutions containing 750 mg L^{-1} of Mg were estimated and compared with those without the chemical modifier (Table 2). A linear relationship between emission intensity (I) and Mn concentration (C, mg L^{-1}) was observed in the range 0.1–7.5 mg L^{-1} ($I = 2262C + 399$) for solutions containing the chemical modifier. The limit of detection was estimated as 0.05 mg L^{-1}, which is 17-fold lower than the one achieved in the absence of Mg. Comparing the calibration curve slopes for solutions with and without Mg, a 15-fold sensitivity improvement was observed when using the modifier. The precisions calculated as % RSD for a solution containing 2.5 mg L^{-1} of Mn (n = 10) with or without the chemical modifier were 3.6 and 6.4%, respectively. As it can be seen, in addition to increasing sensitivity, the application of $Mg(NO_3)_2$ can also improve repeatability in Mn determinations by WCAES.

The procedure's accuracy was evaluated by analyzing certified reference materials of plant with and without Mg addition (Table 3). In the absence of modifier, Mn values obtained were 2-fold higher than the certified ones. On the other hand, no statistically significant differences between determined and certified Mn values were observed, at a 95 % confidence level, for determinations using Mg. These results indicate that high concentrations of Mg also contribute to minimizing matrix effects in Mn determinations.

It is interesting to note that the high recoveries observed when no chemical modifier was employed may be related to the natural presence of high concentrations of

Mg in plant materials, which would cause the same effect observed when using the chemical modifier. Only in this case, signal increases would be observed for the digested sample, but not for the standard reference solutions. Considering the sample mass initially used and dilutions carried out after digestion, Mg concentrations in the sample solutions were approximately 100 mg L^{-1}. On the other hand, this and other matrix effects may be minimized by the overwhelming effect of adding even higher concentrations of Mg to both sample and standard reference solutions. In this case, in addition to the matrix matching effect, high concentrations of Mg may cause the two-step process represented in Eqns. 1-2 to be dominant and override other matrix effects. Therefore, one may say that the effect caused by Mg on Mn emission is in fact a matrix effect, and that in this case, it can be used to the benefit of the analytical procedure (*e.g.* a Mn signal is only observed in the presence of Mg in Fig. 1).

Conclusions

The use of magnesium nitrate as a chemical modifier in Mn determinations by WCAES results in improved sensitivity, precision, accuracy and power of detection. Manganese atoms are trapped in a MgO matrix, which allows the interaction between Mn and Mg^{+} species in the gas phase. The slightly larger Mg ionization potential contributes to increasing the population of excited-state Mn atoms following charge-transfer and electron recombination reactions. In the presence of 750 mg L^{-1} of Mg, a 17-fold limit of detection improvement was achieved when compared to determinations without the chemical modifier. The high concentrations of Mg added to both samples and standard reference materials also contributed to minimizing matrix effects and improving sensitivity in plant material analysis.

This is the first time that $Mg(NO_3)_2$ is employed as chemical modifier in atomic emission spectrometry. This strategy is easily implemented and may result in significant improvements for methods prone to severe matrix effects such as WCAES.

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Figures captions

Figure 1 – Transients emission signals for manganese solutions (5 mg L^{-1}) in presence (—) and absence (---) of magnesium nitrate (750 mg L^{-1}) as chemical modifier.

Figure 2 - Effect of Mg concentration on Mn emission signals (Mn = 5 mg L^{-1}).

Tables

Table 1 - W-coil heating program for Mn determination.

Step	Applied Current (A)	Time (s)
1	3.0	40
2	2.7	30
3	2.5	20
4	2.0	15
5	1.5	10
6	0	10
7	10	4

Table 2 – Analytical features for Mn solutions in presence and absence of magnesium as chemical modifier.

Analytical Features	**Mn/Mg**	**Mn**
Linear range (mg L^{-1})	0.1 – 7.5	2 - 20
Linear equation	S = 2262C + 399	S = 147C + 4
R	0.998	0.997
LOD (mg L^{-1})	0.05	0.86
RSD (%)	3.6	6.4

Table 3 - Manganese determination (mean ± confidence interval, n = 3) in certified reference materials in presence and absence of magnesium nitrate as chemical modifier.

CRM	Certified value	With chemical modifier	Without chemical modifier
Peach Leaves (SRM 1547)	98 ± 3	94 ± 4	219 ± 25
Tomato Leaves (SRM 1573)	238 ± 7	224 ± 13	448 ± 13

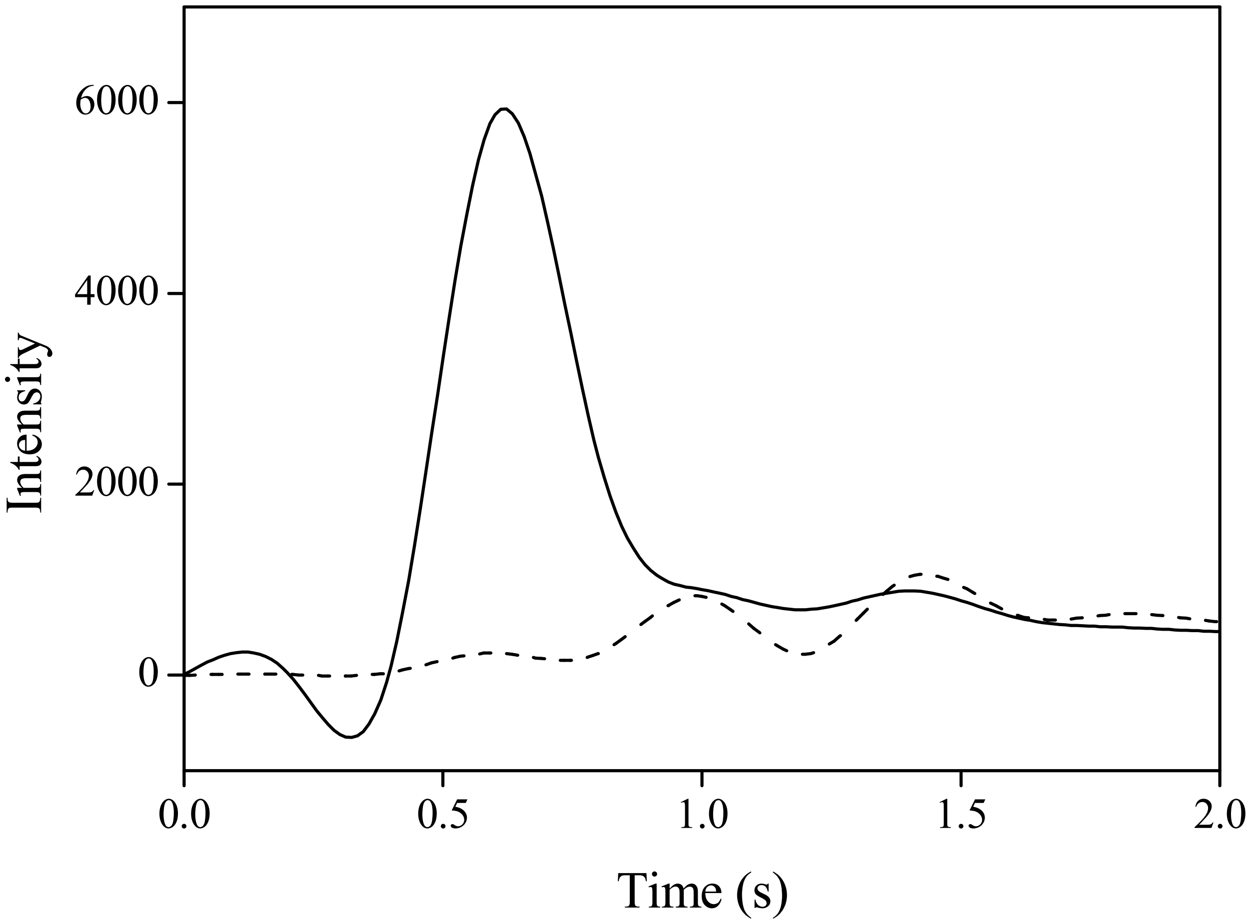

Figure 1

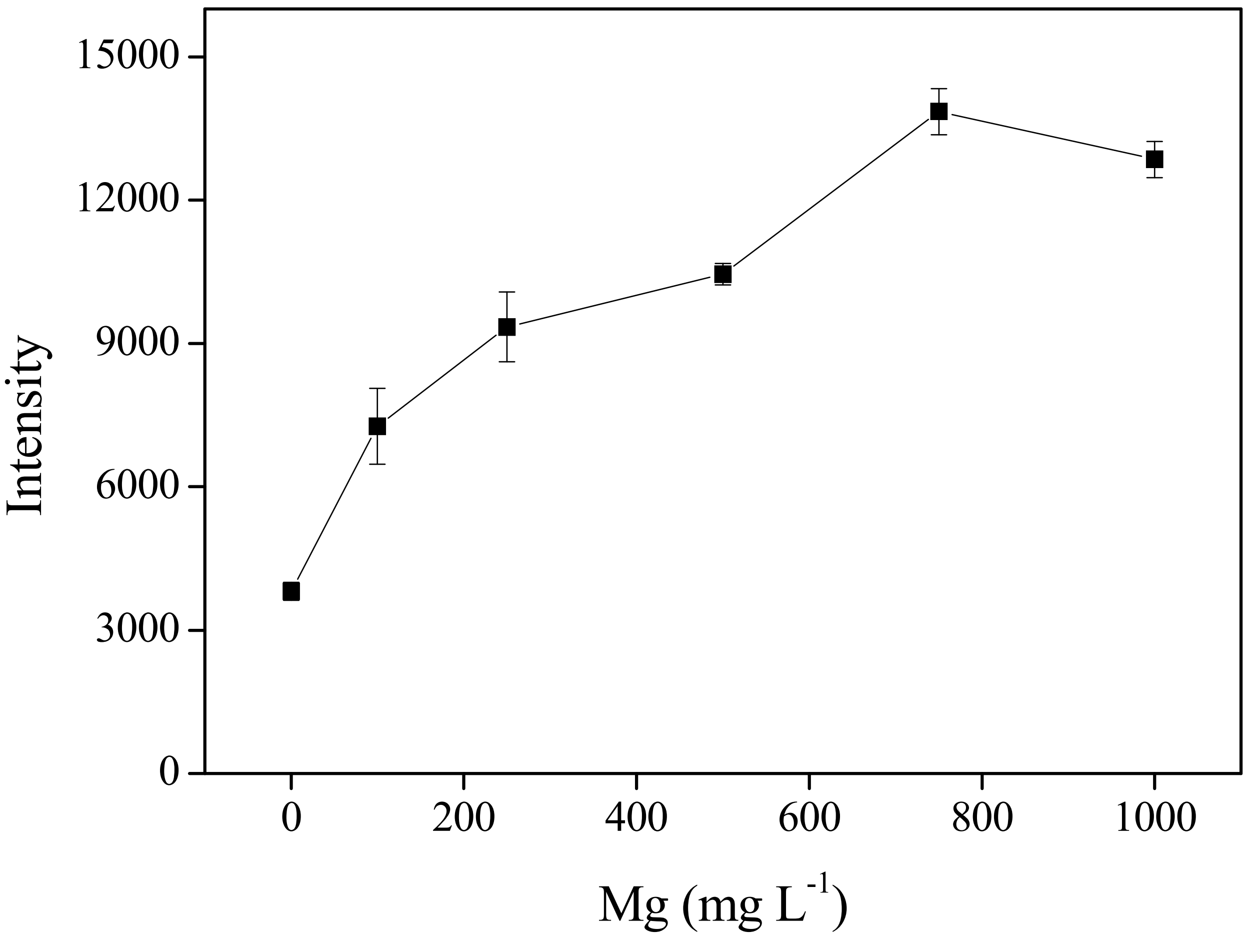
Intensity
15000
12000
9000
6000
3000
0
0
200
400
600
800
1000
Mg (mg L-1)

Figure 2

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The use of magnesium nitrate as a chemical modifier in atomic emission spectrometry to improve sensitivity and minimize matrix effects in Mn determinations is here demonstrated.