

Selective determination of trace magnesium by flame atomic absorption spectrometry after malonate complexation and Sorption on Dowex 50WX8 resin

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Abstract

A simple and selective preconcentration method for magnesium(II) using Dowex 50WX8 ion-exchange resin and complexation by malonate has been developed. The magnesium(II) malonate is eluted from the resin with nitric acid and the magnesium(II) content is determined by flame atomic absorption spectrometry (FAAS). By manipulating flow rate, pH, complexation time and the volumes of sample, complexation agent, and eluent, optimization of the method was achieved. The calibration curve was linear in the range of 0.500 $\mu\text{g mL}^{-1}$ to 10.00 $\mu\text{g mL}^{-1}$ of magnesium(II) with $r = 0.9978$. The limit of detection for magnesium(II) was 0.211 $\mu\text{g mL}^{-1}$. The precision of the method, evaluated as the relative standard deviation for four replicates of 10 $\mu\text{g mL}^{-1}$ magnesium solutions, was lower than 4%. The procedure was validated through recovery studies for magnesium(II) in several Canadian wines with recoveries ranging between 97% and 99%.

Keywords: Magnesium; Preconcentration; Dowex 50WX8; Malonate, Flame Atomic Absorption Spectrometry

Résumé

Nous avons développé une méthode simple et sélective pour la préconcentration du magnésium(II) qui utilise la résine ionique échangeuse Dowex 50WX8 et la complexation par le malonate. Le malonate de magnésium(II) a été élué de la résine par l'acide nitrique

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et le contenu en magnésium(II) mesuré par spectrométrie d'absorption atomique avec flamme (FAAS). La méthode a pu être optimisée en manipulant le débit, le pH, le temps de complexation et le volume de l'échantillon, ainsi que l'agent de complexation et l'éluant. La droite de calibration était linéaire dans la gamme de 0.500 à 10.00 $\mu\text{g mL}^{-1}$ en magnésium(II) avec $r = 0.9978$. La limite de détection du magnésium(II) était de 0.211 $\mu\text{g mL}^{-1}$. La précision de la méthode, évaluée par l'écart type relatif de quatre répétitions sur une solution de magnésium de 10 $\mu\text{g mL}^{-1}$, était inférieure à 4%. La procédure a été validée grâce à une étude de recouvrement du magnésium(II) dans plusieurs vins canadiens avec des valeurs variant entre 97% et 99%.

Introduction

Trace magnesium is vital to the functioning of the human body. It is needed for proper bone formation and in various intracellular enzymatic processes (1). Magnesium plays an important role in regulating the neuromuscular activity of the heart: it maintains normal heart rhythm; it is necessary for proper calcium and vitamin C metabolism; it converts blood sugar into energy (2, 3). Therefore, deficiency of magnesium can lead to high blood pressure (4, 5), increased risk of coronary heart disease (3, 6, 7) and stroke (6, 8), asthma (9) and osteoporosis (10). Trace magnesium is also an essential element to fetal wellbeing during pregnancy and its deficiency has been implicated in pregnancy problems such as pre-eclampsia, pre-term delivery, low birth weight (11, 12), and neonatal mortality (13). In addition, trace elements, including magnesium, in soft drinks and alcoholic beverages have been of great interest due to the possibility of toxicological risks (14). Trace elements

in other matrices such as industrial and environmental samples have also gained a lot of attention because of their effect on human and ecosystem health and thus have become an important part of analytical study (15). The beneficial health effects of magnesium and its disease-prevention qualities emphasize its importance and hence the increased interest in its determination.

In the past, several analytical techniques, such as inductively coupled plasma (ICP) spectrometry, have been utilized to determine trace and ultra trace metal content in aqueous solutions such as wine (16, 17). Even though ICP systems are able to achieve such low levels of detection, the systems are expensive to purchase and maintain (18). As a result, atomic absorption spectrometry (AAS) has been utilized to determine trace metal content in aqueous solutions such as wines (14, 19), and brandies (20). Determining trace metals by flame atomic absorption spectrometry (FAAS) can be amenable to spectral and chemical interferences. For FAAS the problem of direct spectral interference by elements is not very severe (21, 22). Chemical interference is however the biggest source of interference in FAAS. For instance, elements that form oxoanions such as P, B, Si, and Cr can sometimes indirectly interfere by complexing the element of interest. Several approaches can be used to minimize such interference. These include using hotter flames, adjusting the nebulizer to produce a smaller particle size, making observation higher in the flame, and using a releasing agent that would preferentially combine with the interfering element (21, 22). In our work, we did not observe such interferences possibly due to the fuel-to-oxidant ratios and the flame conditions used. In addition, two runs were done with and without addition of a releasing agent, SrCl_2 , to a sample solution. The two runs showed similar results for Mg(II). To carry out selective preconcentration for magnesium(II), a suitable complexation agent is needed. Malonate was chosen as a complexing agent as it is known to form a stable complex with magnesium(II) (23) with the complex having a thermodynamic stability constant, $\log K$, value of 2.90 at 0.01 M ionic strength (24). The fairly high stability constant presumably allows the Mg(II) to be selectively complexed by malonate and thus avoids the complexation of Mg(II) by possible interfering elements.

FAAS does not achieve as low levels of detection as ICP and as mentioned above it suffers from matrix interferences. Selectivity of an element of interest then becomes difficult to achieve. To achieve selectivity preconcentration/separation methods can be used (25). The most widely used preconcentration methods include

co-precipitation, ion-exchange, solvent extraction, and solid phase extraction (25). Previous experiments have shown that factors such as flow rate, pH, complexation time, and the volumes of sample and complexation agent can affect the effectiveness of the preconcentration (15, 25-27).

A number of ion-exchange resins and sorbents have been used for preconcentration and separation methods for trace metals. These include Amberlite XAD resins (25, 27-29), activated carbon (30), octadecyl silica membrane disks (31), silica gel surface (32), cellulose nitrate membrane filter (15), Chromosorb resin (33) and naphthalene-tetraoctylammonium bromide adsorbent (34). In this study we propose the use of Dowex 50WX8, a strongly acidic cation-exchange resin, to separate magnesium(II) from solution after complexation with malonate. The magnesium(II) was determined by flame atomic absorption spectrometry (FAAS). The effects of flow rate, pH, complexation time, and the volumes of sample, chelating agent, and eluent, on the analysis were also studied. The proposed method has been successfully applied to the determination of magnesium(II) in some Canadian wines.

Experimental

Reagents and materials

All chemical reagents used were of analytical grade. Magnesium nitrate hexahydrate, malonic acid (free acid form), concentrated nitric acid (12 M), and concentrated ammonia solution (15 M) were purchased from Fisher Scientific. Filtered 18 M Ω water was used to prepare all solutions. The 400-mesh Dowex 50WX8 resin was purchased from Sigma-Aldrich. The resin was prepared by being washed with approximately 50 mL of water 3 times, followed by 2 washes with approximately 50 mL of 2.4 M nitric acid, and followed by one final wash of approximately 50 mL of water. The malonate buffer (pH 9.15) was prepared by mixing 5.2029 g of malonic acid with 10.00 mL of concentrated ammonia solution and diluting to 500.00 mL in a volumetric flask. A Beckman Φ 340 pH meter with glass electrode was employed for measuring any pH values. Wine samples were obtained commercially through wineries and from British Columbia Liquor Stores. A 50-mL syringe and 0.45- μm syringe filters were used to filter all wine samples.

General procedure

A cut 50-mL Kimax buret fitted with glass wool was used as the preconcentration column. It was filled with

resin slurry to a height of 2.50 cm. This required a resin amount of 1.0737 g. The same resin was used for all samples with frequent washing with water before each experiment. The column was rinsed with 10.00 mL of water before solution was passed through. A pipet bulb was used to maintain the desired flow rate for the solutions. Preconcentration was performed by adding 5.00 mL of the malonate buffer solution (pH 9.15) into a 40.00-mL sample. The solution was gently stirred and allowed to react for 5.00 minutes. After 5.00 minutes, the complexed solution was pushed through the resin with the use of a pipet bulb. The magnesium(II) malonate was eluted from the column with 10.00 mL of 2.4 M nitric acid, yielding an eluent volume of 10.00 mL. The magnesium(II) in the eluent was determined by FAAS.

At the completion of an experiment, the resin column was stored with at least 8.00 mL of water above the top of the resin. To re-use the column for subsequent experiments, it was regenerated by passing through 2.4 M nitric acid and then washed several times with 18 MΩ water.

Experimental conditions and calibration curve

A Varian SpectrAA-55B spectrometer equipped with a magnesium hollow cathode lamp was used for the quantification of the magnesium (II). A set of absorbance readings was collected for each magnesium (II) standard and the sample. The linear regression of the magnesium(II) standards produced a calibration curve having an equation, $A = 0.0271C + 0.0093$, where A and C represent the absorbance and concentration of magnesium(II) respectively. The calibration curve had an r^2 value of 0.9957 i.e. $r = 0.9978$. The uncertainty associated with the slope and intercept were calculated as 1.40% and 19.0% respectively. The calibration curve was linear in the range of $0.500 \mu\text{g mL}^{-1}$ to $10.00 \mu\text{g mL}^{-1}$ of magnesium(II) and a slit width of 1.0 nm was used for all analysis. Under these conditions, as recommended in the Varian instrument analytical methods manual (35), the Mg analytical wavelength of 202.6 nm should be

used rather than the usual analytical wavelength of 285.2 nm. Using the 202.6 nm analytical wavelength yielded satisfactory results in our case. The flame utilized was an air/acetylene mixture. The operating parameters used for determination of magnesium(II) are given in Table 1. The error bars in the figures represent the standard deviation of several determinations.

Results and Discussion

Effect of pH on the percent recovery

The influence of pH of the aqueous solution on the percentage recovery of the magnesium was investigated in the pH range of approximately 6 – 11. This high pH region was chosen for study so as to ensure that all the malonate is in the anionic (L^{2-}) form. Therefore, the single equilibrium involved is between the Mg^{2+} and L^{2-} (malonate) to yield MgL (24). The desired pH was obtained by adding different amounts of 6 M nitric acid and 6 M aqueous ammonia solutions to the complexation agent before being added to the sample. The results are depicted in Figure 1. A pH value of approximately 9.2 gave the highest percentage recovery. At this pH, the precipitation of magnesium hydroxide was not observed. This precipitation was probably prevented since all the malonic acid (H_2L) is essentially in the malonate (L^{2-}) form. Furthermore, the stability constant of MgL is high, which facilitates the formation of the magnesium(II) malonate.

Effect of complexation time on the percent recovery

Using a sample volume of 40.00 mL, the effect of the complexation time on the preconcentration and sorption of the magnesium ions onto the Dowex 50WX8 resin was studied. A 5.00-mL malonate solution buffered at pH 9.15 and an approximate flow rate of 1.25 mL sec^{-1} were used for this investigation. The results are shown in Figure 2. Complexation time variations from 5.00 to 20.00 minutes had no significant effect on the recoveries.

Table 1. Instrument settings for FAAS determination of magnesium.

Parameters	
Measurement mode	Absorbance
Reading precision (PROMT mode)	5%
Wavelength (nm)	202.6
Slit width (nm)	1.0
Active current for lamp (mA)	7
Pre-read delay time (sec)	3.0
Read time (sec)	3.0

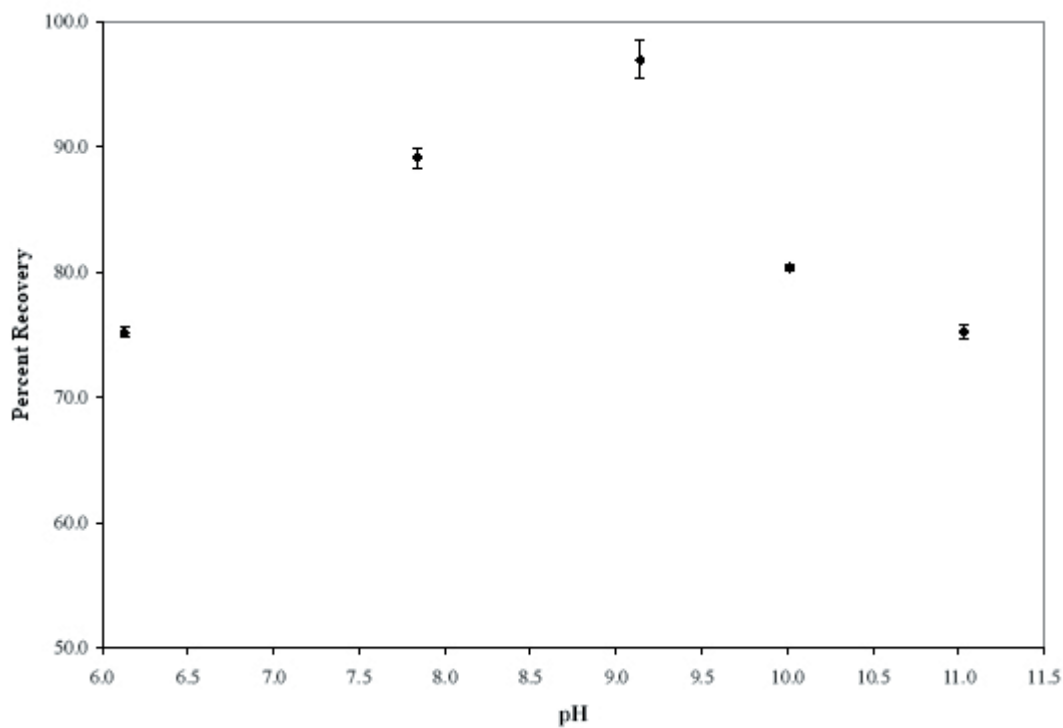


Figure 1. The effects of pH on recoveries of Mg(II) (sample volume: 40.00 mL, complexation agent volume: 5.00 mL, N = 8).

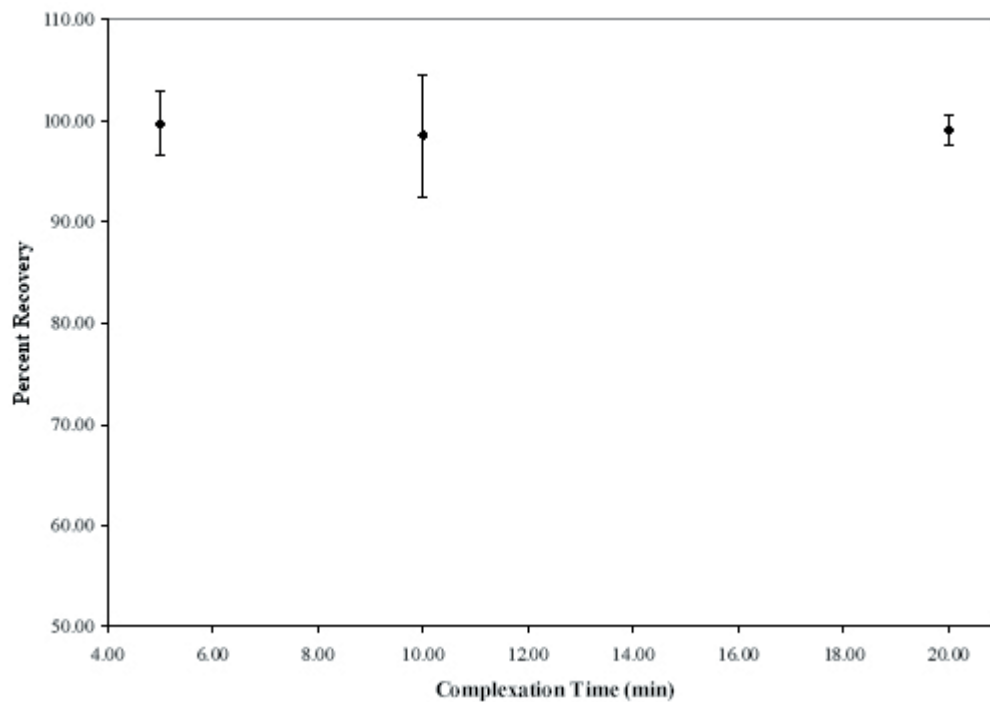


Figure 2. The effect of complexation time on recoveries of Mg(II) (sample volume: 30.00 mL, complexation agent volume: 5.00 mL, pH 9.15, N = 4).

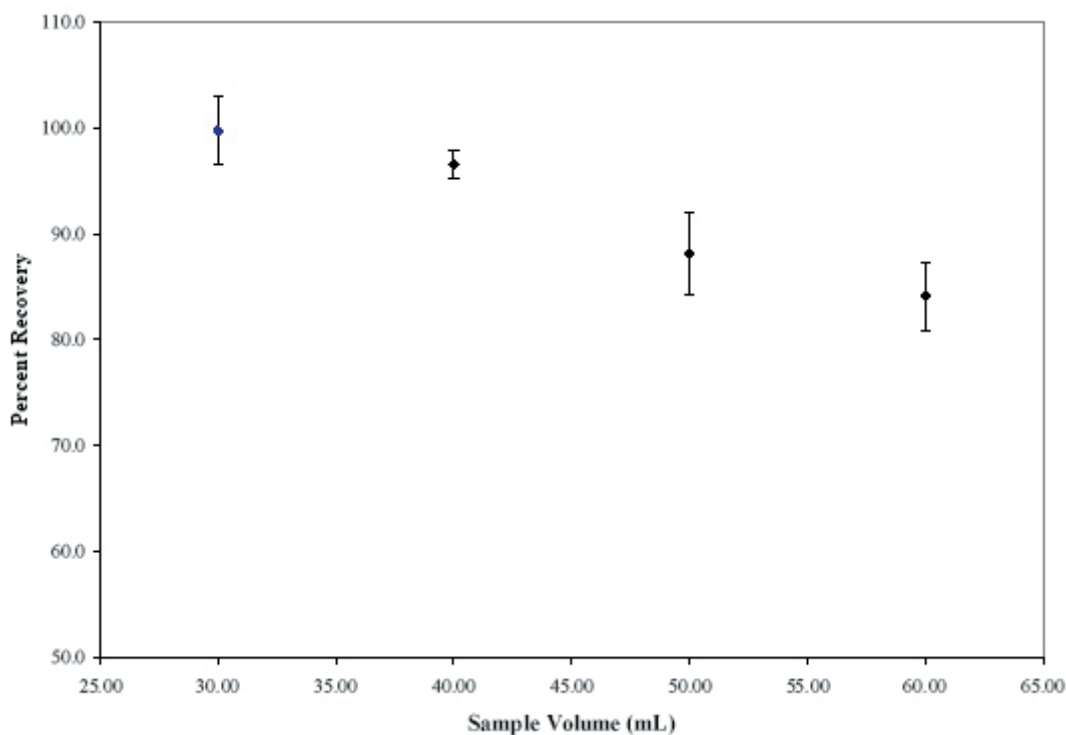


Figure 3. Percent recovery of Mg(II) with variations in sample volume (complexation agent volume:5.00 mL, complexation time: 5.00 min, pH 9.15, N = 8 for all samples except for 30.00 mL where N = 6).

A complexation time of 5.00 minutes was the shortest amount of time that still provided a narrower range of percent recovery in comparison to 10.00 minutes, and had a higher percent recovery average than 20.00 minutes. As a result, all subsequent experiments were performed with a 5.00-minute complexation time.

Effect of sample volume on the percent recovery

The effect of the sample solution volume on the preconcentration and sorption of the magnesium ions onto the Dowex 50WX8 was studied. A 5.00-mL aliquot of the malonate solution buffered at pH 9.15 and an approximate flow rate of 1.25 mL/sec was used in the sample volume range of 30.00 - 60.00 mL in 10.00-mL intervals. The results are depicted in Figure 3. It can be seen that there was a decreasing trend in the percent recovery as the sample volume increased, while keeping the other conditions constant. It can also be seen from Figure 3 that sample volumes of 30.00 mL and 40.00 mL gave higher average percent recoveries than the other volumes. Since the 40.00-mL samples had a smaller spread in percent recovery and thus a better precision than the 30.00-mL samples, 40.00 mL was chosen as the optimal sample volume for this study. Based on this optimal sample volume of 40.00 mL and the final eluent

volume of 10.00 mL used in this study, an enrichment factor of 4 is obtained.

Effect of complexation agent volume on the percent recovery

For completeness, the volume of complexation agent i.e. the malonate buffer (pH 9.15), was also investigated. As can be seen in Figure 4, 5.00-mL samples produced the highest percentage recoveries using a sample volume of 40.00 mL. As a result, 5.00 mL was chosen as the optimal volume for the malonate complexation agent.

Effect of flow rate on the percent recovery

The influence of flow rate on percent recovery was also studied. The two flow rates studied were gravity influenced ($\sim 2.00 \text{ mL min}^{-1}$) and pushing the solution through the column with the use of a pipet bulb ($\sim 1.25 \text{ mL sec}^{-1}$). Flow rate was determined to have no significant effect on the recoveries. All subsequent experiments were performed at $\sim 1.25 \text{ mL sec}^{-1}$.

Table 2 summarizes all the optimal experimental conditions obtained in this study using a $5 \mu\text{g mL}^{-1}$ magnesium(II) standard solution.

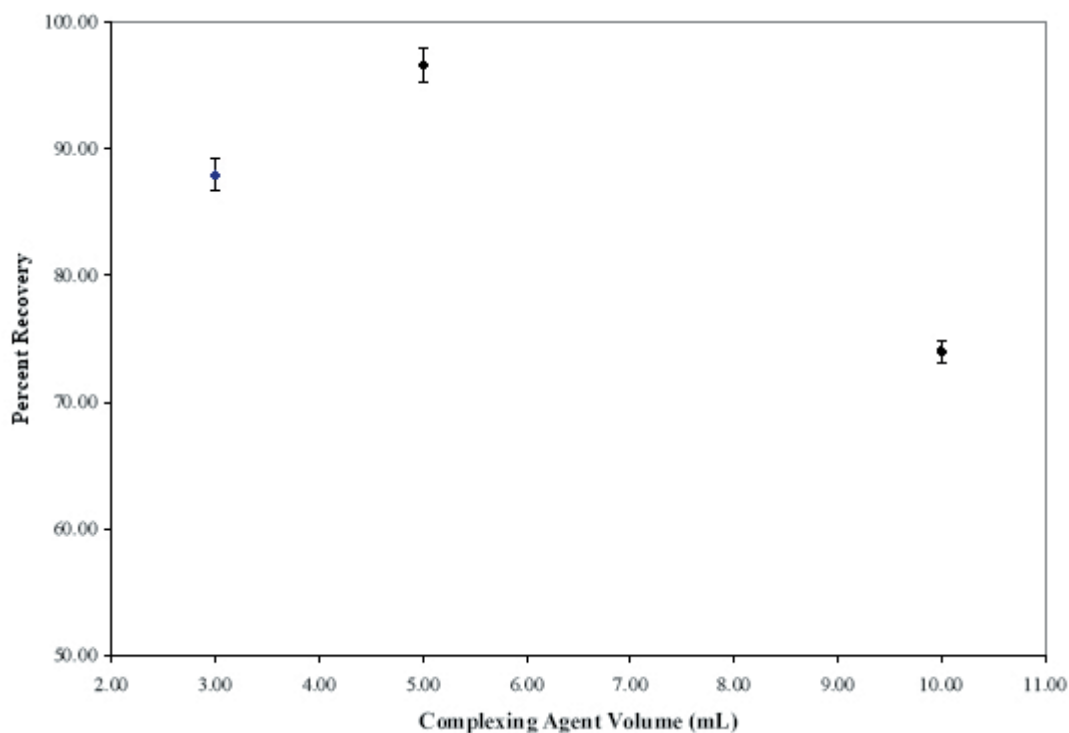


Figure 4. The influence of complexation agent volume on percent recovery of Mg(II) (sample volume: 40.00 mL, pH 9.15, N = 4 except for 5.00 mL where N = 8).

Table 2. Experimentally determined optimized conditions for preconcentration and determination of magnesium(II).

Parameter	Optimized Value
Sample Volume	40.00 mL
Complexation Agent Volume	5.00 mL
Eluent Volume	10.00 mL
Complexation Time	5.00 min
pH	9.15
Flow Rate	~1.25 mL/sec

Table 3. Analysis of diluted wine samples spiked with magnesium(II).

Wine	Average non-spiked diluted wine. Magnesium concentration \pm standard deviation ($\mu\text{g mL}^{-1}$)	Average spiked diluted wine. Magnesium concentration \pm standard deviation ($\mu\text{g mL}^{-1}$)	Percent recovery of magnesium
<i>B</i>	4.46 ± 0.01	5.40 ± 0.03	97.8
<i>D</i>	2.45 ± 0.07	3.37 ± 0.05	98.9

All parameters used were of the optimized values. Wine samples were diluted by a factor of 20 with a spike of $1.00 \mu\text{g mL}^{-1}$ magnesium(II). (For wine *B*: N = 8, for wine *D*: N = 4).

Table 4. Calculated concentrations of magnesium in wines (N = 4 for each wine).

Wine	Concentration of magnesium ($\mu\text{g mL}^{-1}$)
A) Organic Riesling Wine 2001	100.5 \pm 0.7
B) Organic Gewurztraminer 2001	89.2 \pm 0.2
C) Dry Red 2000	79.4 \pm 6.8
D) Dry White 2000	48.9 \pm 1.3
E) Savion Blanc 2001	98.1 \pm 2.1

Recovery of spikes from wine samples

For recovery studies, 20.00 mL of 10.00 $\mu\text{g mL}^{-1}$ magnesium (II) standard solution was spiked into each of two sets of two different wine samples: an organic white wine, *B*, and a non-organic white wine, *D*. A 10.00-mL aliquot was used for each wine sample. The volumes were then made up to 200.00 mL with water in a volumetric flask. This effectively spiked each sample with 1.000 $\mu\text{g mL}^{-1}$ of magnesium. The prepared solutions were then subjected to the preconcentration procedure described in this paper. The values obtained for these samples are shown numerically in Table 3.

Application

The applicability of the proposed method was checked by the analysis of five Canadian commercial wines. The goal here is to find out if the proposed method yields reasonable and typical magnesium(II) values in the wines. Two of the wines are organic white wines labeled *A*, *B*; one is a non-organic (i. e. conventional) red wine labeled *C*; and two are non-organic white wines labeled *D*, *E*. The actual names of the wines are presented in Table 4. All the wines were produced from wineries located in the Okanagan region of British Columbia.

A 10-mL aliquot of each wine sample was filtered through a 0.45- μm syringe filter and diluted with water to represent a final sample volume of 200.00 mL in a volumetric flask. The wine samples were then analyzed using the proposed method and the magnesium(II) concentrations obtained are shown numerically in Table 4. These magnesium(II) values were found to be typical and comparable to magnesium(II) values in wines determined by a flow-injection method (36). This comparison verifies the accuracy of the proposed method.

The two organic white wines, wines *A* and *B*, had magnesium(II) concentrations of approximately 100 and 90 $\mu\text{g mL}^{-1}$ respectively. The concentration of magnesium in the non-organic white wines, wines *D* and *E*, were quite different in value. It was observed that wine *E* may

have had well water used in its production, attributing to it having a much larger magnesium(II) concentration than wine *D*. The non-organic red wine, wine *C*, had a magnesium(II) concentration lower than the organic white wines (approximately 80 $\mu\text{g mL}^{-1}$), but higher than the non-organic white wine that may not have had well water used in its production.

Conclusion

A preconcentration/separation method using malonate to selectively complex magnesium(II) and sorption on a Dowex 50WX8 ion-exchange resin has been developed for the determination of magnesium(II) in aqueous samples. To the best of our knowledge, the use of malonic acid, in the form of malonate, combined with Dowex ion-exchange resin for selective determination of trace divalent metal content such as magnesium(II) has not been studied. Thus, making this study the first of its kind as well as providing an alternative selective method for determining trace magnesium(II) in aqueous solutions. Using this method allowed the successful determination of trace magnesium(II) in some organic and conventional Canadian wines. This method opens up the possibility of applying the same preconcentration technique to other divalent cations in a variety of other aqueous solutions.

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References

1. A. Grollman and E. F. Grollman, "Pharmacology and Therapeutics", 6th ed. Lea, Philadelphia (1965).
2. P. O. Wester, *Am. J. Clin. Nutr.*, **45**, 1305 (1987).
3. N. E. Saris, E. Mervaala, H. Karpanen, J. A. Kharwaja and A. Lewenstam, *Clin. Chim. Acta*, **294**, 1 (2000).
4. Y. Yamori, N. Nara and S. Mizushima, *Health Rep.*, **6**, 22 (1994).
5. S. Douban, M. A. Brodsky, D. D. Whang, and R. Whang, *Am. Heart J.*, **132**, 664 (1996).
6. L. J. Appel, *Clin. Cardiol.*, **22**, 1111 (1999).
7. E. S. Ford, *Int. J. Epidemiol.*, **28**, 645 (1999).
8. A. Ascherio, E. B. Rimm, M. A. Hernan, E. L. Giovannucci, I Kawachi, M. J. Stampfer and W. C. Willett, *Circulation*, **98**, 1198 (1998).
9. P. Fantidis, J. Ruiz Cacho, M. Marin, R. Madero Jarabo, J. Solera and E. Herrero, *Roy. Soc. Med.*, **88**, 441 (1995).
10. R. K. Rude and M. Olerich, *Osteoporosis Int.*, **6**, 453 (1996).
11. P. F. W. Chien, K. S. Khan and N. Arnott, *Brit. J. Obstet. Gynaec.*, **103**, 1085 (1996).
12. W. J. Fawcett, E. J. Haxby and D. A. Male, *Brit. J. Anaesth.*, **83**, 302 (1999).
13. R. A. Almonte, D. L. Heath, J. Whitehall, M. J. Russell, S. Pathole and R. Vink, *Biol. Neonatorum*, **76**, 26 (1999).
14. S. Frias, J. E. Conde, M. A. Rodriguez, V. Dohnal and J. P. Perez-Trujillo, *Nahrung*, **46**, 370 (2002).
15. M. Soylak, U. Divrikli, L. Elci and M. Dogan, *Talanta*, **56**, 565 (2002).
16. G. Thiel, I. Blechschmidt, F. Alt, K-H. Bauer, H. Eschnauer and K. Danzer, Institut fur Anorganische u. Analytische Chemie (1998).
17. V. F. Taylor, H. P. Longrich and J. D. Greenough, *J. Agric. Food Chem.*, **51**, 856 (2003).
18. T. F. Kraemer, M. W. Doughten and T. D. Bullen, *Environ. Sci. Technol.*, **36**, 22 (2002).
19. I. Karadjova, B. Izgi and S. Gucer, *Spectrochimica Acta Part B*, **57**, 581 (2002).
20. A. M. Camean, I. Moreno, M. Lopez-Artiguez, M. Repetto and A. G. Gonzalez, *Talanta*, **54**, 53 (2001).
21. E. H. Evans, ed., "An Introduction to Analytical Atomic Spectrometry", John Wiley and Sons, New York, 1998, p. 46.
22. D. A. Skoog, F.J. Holler and T. A. Nieman, "Principles of Instrumental Analysis, 5th ed., Harcourt Brace College Publishers, Toronto, 1998, p. 218.
23. R. K. Cannan and A. Kibrick, *J. Am. Chem. Soc.*, **60**, 2314 (1938).
24. H. Ren and B. Kratochvil, *J. Chem. Eng. Data*, **40**, 1091 (1995).
25. A. Uzun, M. Soylak and L. Elci, *Talanta*, **54**, 197 (2001).
26. M. Soylak, A. U. Karatepe, L. Elci and M. Dogan, *Turk. J. Chem.*, **27**, 235 (2003).
27. S. L. Costa Ferreira, H. Costa dos Santos, J. Reis Ferreria, N. M. Lopo de Araujo, A. Celso Spinola Costa and D. Santiago de Jesus, *J. Braz. Chem. Soc.*, **9**, 525 (1998).
28. E. J. dos Santos, A. B. Herrmann, A. S. Ribeiro and A. J. Curtius, *Talanta*, **65**, 593 (2005).
29. I. Narin, M. Tuzen and M. Soylak, *Talanta*, **63**, 411 (2004).
30. H. C. dos Dantos, M. G. A Korn and S. L. C. Ferreira, *Anal. Chim. Acta*, **426**, 79 (2001).
31. A. R. Khorrami, H. Naeimi and A. R. Fakhari, *Talanta*, **64**, 13 (2004).
32. H. F. Maltez and E. Carasek, *Talanta*, **65**, 537 (2005).
33. J. Yao, Y. Liu, Y. Tuo, F. Zhou, J. Zhang, Y. Xiao, S. Xiao, and Z. Tan, *Can. J. Anal. Sci. Spectrosc.*, **49**, 267 (2004).
34. N. Pourreza and H. Zavvar Moussavi, *Talanta*, **64**, 264 (2004).
35. "Flame Atomic Absorption Spectrometry: Analytical Methods", Varian Australia Pty Ltd, Victoria, Australia, 1998, p. 37.
36. D. G. Themelis, P. D. Tzanavaras, A. V. Trellopoulos and M. C. Sofoniou, *J. Agric. Food Chem.*, **49**, 5152 (2001)