Comparative Study of Two Inductively Coupled Plasma Atomic Emission Spectrometers Using Ionic-to-Atomic Line Intensity Ratios Under Robust and Non-Robust Conditions

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Summary: The Mg (II) 280.270 nm/ Mg (I) 285.213 nm intensity ratio was used for the comparative study of the matrix effects using two inductively coupled plasma atomic emission spectrometers (ICP-AES) with different torch sizes, under robust and non-robust conditions. We observed that in the presence of a matrix, i.e., 5mg ml^{-1} Na, the values of the ratio obtained were around 7 and 12 for mini-torch and conventional torch ICP systems, respectively. It has also been observed that under robust conditions the matrix effect on different analytes decreased considerably for both ICP systems. Influence of matrix effect, under robust conditions, on the intensity ratios of various ionic-to-atomic lines such as, Cd (II) 226.502 nm/ Cd (I) 228.802 nm, Cr (II) 267.716 nm/ Cr (I) 357.868 nm, Mg (II) 280.270 nm/ Mg (I) 285.213 nm, Ni (II) 231.604 nm/ Ni (I) 232.003 nm, Ni (II) 231.604 nm/ Ni (I) 232.138 nm, Pb (II) 220.353 nm/ Pb (I) 216.999 nm, and Zn (II) 206.200 nm/ Zn (I) 213.857 nm has also been investigated and the ratios were found to vary similarly. It was concluded that the matrix effect due to 5 mg ml^{-1} Na could be minimized efficiently on a mini-torch ICP system under robust conditions and the residual effect may be due to the sample introduction system.

Introduction

During analysis, inductively coupled plasma (ICP) user must plan systematic actions to verify that the ICP system will satisfy given requirements for analytical performance and instrument maintenance. The analysts are mostly concerned with achieving good accuracy and precision for the measurement of elemental concentration in their samples. Good accuracy may be obtained not only by the elimination of systematic errors, i.e. bias, but also by removing matrix effects. The problem of matrix effects has been of major concern in inductively coupled plasma atomic emission spectrometry (ICP-AES). The matrix effects are mainly caused by the presence of elements in high concentration, especially easily ionized elements (EIEs), which may result in enhancement or suppression of analyte signal intensity.

The matrix effects may also be observed when the concentrations of major elements in the standard solutions are different from the sample solutions. In such a case, matrix matching is a recommended way to operate. However, it is not always possible to ensure a perfect matrix matching, particularly when the various processes of sample preparation are not fully controlled. Therefore, it is necessary to obtain ICP operating conditions that could allow some possible changes in the nature or concentration of the matrix components without a significant change in the analyte signal. These conditions are usually called robust conditions and under which plasma parameters, such as temperature and electron number density, are not modified [1-3].

Sophisticated techniques have been used to verify temperature and electron number density, such as measurement of the Stark effect on H_β line for the electron density along with the use of Abel inversion to obtain spatially resolved information [4] and the use of the Boltzmann plot for the excitation temperature. More recently, diagnostic research has been carried out using so-called active methods, mainly based on the use of laser, such as laser induced fluorescence and Thomson and Rayleigh scattering [5-7]. These experiments are time consuming and an ICP user may not be able to modify a commercially available ICP system to undertake such studies.

The use of ionic-to-atomic line intensity ratio is a simpler approach that has been widely applied in ICP-AES. Initially, this approach was

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used to elucidate the departure from local thermodynamic equilibrium (LTE) in an ICP [4, 8-15]. Ionic-to-atomic line intensity ratio was also used to study matrix interferences [2, 14, 16-21]. The Mg (II) 280.270 nm / Mg (I) 285.213 nm ratio has been the most popular choice as a criterion for plasma robustness, energy transfer and residence time. There are three reasons for this choice: (i) the two wavelengths are relatively close, (ii) the intensities of the ionic and atomic lines are of the same magnitude, and (iii) transition probability values are known with an acceptable accuracy so as to compute theoretical ratios using Saha equation. An advantage of ionic-to-atomic line intensity ratio is that it is independent of the type of detector used and therefore, the absolute value of the ratio can be used to compare ICP systems and their operating conditions [22-23]. It has been shown [2] that in a conventional (radial) observational mode of the ICP, the use of the Mg (II) / Mg (I) ratio is an efficient way to study the plasma conditions, in order to minimize the matrix effects. The ratio has also been used to assign possible origins of the matrix effects, such as, change in plasma conditions, or change in aerosol formation, transport and filtering [2-3, 19, 24].

Dennaud et al. [21] used Mg (II) / Mg (I) line intensity ratio to compare two axially viewed ICP systems in terms of matrix effects. The purpose of the present work was to compare the operating conditions of two commercially available ICP systems, one with a conventional torch and the other with a mini-torch, both operating in radial viewing mode, by studying their behaviours towards matrix effects due to a 5mg ml^{-1} concentration of Na, under robust and non-robust conditions, employing Mg (II) / Mg (I) line intensity ratio. Mini-torch ICP systems were developed during 1980s [25-27] after the realization of high cost of argon and high radio frequency power generators used in conventional systems. A mini-torch could be operated at an outer gas flow rate of 8 l min^{-1} and a power of 1 kW as compared to 16 l min^{-1} and 1.5 kW respectively for a conventional system, thus reducing the running cost considerably. The detection limits achievable with a mini-torch ICP are comparable with those obtained by the conventional torch systems [28] and even better in many cases [29, 30]. In view of these advantages of a mini-torch system, it is important to investigate the operating conditions where the matrix effects in the plasma could be reduced and compared with those of a conventional ICP system.

Concept of Robust and Non-Robust Conditions

If the equilibrium was attained in an ICP, it could provide evidence that atomization, excitation and ionization processes would be as efficient as possible and thus robust plasma conditions would be observed. There is a significant influence of both the power and the carrier gas flow rate in determining the robust or non-robust operating conditions [3] as these correspond respectively to efficient and inefficient energy transfer between the plasma surroundings and the central channel. Robustness is obtained when any change in the composition of the matrix does not lead to significant variation in the analytical line intensity. A way of achieving or approaching robust conditions is to use a combination of a high power and long residence time [3, 31]. The concept of residence time is related to the acceleration of the carrier gas flow rate within the load coil from a few to 20-30 m s^{-1} [1]. For a given injector bore, an increase in the residence time is obtained by decreasing the carrier gas flow rate. Therefore, high values of ionic-to-atomic ratio are usually obtained for high rf powers and low carrier gas flow rates, along with an injector of large internal diameter [2, 32]. Non-robust conditions should be avoided for analytical applications; however, they can be useful to enhance matrix effects so as to facilitate their study.

Results and Discussion

Comparison of Mg II / Mg I Ratio

It has been shown [31] that Mg (II) to Mg (I) intensity ratio is a useful indicator of changes in the plasma excitation conditions. In the present studies, 10 µg ml^{-1} Mg in de-ionized water was used to measure Mg (II) / Mg (I) ratio as a function of power and carrier gas flow rate. In the commercial ICP systems, normally used for analytical applications, the observation height is usually optimized using ionic manganese line. Therefore, during the present study, observation heights of both the ICP systems were optimized by maximizing signal to background ratio (SBR) for Mn (II) 257.610 nm line. Keeping the power at 0.65

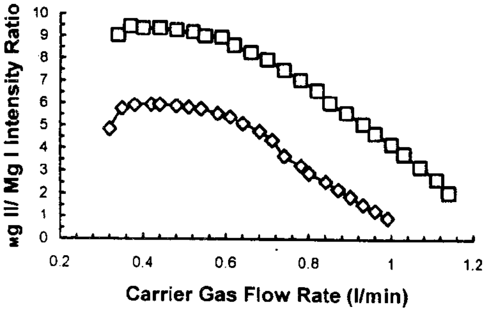

Fig. 1: Comparison of the Mg (II) 280.270 nm/ Mg (I) 285.213 nm line intensity ratio for Mini-torch ICP (◊) and Conventional-torch ICP (□) as a function of carrier gas flow rate. Power for the two systems was 0.65 and 1.2 kW respectively.

kW and 1.2 kW which are the normal working powers for the mini-torch ICP and the conventional-torch ICP respectively, the Mg (II) / Mg (I) intensity ratios were measured on both the ICP systems as a function of carrier gas flow rate and are compared in Fig. 1. These ratios were average of three determinations. It can be seen that the ratios measured on conventional system are higher than those of the mini-torch ICP, and the difference between the two sets of ratios is approximately 3.5 for almost all the values of carrier gas flow rate. This perhaps is not surprising since the mini-torch plasma operates at nearly half the rf power as compared to that of the conventional torch system. This has been reported that robust conditions could be observed for Mg (II) / Mg (I) ratios greater than 8 [2]. This value has been assessed for a conventional torch in radial viewing mode. Consequently, from Fig.1, it seems that for the mini-torch ICP, robust conditions would be achieved at relatively lower values. Maximum ratios of 6 and 9 for mini-torch and the conventional systems respectively, were observed at carrier gas flow rate of 0.4 l min^{-1}.

In Fig. 2, the measured Mg (II) / Mg (I) ratios (average of three determinations) are shown as a function of rf power for mini-torch ICP. Since the mini-torch plasma can only be operated in a limited power range due to plasma stability consideration, the power was varied only from 0.55 kW to 0.7 kW. Similarly, the Mg (II) / Mg (I) ratios measured on the conventional-torch ICP by varying power from 0.7 to 1.6 kW are shown in Fig. 3. Data for both the systems were obtained at carrier gas flow rate of 0.4 l min^{-1}. Following the robust condition of high power and low carrier gas flow rate, it seems reasonable from the data in Figs. 1-3 that the values of 0.7 kW and 0.4 l min^{-1} for the mini-torch; and 1.5 kW and 0.4 l min^{-1} for the conventional-torch ICP, can be chosen to represent robust conditions. The Mg (II) / Mg (I) ratios obtained under robust conditions, were ~7 and ~12 for the mini-torch and conventional systems respectively.

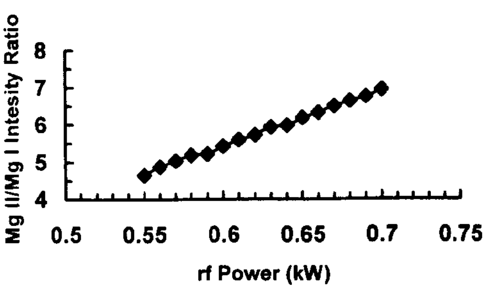

Fig. 2: Mg (II)/ Mg (I) ratio observed on Mini-torch ICP system as a function of rf power. Carrier gas flow rate was 0.4 l/min.

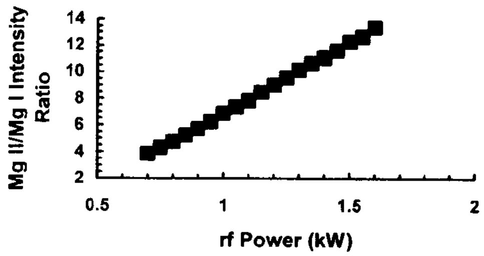

Fig. 3: Mg (II)/ Mg (I) ratio observed on Conventional-torch ICP system as a function of rf power. Carrier gas flow rate was 0.4 l/ min.

Influence of the Robust/Non-Robust Conditions on Atomic and Ionic Lines

This experiment was carried out to study the effect of 5 mg ml^{-1} Na matrix on various atomic and ionic lines under robust and non-robust conditions, using both mini-torch and conventional torch ICP systems. Several atomic and ionic lines of Cr, Cd, Mg, Ni, Pb and Zn are listed in Table- 1.

Table-1: Atomic and ionic lines selected for the study of the sensitivity of the ionic-to-atomic line intensity ratios with reference to matrix effect.

Line (nm)	E_{exc} (eV)	E_{ion} (eV)	E_{sum} (eV)
Cr (I) 357.868	3.46	-	3.46
Mg (I)285.213	4.35	-	4.35
Ni (I) 232.003	5.34	-	5.34
Cd (I) 28.802	5.42	-	5.42
Ni (I) 232.138	5.61	-	5.61
Pb (I) 216.999	5.71	-	5.71
Zn (I) 213.857	5.8	-	5.8
Cr (II) 267.716	4.42	7.65	12.07
Mg (II) 80.270	6.15	6.77	12.92
Cd (II) 26.502	6.39	7.63	14.02
Ni (II) 231.604	5.47	8.99	14.46
Pb (II) 20.353	7.37	7.42	14.79
Zn (II) 06.200	6.01	9.39	15.40

These lines were selected such as to cover a wide range of energy sum as $E_{sum,}$ consisting of excitation energy as E_{exc} and ionization energy as E_{ion}. Line intensities with and without matrix were measured on both ICP systems under robust as well as no-robust conditions. The intensity ratios of signals with matrix to without matrix were normalized to 100, where the value of 100 represents no matrix effect on the original signal due to sodium. The data for the two ICP systems under robust and non-robust conditions were plotted as a function of energy sum as shown in Fig. 4.

Under non-robust conditions, there is an enhancement of line intensities for both the mini-torch and the conventional-torch ICPs. The enhancement effect is clearly line dependent, and follows almost the same pattern for both the systems. On the other hand, under robust conditions, there is a marked decrease in the matrix effect and the data for both the systems explain a light depressive effect on all the signals, except on the atomic lines of Cr and Pb for the mini-torch ICP. A comparison of the percentage change of atomic and ionic line intensities due to 5 mg ml^{-1} Na under robust and non-robust conditions is given in Table-2, for both ICP systems.

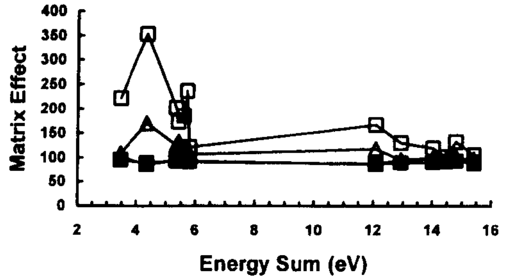

Fig. 4: Matrix effect (normalized intensity ratio with to without matrix) on the original signals due to 5 mg ml^{-1} Na on the atomic and ionic lines given in Table 2, for mini-torch ICP (▲, △) and conventional-torch ICP (■, □), under robust (solid symbols) and non-robust conditions.

Under non-robust conditions, the atomic lines on both the systems show in general, a significant enhancement effect than the ionic lines. Maximum enhancement was observed for Mg (I) 285.213 nm line on both the systems. On mini-torch system, there was an enhancement of all line intensities except Ni and Cd ionic lines, which were

Table- 2: Comparison of the percentage change of atomic and ionic line intensities due to 5 mg ml^{-1} Na under robust and non-robust conditions using the two ICP systems. Negative sign signifies the depressive effect.

Line (nm)	E_{exe} or E_{sum}	Robust		Non-Robust	
		Mini-Torch ICP	Conventional-Torch ICP	Mini-Torch ICP	Conventional-Torch ICP
Cr (I) 357.868	3.46	1.1	-4.7	8.2	121.4
Mg (I) 285.213	4.35	-4.2	-11.3	69.2	253.5
Ni (I) 232.003	5.34	-6.5	-7.3	24.7	101.0
Cd (I) 228.802	5.42	-8.4	-8.2	31.5	71.8
Ni (I) 232.138	5.61	-1.2	-5.5	18.0	84.7
Pb (I) 216.999	5.71	2.4	-7.0	18.3	135.4
Zn (I) 213.857	5.80	-8.1	-9.9	6.1	20.9
Mg (II) 280.270	12.07	-14.3	-13.3	16.6	65.6
Cr (II) 267.716	12.92	-5.4	-11.4	5.0	29.1
Ni (II) 231.604	14.02	-4.2	-10.7	-1.2	18.6
Cd (II) 226.502	14.46	-5.6	-8.8	-2.7	1.3
Pb (II) 220.353	14.79	-2.8	-7.6	1.5	31.7
Zn (II) 206.200	15.40	-3.0	-9.1	-12.5	5.2

depressed very slightly. The depressive effect on Zn ionic line was about 12 percent. There was a negligible enhancement of atomic Zn and ionic Pb lines. For the conventional system, there was a significant enhancement of all the line intensities except Cd and Zn ionic lines where the enhancement was negligible. However, the enhancement of Ni ionic line was 19 %.

Under robust conditions for both the ICP systems, the matrix effect has decreased considerably. On mini-torch ICP, the change in line intensities due to the matrix lies between the extreme limits of 2.4 % (enhancement) for Cr (I) 357.868 nm and -14 % (depressive effect) for Mg (II) 280.270 nm. From Table-2, it is clear that all the analytes under investigation in the presence of 5 mg ml^{-1} Na, can be determined within an accuracy of ± 8 % using atomic or ionic lines except Mg (II) line, which is quite acceptable for most analytical applications. In the case of conventional-torch system, the depressive effect on most of the lines is quite tolerable and lies below 9 % except for Mg (I), Mg (II), Cr (II) and Ni (II) where the depressive effect is within 11 % to 13 %. It appears that for both the ICP systems the effect of robust condition on atomic and ionic lines is similar. Since the ionisation and excitation conditions are not modified, the remaining depressive effect could probably be assigned mainly to aerosol formation and transport. A similar residual depressive effect due to sodium was observed through studies on axially viewed ICP under robust conditions [21], in which case the depressive effect was as high as 50 %.

Comparison of the Sensitivity of Ionic-to-Atomic Line Intensity Ratios to Matrix Effects

Over the years, Mg (II) / Mg (I) ratio has been proved to be useful in the studies of matrix effects. Recently, work has been carried out on axially viewed ICP systems [21] to verify the suitability of other atomic and ionic line pairs in this regard. It could be interesting to carry out such studies using mini-torch and conventional torch ICP systems in radial viewing mode. The selected line pairs for the present work are given in Table-3, and the matrix effect was studied using 5 mg ml^{-1} Na.

Table-3: Line pair used in the study of the sensitivity of the ionic-to-atomic line intensity ratios with reference to matrix effect

Ionic Lines (nm)	Energy Sum (eV)	Atomic Lines (nm)	Exc. Energy (eV)
Cd (II) 226.502	14.47	Cd (I) 228.802	5.42
Cr (II) 267.716	12.92	Cr (I) 357.868	3.46
Mg (II) 280.270	12.07	Mg (I)285.213	4.35
Ni (II) 231.604	14.03	Ni (I) 232.003	5.34
Ni (II) 231.604	14.03	Ni (I) 232.138	5.61
Pb (II) 220.353	14.79	Pb (I) 216.999	5.71
Zn (II) 206.200	15.4	Zn (I) 213.857	5.80

Ionic-to-atomic line intensity ratios for the selected line pairs were calculated from data obtained in the presence of 5 mg ml^{-1} Na, under robust and non-robust conditions for the two ICP systems and are shown as bar diagram in Fig. 5. The ratios have been normalized to those obtained in de-ionized water, therefore, a ratio of 100 signifies no matrix effect. Under non-robust

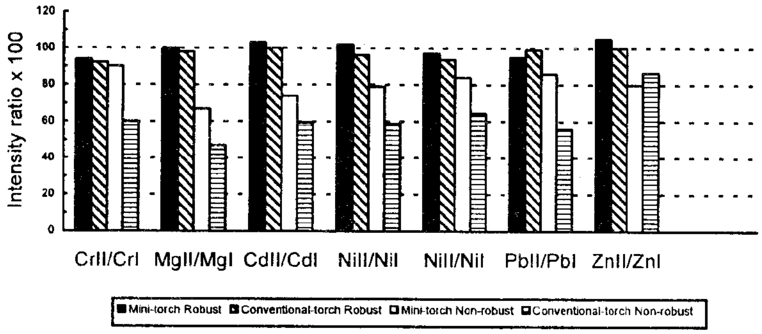

Fig. 5: Ionic-to-atomic line intensity ratios of lines given in Table-2 due to 5 mg ml^{-1} Na. The ratios were normalized to those obtained in water. Data for two Ni (II) / Ni (I) ratios correspond to Ni (II) 231.604/ Ni (I) 232.003 and Ni (II) 231.604/ Ni (I) 232.138 respectively.

conditions, the data for both the systems exhibit considerable depressive matrix effect. In the case of mini-torch ICP, the depressive effect ranges from 10 for Cr (II) / Cr (I), to 33 for Mg (II) / Mg (I) ratio. However, for the conventional-torch system the depressive effect is more pronounced and is in the range of 13 for Zn (II) / Zn (I) and 53 for Mg (II) / Mg (I). Under robust conditions, there is a noticeable improvement in the intensity ratios for both the ICP systems. The matrix effect for the mini-torch ICP has decreased to within ± 6 % and for the conventional-torch system the maximum matrix effect is -8 %. It does seem that under robust conditions, all the line pairs in the present studies behave in a similar fashion, for both the ICP systems.

Experimental

Two commercially available ICP systems, the mini-torch ICP operating at 27.12 MHz and the conventional-torch ICP operating at 40 MHz frequency, were used in radial viewing mode. The main characteristics of the two instruments are compared in Table- 4. Viewing heights above the load coil were obtained for both the systems by maximizing signal-to-background ratio of Mn (II) 257.610 nm line.

Test solutions were prepared using 1mg ml^{-1} standard stock solutions of Penreac. For Mg (II)/ Mg (I) ratio measurement, 10 µg ml^{-1} Mg solution was used. Two multi-element solutions of Cr, Cd, Mg, Ni, Pb and Zn each with 10 µg ml^{-1} concentration were prepared in de-ionized water for measurements of ionic-to-atomic line intensity ratios. One of these solutions also contained 5 mg ml^{-1} Na as matrix element, prepared from extra pure sodium nitrate of Penreac origin.

Conclusions

The Mg (II) / Mg (I) intensity ratio has been found very useful for the comparison of two ICP systems with torches of different size. Under robust conditions, the values of the ratio obtained were around 7 for mini-torch ICP and about 12 for conventional-torch ICP system. It has been reported that for a conventional system in radial viewing mode, robust conditions would be observed for Mg (II) / Mg (I) ratios above 8 and at high power usually above 1.2 kW [2, 21]. This assessment could be valid for a conventional ICP torch. Present studies, however, show that for a mini-torch system, robust conditions could be achieved for a ratio of 7 at 0.7 kW power.

The influence of 5 mg ml^{-1} Na on atomic and ionic lines of Cr, Cd, Mg, Ni, Pb and Zn has

Table- 4: Instrumental details and characteristics of two ICP systems used in the present studies.

	Mini-Torch ICP	Conventional-Torch ICP
Optical mount	Czerny-Turner, vacuum	Czerny-Tumer, nitrogen purge
Focal length (m)	1	0.75
Grating (grooves mm^{-1})	Holographic, 2400	Holographic, 1800
Detector	PMT, R955 Hamamatsu	PMT
RF Generator	27.12 MHz, air cooled, crystal controlled solid state	40 MHz, air cooled, free running, solid state
RF Power, kW		
robust condition	0.7	1.5
non-robust condition	0.6	0.8
Torch	10.5 mm, mini-torch	18 mm, conventional
injector i.d. (mm)	1.4	1.4
Observation height above load coil (mm)	9	9
Nebulizer	Glass concentric	Glass concentric
Spray chamber	Conical glass 45 cm^3, impact sphere	Glass cyclonic
Outer argon gas flow, l min^{-1}	7.5	15
Intermediate gas flow, l min^{-1}	0.8	1.5
Carrier gas flow, l min^{-1}		
robust condition	0.4	0.4
non-robust condition	0.9	1.0

been investigated using both the ICP systems under non-robust as well as robust operating conditions. The matrix effect on all the analyte lines was found to decrease considerably when robust conditions were used. It may be concluded from Table-2 that in both the ICP systems under robust conditions, most of the analytes could be determined with an accuracy of about 10% in the presence of 5 mg ml^{-1} Na.

Influence of 5 mg ml^{-1} Na matrix on the ratios of various atomic and ionic line pairs was investigated under robust and non-robust conditions using both the ICP systems. It was found that the behaviour of all the line pairs on both the systems is very similar. This, however, is contrary to earlier work on axially viewed ICP where Cr (II) / Cr (I) ratio was found to behave very differently from the other ratios [21]. The present work, however, seems to indicate that ionic-to-atomic line intensity ratios other than Mg (II) / Mg (I) ratio may be used to study plasma excitation conditions. It would be interesting to investigate the behaviour of various ionic-to-atomic line intensity ratios in the presence of different matrices, especially using mini-torch ICP system.

From the results obtained in the present study, it is safe to conclude that the matrix effects due to 5 mg ml^{-1} Na can be minimized using robust conditions on a mini-torch ICP system as efficiently as on a conventional torch ICP. Since the excitation and ionization mechanisms are not modified under robust condition, the residual matrix effect of around 10 % may be assigned mainly to aerosol formation and transport.

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