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Direct determination of manganese in produced waters from petroleum exploration by Electrothermal Atomic Absorption Spectrometry using Ir–W as permanent modifier

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ABSTRACT

This present work reports the development and evaluation of a method for the direct determination of manganese in waters extracted during petroleum exploitation by Electrothermal Atomic Absorption Spectrometry (ET AAS) using Ir–W as permanent modifier. These waters, usually called produced waters, contain a wide range of organic and inorganic substances and are characterized by their high salinity. In order to achieve suitable experimental conditions for the method application, studies about the effect of operational variables (chemical modifier, pyrolysis and atomization temperatures) were performed, as well as the establishment of convenient calibration strategy. The best results were verified when the temperatures of pyrolysis and atomization were 1000 °C and 2300 °C, respectively, and using Ir–W as permanent modifier. The results showed that manganese can be determined by the standard addition method or employing external calibration with standard solutions prepared in the same salinity of the samples (with NaCl). Three real samples with salinities varying between 74 and 84‰ were successfully analyzed by the developed procedure. The limits of detection and quantification were 0.24 and 0.80 $\mu g\,L^{-1}$, respectively, in purified water, and 0.34 and 1.1 $\mu g\,L^{-1}$, respectively, in 0.4 $mol\,L^{-1}$ NaCl medium (approximately 23‰ salinity).

1. Introduction

The exploration of petroleum remains as one of the most important activities in the modern society because the large use of petroleum-derived products in different fields. In order to supply the demand, the search for new reservoirs has increased in the last years. In Brazil, the discovery of new petroleum deposits under the sea has opened several new opportunities, but it also has demanded the development of new technologies for the exploration, processing and control of the petroleum, along with its derivatives and the wastes generated from this activity.

One of the main problems associated with the exploration of petroleum found under the seawater is how to deal with the water extracted with the oil. Because of the location of the deposits, large amounts of water are extracted in the drilling process. Moreover, secondary recovery of the petroleum is usually performed by pumping seawater into the wells in order to increase the internal pressure and make possible the recovery of additional quantities of oil. Obviously, the water injected into the wells is removed with petroleum. This water is named produced water and has a very complex composition [1].

Produced waters can have a wide range of chemical substances such as chemicals added during oil recovery (methanol, glycol, poly-electrolytes, etc.), organic salts, aliphatic and aromatic hydrocarbons, heavy metals and, occasionally, radioactive materials usually called NORM (Normally Occurred Radioactive Materials). A remarkable characteristic of the produced waters extracted in offshore operations is the high salinity [2–4]. During drilling operations the amount of water extracted, in offshore platforms, is much larger than the amount of oil. The volume of produced water extracted can vary from 2000 to 40,000 m^3/day, depending on the dimensions of the reservoir, geological characteristics of the region and the capacity of the exploration unity [4,5]. As mentioned previously, this high amount of water is a great problem because it cannot be directly poured back into the sea and must be characterized and treated before discharging [6,7].

The determination of metals in produced waters from petroleum exploration is not a simple task because of the high salinity of the samples and the very low concentration of the metals, characteristics that make difficult the direct application of current techniques employed for the trace level determination of metals such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS),

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Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) or Electrothermal Atomic Absorption Spectrometry (ET AAS).

The ET AAS can be considered one of the most important analytical techniques used for trace metal determination in saline water samples [8–12]. The use of different chemical modifiers is, in general, mandatory because of the deleterious effect of the NaCl on the absorbance signals of great number of metals in the ET AAS technique. The use of permanent chemical modifiers for the direct determination of several analytes in different matrices by ET AAS has increased in the last decade [13]. They present some interesting advantage over the conventional chemical modifiers such as the lower blank values, lower time spent in the sample injection, longer signal term stability and remarkable increase of the graphite tube lifetime [13–18]. However, there are no papers describing the use of permanent modifiers for the direct determination of metals in saline water samples.

The determination of metals in produced waters by ET AAS is not a common subject found in the current literature. Trefry et al. [19] studied the bioaccumulation of heavy metals in some aquatic organisms due to the discharge of produced waters in the Gulf of Mexico. Several metals were determined in 37 samples by ET AAS. Nevertheless, no information regarding the method development or performance is given in the paper. Our research group has also developed methods for the analysis of different metals in produced waters by ET AAS, employing different strategies [20–22].

This present work aims to develop a methodology to perform direct determination of Mn in produced waters obtained from offshore petroleum exploration. The thermal stabilization of Mn in the samples was achieved by using the Ir–W permanent modifier and the method was successfully applied in the determination of the analyte in three samples, with salinities that varied between 74 and 84‰.

2. Experimental

2.1. Apparatus

A Varian (Mulgrave, Australia) electrothermal atomic absorption spectrometer, model Spectra AA240Z, equipped with a Varian GTA 120 graphite furnace unity and a Varian manganese hollow cathode lamp was used throughout the experimental work. The spectrometer was coupled to a PSD 120 auto sampler also supplied by Varian. Integrated absorbance measurements were made by using Varian graphite tubes coated with pyrolytic graphite (Part No. 63-100011-00) and the background correction was performed with a Zeeman-effect based corrector. Argon (99.99%, Linde Gases, Macaé, Brazil) was used as protective gas and the instrumental operating conditions were: 5 mA lamp current, 0.2 nm slit width and 279.5 nm wavelength.

The salinity was estimated by measuring the conductivity of the samples (at 25 °C), comparing the results with a convenient standard. For this purpose, an Analyser 650 conductivity meter (São Paulo, Brazil) equipped with a two-band platinum electrode (covered with platinum black) with 1 cm of cell constant was employed.

2.2. Reagents and solutions

Purified water obtained with a Direct-Q 3 Water System (Millipore, Milford, MA, USA) was employed during the experimental work. All reagents were of analytical grade and used without further purification.

Aqueous stock manganese solution of 1000 μg mL^{-1} was supplied by Tedia (Fairfield, OH, USA). Standard solutions were daily prepared by suitable dilution of the stock solution with water.

Table 1
Temperature program used in the coating procedure of the graphite tube with Ir and Ir–W.

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow rate (mL min^{-1})
1	90	5	30	200
2	140	5	30	200
3	1000	10	10	200
4	2000	0	5	0
5	50	0	10	200

Table 2
Temperature program used in the determination of Mn in produced waters by ET AAS.

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow rate (mL min^{-1})
Drying	80–140	40	10	300
Pyrolysis	[a]	0	15	300
Atomization	[a]	0	5	0
Cleaning	2500	0	4	300

[a] Parameters under study.

Iridium and tungsten solutions used for the permanent modification of the graphite tubes were prepared by adequate dilution of the 1000 μg mL^{-1} stock solutions (supplied by Merck, Darmstadt, Germany) of each element with purified water.

2.3. General procedure

2.3.1. Permanent modification of the graphite tube

Two distinct approaches for permanent modification of the graphite tubes were tested in this present work: (i) permanent modification with a solution containing only iridium and (ii) permanent modification with a solution containing iridium and tungsten. In both cases, the temperature program used for the tube coating was the same employed previously by this research group [20]. The coating procedure of the tubes was performed by injecting 40 μL of a 500 μg mL^{-1} Ir solution or, 40 μL of a solution containing 500 μg mL^{-1} of Ir and 500 μg mL^{-1} of W into the graphite tube. So, the graphite tube was submitted to the temperature program reported in Table 1. This procedure was repeated 25 times before using each tube for analytical measurements.

2.3.2. Determination of manganese by ET AAS

For the measurement of Mn, 20 μL of sample or standard solution were inserted into the graphite tube permanently modified with Ir–W. Afterwards, the temperature program was run and the integrated absorbance was measured. Operational conditions used were those suggested by the manufacturer, except otherwise mentioned. The temperature program used is listed in Table 2.

2.4. Sample collection and storage

The samples of produced waters were supplied by Petrobras. According to Petrobras, the samples were previously treated in order to eliminate the high content of oil mixed with the water. Afterwards, the samples were collected in decontaminated polyethylene flasks, acidified with concentrated nitric acid to pH 1.8–2.0 and maintained in the refrigerator at 4 °C.

3. Results and discussion

3.1. Evaluation of Mn thermal behavior

Manganese determination in saline samples is classically carried out in the presence of chemical modifiers, which are used to keep

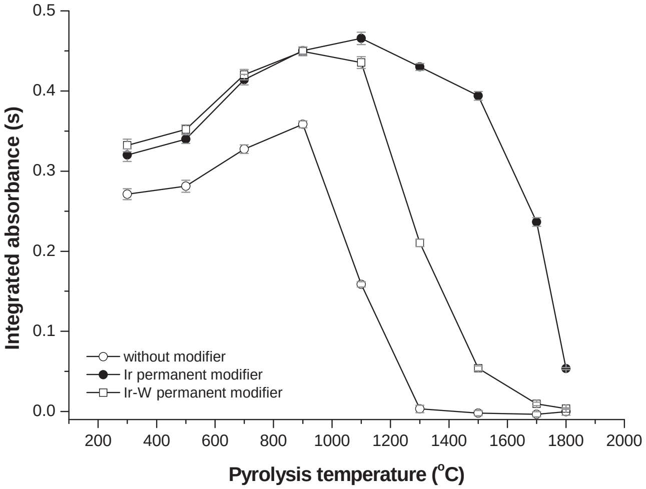

Fig. 1. Pyrolysis curves for manganese in purified water. [Mn] = 5 μg L^{-1}.

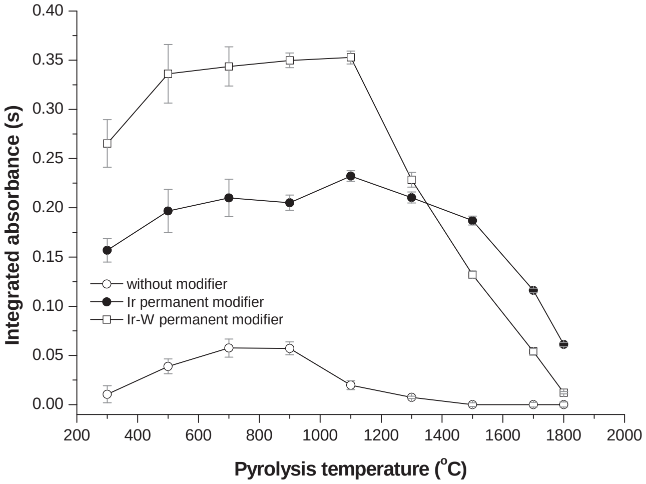

Fig. 2. Pyrolysis curves for manganese in 0.8 mol L^{-1} NaCl solution (approximately 47‰ salinity). [Mn] = 5 μg L^{-1}.

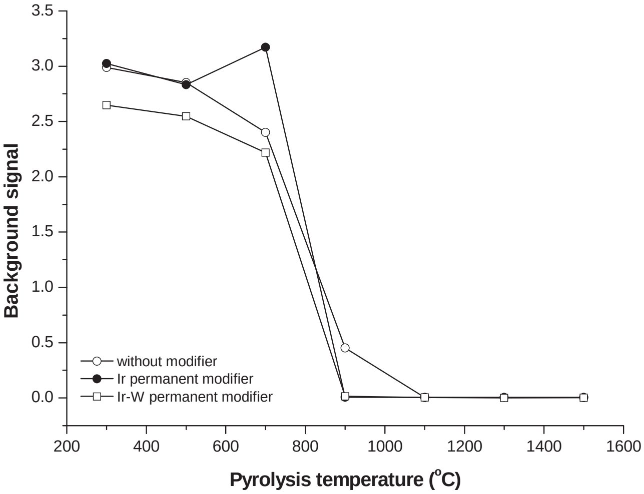

Fig. 3. Background signals obtained in the pyrolysis curve for manganese in 0.8 mol L^{-1} NaCl medium. [Mn] = 5 μg L^{-1}.

Mn stable during pyrolysis or to enhance the volatility of the NaCl matrix and therefore, improving the background reduction during atomization [23–26]. Although the permanent modification of graphite tubes was already used to determine Mn in different kind of samples [27,28], this approach has not been applied in Mn determination in saline waters such as produced waters or seawater. Therefore, as mentioned before, this present work aims the development of a methodology for direct Mn determination in saline waters derived from petroleum exploration.

The first step of this work was to verify (and compare) the thermal behavior of the Mn by constructing pyrolysis curves in pure water and in saline solution (0.8 mol L^{-1} NaCl), in the presence and absence of the modifiers under investigation. For the saline solutions, the behavior of the background signal was also evaluated. The results obtained in such experiments are shown in Figs. 1 and 2 for pure water and saline solution, respectively. Fig. 3 shows the result for the background in saline solution. Solutions with Mn concentration of 5 μg L^{-1} were employed in all experiments.

As it can be seen in Fig. 1, there was a remarkable difference in the Mn behavior in the presence and absence of the permanent modifiers tested when the Mn standard solution was prepared with pure water. When the modifier was not used, the analytical signals (as integrated absorbance) were systematically lower than those signals obtained when the graphite tubes were treated with Ir or Ir–W permanent modifiers. Such signals were approximately 15–20% lower, evidencing that a small fraction of the Mn is volatilized during the pyrolysis, even at temperatures as low as 300 °C. Also, this fact demonstrates that the use of modifiers is really necessary for the Mn determination without losing sensitivity, especially if the complexity of samples like produced waters is taking into account.

When the Ir and Ir–W permanent modifiers are compared, it is possible to realize that there was no difference in terms of efficiency in the range of 300–1100 °C. The signals generated in both cases were very similar in terms of magnitude and profile. Nevertheless, in pyrolysis temperatures higher than 1100 °C, the use of the Ir permanent modifier showed to be more adequate because a noticeable decrease in the sensitivity was noted when the Ir–W permanent modifier was employed. Using the Ir permanent modifier, the signal only decreased when a pyrolysis temperature of 1300 °C was set.

Although the preliminary results in pure water indicated that Ir permanent modifier would be the best choice for the system, the data obtained for the Mn in saline solution presented different behavior. Fig. 2 shows for the 0.8 mol L^{-1} NaCl solution (approximately 47‰ salinity), that the Mn signal practically disappeared in the absence of the modifiers. This result evidenced that the presence of chloride made the Mn less thermally stable, leading to its volatilization from solution even in temperatures as low as 300 °C.

As expected, the Ir and Ir–W permanent modifiers increased the thermal stability of Mn during the pyrolysis in the saline medium. However, in opposition to the data observed in pure water, Ir–W permanent modifier was more effective in the stabilization of Mn, allowing that the pyrolysis temperature could be elevated up to 1100 °C. It is important to remark that signals obtained with the Ir–W permanent modifier in the saline medium were only approximately 20% lower than those observed in pure water (at 1100 °C pyrolysis), showing that this permanent modifier was really efficient to minimize the Mn volatilization in the chloride form. Similar phenomenon occurred when Pb was directly determined by ET AAS in produced waters [20], using the same modifier.

Fig. 3 shows the variation of the background signal with the variation of pyrolysis temperature for the Mn standard solution prepared in the saline medium. From the data, it is possible to realize that high background signals are generated by NaCl, probably due to unspecific molecular absorption at the wavelength employed for Mn determination, which was 279.6 nm. Also, the obtained results demonstrated that the background signal due

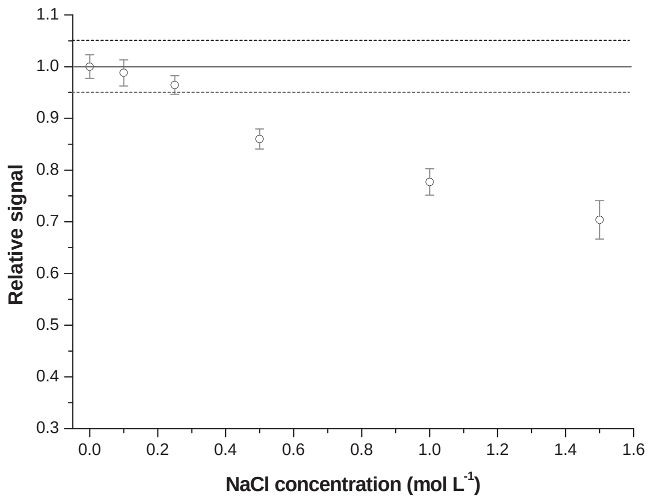

Fig. 4. Effect of the salinity on the analytical signal for manganese using the Ir–W permanent modifier. [Mn] = 5 μg L^{-1}.

to NaCl can be reduced by increasing the pyrolysis temperature. The comparison between the modification strategies under evaluation showed that the most efficient and fast elimination of the background due to NaCl was obtained when the Ir–W permanent modifier was used. In this case, the background signal was reduced to almost zero at the pyrolysis temperature of 900 °C. In the case of the Ir permanent modifier, the background signal first increased and then decreased to values close to zero, also at 900 °C, but with analytical signal lower than that obtained with the Ir–W permanent modifier. So, the Ir–W permanent modifier was chosen as permanent modifier for the proposed methodology and the temperature of 1000 °C was set as the best pyrolysis temperature.

With the pyrolysis conditions optimized, an atomization curve was built up in order to attain the best atomization temperature for the method. Again, in this experiment, Mn solutions prepared in pure water and in saline solution (0.8 mol L^{-1} NaCl) were tested. The best signals were observed at the atomization temperature of 2300 °C, which was used in all further experiments. It was also possible to realize that the presence of NaCl caused matrix interference. Analytical signals were approximately 20% lower when the Mn saline solutions were injected into the graphite tube modified with Ir–W (at the atomization temperature of 2300 °C).

3.2. *Effect of the salinity*

In order to evaluate the effect of the salinity on the sensitivity of the methodology, an experiment was performed by measuring the Mn signal in standard solutions prepared in different concentrations of NaCl. In this experiment, the Ir–W permanent modifier was employed and the NaCl concentration varied from 0 (pure water) to 1.5 mol L^{-1} (approximately 88‰ salinity). The results obtained in this experiment are shown in Fig. 4. For NaCl concentrations lower than 0.25 mol L^{-1}, the effect of NaCl can be considered negligible, since the signal decreased less than 5%. However, in NaCl concentrations higher than 0.25 mol L^{-1}, the absorbance signal decreased more, evidencing that the saline matrix caused interference on the Mn measurement.

3.3. *Evaluation of the calibration strategy*

After optimizing the operational parameters, the developed methodology was employed in the determination of Mn in three samples of produced waters with different salinities (74–84‰). During application, a detailed study about suitable calibration strategy was carried out through the standard addition and external calibration methods for the Mn quantification in the samples. It is important to remark that all samples were diluted four times with purified water before the application of the quantification strategies because of the high concentration of Mn in the samples.

The first quantification strategy tested for the Mn determination in the samples was the application of external calibration. For this test, the analytical curve was built up using standard solutions of Mn(II) prepared in a 0.40 mol L^{-1} NaCl (approximately 23‰ salinity) medium, which is a salinity very close to the salinities of the solutions measured (original salinity of the samples divided by 4, the dilution factor). As it can be seen in Table 3, the analytical curve prepared in the NaCl medium presented a slope very different from the slope of the analytical curve prepared in water, evidencing, as expected, that the presence of NaCl in a concentration higher than 0.25 mol L^{-1} reduces the sensitivity for the Mn determination by ET AAS, even when a Ir–W permanent modifier is used. Additionally, in order to test if the matrix matching procedure was efficient to calibrate the system, a recovery test was performed by spiking the samples with 2.5 μg L^{-1} of Mn and calculating the recoveries using the analytical curve in NaCl medium. Recovery percentages between 89 and 96% were obtained by using analytical curves prepared in the same media of the samples. This fact indicated that the matrix interferences due to salinity can be reduced by matching the salinity of the standard solutions used in the calibration with the salinity of the samples. Also, it can be concluded that no other matrix interference than salinity was present.

Also, the determination of Mn in the samples using the standard addition method was performed. Table 3 also shows the Mn concentrations obtained by using this approach and the equations of all standard addition curves. The Mn concentrations in the samples obtained by standard addition were similar (at 95% confidence level, Student's *t*-test) to the concentrations obtained when the external calibration approach was used, reinforcing the idea raised previously that the preparation of Mn standard solutions with the same salinity of samples is enough to overcome the matrix interference. Therefore, two important conclusions could be drawn: (i) samples can be analyzed by the standard addition method, independently of their salinities and (ii) previous evaluation of the sample salinity is required when the determination of Mn is carried out by the external calibration approach, in order to make possible to prepare standard solutions in the same medium to minimize possible matrix effects.

3.4. *Analytical features of the methodology*

After performing all studies, it was verified that the direct Mn determination in produced waters from petroleum exploration by ET AAS can be carried out employing graphite tube permanently modified with Ir–W. Using this modification approach, an atomization temperature of 2300 °C and a pyrolysis temperature of 1000 °C were set. In such conditions, analytical curves were built up in both purified water and saline solution (0.8 mol L^{-1} NaCl) to derive the general equations and the detection limits of the methodology. Such equations are shown in Table 3. The limits of detection (3σ criterion) and quantification (10σ criterion), estimated from ten measurement of the 2.5 μg L^{-1} Mn standard solution were 0.24 and 0.80 μg L^{-1}, respectively, for purified water and, 0.34 and 1.1 μg L^{-1}, respectively, for 0.4 mol L^{-1} NaCl medium. The characteristic masses, derived from these same analytical curves were 1.2 pg (water) and 1.4 pg (0.4 mol L^{-1} NaCl). The R.S.D., calculated after 10 measurements of the 2.5 μg L^{-1} Mn solutions were 3.1% for purified water and 4.4% for 0.4 mol L^{-1} NaCl medium.

Table 3
Results (mean ± standard deviation for $n = 3$) obtained in the analysis of real samples of produced waters by external calibration and standard addition methods. [Mn] = manganese concentration in $\mu g\,L^{-1}$.

Method	Media	Equation	Mn found ($\mu g\,L^{-1}$)[b]
Analytical curve (2.5–10 $\mu g\,L^{-1}$)	Purified water	$A = 0.072[\mathrm{Mn}] + 0.007$; $r = 0.995$	
	0.40 $mol\,L^{-1}$ NaCl	$A = 0.061[\mathrm{Mn}] + 0.005$; $r = 0.999$	
	S1 (82‰)[a]		35.0 ± 1.7
	S1 + 2.5 $\mu g\,L^{-1}$		92%[c]
	S2 (84‰)[a]		19.4 ± 0.8
	S2 + 2.5 $\mu g\,L^{-1}$		89%[c]
	S3 (74‰)[a]		21.7 ± 0.9
	S3 + 2.5 $\mu g\,L^{-1}$		96%[c]
Standard addition (2.0–6.0 $\mu g\,L^{-1}$)	S1 (82‰)[a]	$A = 0.061[\mathrm{Mn}] + 0.502$; $r = 0.996$	33.4 ± 1.1
	S2 (84‰)[a]	$A = 0.062[\mathrm{Mn}] + 0.299$; $r = 0.999$	19.2 ± 0.7
	S3 (74‰)[a]	$A = 0.059[\mathrm{Mn}] + 0.331$; $r = 0.994$	20.7 ± 0.9

[a] S1, S2 and S3 are the produced water samples with their respective original salinities between parentheses. It is important to remember that the solutions measured in the quantification had a salinity four times lower than the original, due to the dilution.

[b] Manganese concentrations found in the original samples already taking into account the dilution.

[c] Recovery percentages obtained after Mn determination in the spiked samples.

4. Conclusion

The results obtained in this present work showed that is possible to perform the direct determination of manganese in the highly saline produced waters obtained from petroleum exploration by employing the Electrothermal Atomic Absorption Spectrometry technique. In this case, the use of a convenient modification strategy is mandatory, once very low analytical signal was observed when the manganese was measured in the presence of high concentrations of NaCl. The utilization of the Ir–W permanent modifier afforded better performance and allowed the use of a pyrolysis temperature of 1000 °C, which was enough to reduce drastically the background. Even using this pyrolysis temperature, the sensitivity of the method decays when NaCl is present in concentrations higher than 0.25 $mol\,L^{-1}$.

Another important condition to be observed is the calibration strategy. It was observed that the determination can be carried out employing external calibration with Mn standard solutions prepared in the same media (in terms of salinity) of the samples. Also, the use of the standard addition method showed to be efficient for the quantification. In this context, it is possible to conclude that the measurement of the salinity of the samples is an important step when the Mn determination in produced waters is carried out by ET AAS.

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