Talanta 85 (2011) 1100–1104

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Directly suspended droplet microextraction in combination with microvolume UV–vis spectrophotometry for determination of phosphate

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ARTICLE INFO

Article history:
Received 17 March 2011
Received in revised form 9 May 2011
Accepted 17 May 2011
Available online 26 May 2011

Keywords:
Directly suspended droplet microextraction
Microvolume spectrophotometry
Phosphate
Dissolved reactive phosphorus
Preconcentration

ABSTRACT

A miniaturized methodology for the determination of phosphate in waters has been developed by combining directly suspended droplet microextraction (DSDME) with microvolume spectrophotometry. The method is based on the extraction of the ion pair formed between 12-molybdophosphate and malachite green onto a microdrop of methyl isobutyl ketone and subsequent spectrophotometric determination with no dilution. An enrichment factor of 325 was obtained after 7.5 min of microextraction. The detection limit was 6.1 nM phosphate and the repeatability, expressed as relative standard deviation, was 2.7% ($n = 6$). The method was successfully applied to the determination of dissolved reactive phosphorus in different freshwater samples.

1. Introduction

Phosphorus is an essential element for living organisms that can limit the primary productivity of a water body. Phosphorus is delivered to the aquatic environment mainly from industrial and municipal sources and over-fertilization. Increased concern has arisen due to the eutrophication impacts produced when phosphorus is excessively discharged into the environment [1–3]. As a result of its impact over aquatic systems, control of phosphorus levels in environmental waters is an issue that requires specific attention.

Spectrophotometry is by far the most common analytical technique used for phosphate determination in water samples. Spectrophotometric methods are based on the formation of a heteropolyacid by reaction of phosphate with ammonium molybdate in acidic medium [1]. Even though this method has been internationally accepted due to its simplicity and selectivity, its sensitivity is limited. Different strategies have been developed to provide alternative methodologies capable of determining phosphate in water samples at ultratrace levels, bearing on mind the fundamental role that phosphate plays in the environment at such low concentrations [4]. Thus, the sensitivity of analytical methods for detection of phosphate has been enhanced in the following ways: (i) by optimizing the chemistry using cationic dyes [5–9]; (ii) using preconcentration approaches such as liquid–liquid extraction (LLE) [5,6], solid-phase extraction (SPE) [10], cloud-point extraction (CPE) [11,12] or the magnesium-induced-coprecipitation (MAGIC) method [13,14]; (iii) by making use of sensitive detection techniques, such as chemiluminescence [15,16], fluorescence quenching [17,18] or liquid-waveguide capillary cell (LWCC) systems [19–21].

In the last years, liquid-phase microextraction (LPME) has received considerable attention due to the several benefits derived from the reduced extractant phase-to-sample volume ratio, i.e., excellent enrichment factors, negligible solvent consumption and waste generation [22]. Different LPME approaches have been developed for the extraction and preconcentration of target analytes, including single-drop microextraction [23], hollow fibre liquid-phase microextraction [24], dispersive liquid–liquid microextraction [25], solidified floating organic drop microextraction [26]. Directly suspended droplet microextraction (DSDME) has been recently presented by Yangcheng et al. [27] as an attempt to provide a simple and miniaturized sample preparation technique that could solve the drawbacks inherent with other LPME approaches where the extractant phase is directly exposed to the needle of the microsyringe or several steps are needed to perform the microextraction process. In DSDME, a microdrop of a low density organic solvent is directly exposed to a continuously stirred sample solution, in such a way that the extraction is performed without risk of drop dislodgement. Thus, the sample can be vigorously stirred during the DSDME process in order to enhance the extraction kinetics and, therefore, the extraction efficiency. DSDME has been scarcely employed so far [27–29] in spite of its potential

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doi:10.1016/j.talanta.2011.05.032

usefulness in sample preparation and, to the best of our knowledge, DSDME has not been combined with spectrophotometric systems.

In this sense, the combination of microextraction approaches with commercially available miniaturized UV–vis spectrophotometers involves a step towards the improvement of routine spectrophotometric-based methodologies, as demonstrated in previous studies [30–32]. In this work, the miniaturization of the spectrophotometric method for phosphate determination in water samples is proposed by combination of DSDME and microvolume UV–vis spectrophotometry. The method is based on ion pair formation of 12-molybdophosphate with a cationic triphenylmethane dye, malachite green, and its subsequent extraction onto a microdrop of low density organic solvent.

2. Experimental

2.1. Reagents and solutions

All chemicals were of analytical reagent grade. Deionized water obtained from a Milli-Q water purifier (Millipore, Molsheim, France) was used throughout. A stock standard solution of phosphate (3 mM) was prepared from potassium dihydrogen phosphate (Merck, Darmstadt, Germany). Working standards were daily prepared by appropriate dilution of the stock solution with deionized water.

The mixed reagent solution was prepared as follows: 8.6 g of ammonium heptamolybdate tetrahydrate (Prolabo, Paris, France) was dissolved in water, followed by dropwise addition of 8.6 mL of concentrated sulphuric acid (Prolabo), 0.023 g of malachite green oxalate (Ugine Kuhlmann, Paris, France) and 2 g of tartaric acid (Probus, Badalona, Spain)), and made up to 100 mL with deionized water. The solution was stored for 1 h and filtered through a 0.45 μm membrane filter [5].

1-octanol (Merck), 1-butanol (Prolabo), methyl isobutyl ketone (MIBK) (Prolabo) and toluene (Prolabo) were tried as potential extractants of the ion pair formed between 12-molybdophosphate and malachite green.

Sodium chloride (Sigma Aldrich, St. Louis, MO, USA) was tried as salting-out agent. Sodium dodecyl sulphate (SDS) (Fluka, Buchs, Switzerland) was tried to enhance the sensitivity of the molybdate-malachite green method.

2.2. Apparatus

A Nanodrop (Thermo Scientific, Wilmington, DE, USA) model ND-1000 Spectrophotometer was used for phosphorus determination after DSDME. The characteristics of the analytical instrument are described elsewhere [33]. Absorbance measurements were carried out at 627 nm.

A 10 μL Hamilton Gastight syringe (Hamilton Bonaduz AG, Bonaduz, Switzerland), with a flat needle tip was used to withdrawn the enriched drop at the end of the DSDME process.

2.3. DSDME procedure

5 mL of water sample and a stir bar (10 mm × 3 mm) were placed in a 7 mL glass vial. Then, 500 μL of H_2SO_4 4.5 M and 500 μL of the mixed reagent solution were added to form the coloured 12-molybdophosphate-malachite green ion pair. The magnetic stirrer was subsequently turned on and the stirring rate fixed to 1200 rpm in order to form a steady vortex. Then, 100 μL of MIBK is injected at the bottom of the vortex and the vial is capped during the extraction process. After 7.5 min, the cap is removed and 2 μL of the remaining microdrop is taken back into the syringe and deposited on the lower pedestal of the microvolume spectrophotometer for analysis.

3. Results and discussion

3.1. Optimization of the DSDME method

The proposed method lies in the formation of 12-molybdophosphate-malachite green ion pair and its extraction onto a microvolume of organic solvent. Experimental parameters that can affect the extractability of the coloured ion pair, including organic solvent type and volume, extraction time, stirring rate, as well as addition of NaCl and SDS to the sample solution were optimized independently. Optimization studies were performed with a 0.5 μM phosphate aqueous standard unless otherwise stated. Three replicates were performed in all cases.

3.1.1. Selection of organic solvent

In DSDME, organic solvents must fulfil some initial requirements to be used. The extractant phase should have lower density than water, low volatility and water solubility. In addition, the extractant phase should show appropriate extraction efficiency of the target analyte. On the basis of these considerations, four organic solvents with different physicochemical properties were tested, including 1-octanol, 1-butanol, MIBK and toluene. Bearing in mind the different water solubility of the organic solvents tested, standard solutions were saturated with the corresponding organic solvent prior to the DSDME process for comparison purposes [34]. To facilitate the uptake of the enriched extractant phase at the end of the DSDME process, the stirring rate of the sample solution was fixed at 600 rpm (lower stirring rate needed to form a stable and well-defined drop), given that 1-octanol was the only organic solvent that formed a well-defined drop when the agitation of the sample solution is stopped.

These observations are consistent with those previously reported by other researchers [35]. Nevertheless, among the studied solvents, only MIBK and 1-butanol were found to be appropriate extractant phases of the ion pair. MIBK was finally selected due to its lower water solubility, which allows a lower solvent consumption per analysis.

3.1.2. Organic solvent volume

The organic solvent volume has great impact on the extraction of target analytes, since the kinetics of extraction depends upon the interfacial area (A) and the organic solvent volume (V^{extr}) in accordance with the following equation:

$$k = \frac{A}{V^{extr}} \tilde{\beta}^{extr} \left(1 + K \frac{V^{extr}}{V^{w}}\right) \quad (1)$$

Where k is the observed rate constant, V^{w} is the sample volume, and $\tilde{\beta}^{extr}$ the overall mass transfer coefficient with respect to the extractant phase [36].

In addition, the organic solvent volume defines the potential enrichment factor at a fixed sample volume, according to the equation:

$$EF = \frac{C^{extr}}{C_0^{w}} = \frac{K}{1 + K(V^{extr}/V^{w})} \quad (2)$$

The impact of MIBK volume on the extraction efficiency of the ion pair was studied in the range 80–160 μL. As shown in Fig. 1, the analytical signal increases on decreasing volume of MIBK. These results are consistent with Eq. (1), since a larger interfacial area-to-drop volume ratio is provided by smaller drops. Additionally, the dissolution of the drop is more pronounced when shorter microdrop volumes are used, thus giving rise to increased analyte concentration in the drop [37]. However, the use of MIBK volumes lower than 100 μL brings about higher blank values and a worse repeatability presumably due to the difficulty to uptake the

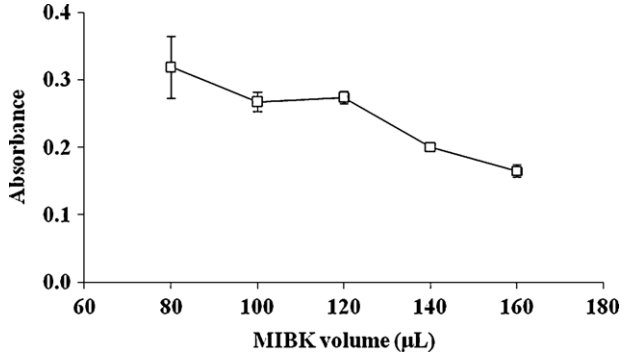

Fig. 1. Effect of the extractant phase volume. DSDME conditions: Extractant phase, MIBK; stirring rate, 1200 rpm; extraction time, 5 min. Error bars represent the standard deviation for $N = 3$.

enriched extractant phase separated for water sample. According to these results, a 100 μL volume of MIBK was selected as the most suitable.

3.1.3. Stirring rate

According to the Withman two-film theory, steady-state diffusion is produced across stagnant solvent layers of thickness adjacent to the interface in the extractant phase and sample solution, respectively [36]. Agitation of the sample solution allows enhancing the extraction kinetics as a result of the reduction of the Nernst diffusion film. In this work, the effect of the stirring rate was studied in the range 600–1350 rpm. Larger stirring rates were not studied due to the difficulty to keep constant stirring during the extraction process, which results in drop breakup and subsequent dispersion into the sample solution. As shown in Fig. 2, the increase in the stirring rate brings about an increase in the analytical signal as a result of the enhanced mass transfer. It can be also observed that homogenization of the ion pair in the drop does not occur at low stirring rates, which means that diffusion of the coloured compound from the surface towards the center of the microdrop is slow. Hence, a stirring rate of 1200 rpm was selected for further studies.

3.1.4. Effect of time

Like in conventional LLE, mass transfer of the analyte between the two immiscible phases involved (sample solution and organic solvent) is time dependent in DSDME. The effect of the extraction time was investigated up to 12.5 min. Extraction efficiency increases with increasing extraction time (Fig. 3). Equilibrium conditions are not achieved within 12.5 min (i.e. the maximum microextraction time tried). Bearing in mind that the whole analysis time depends directly on the time needed to perform the

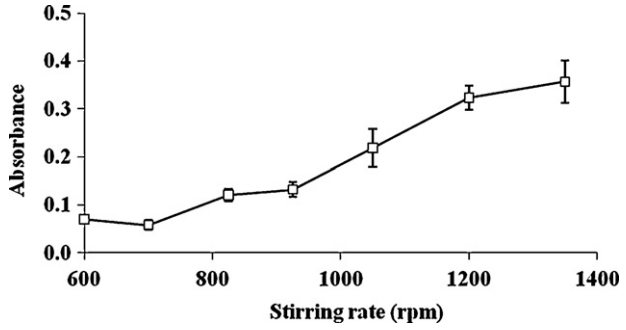

Fig. 2. Effect of the agitation of the sample. DSDME conditions: Extractant phase, MIBK; extractant phase volume, 100 μL; extraction time, 5 min. Error bars represent the standard deviation for $N = 3$.

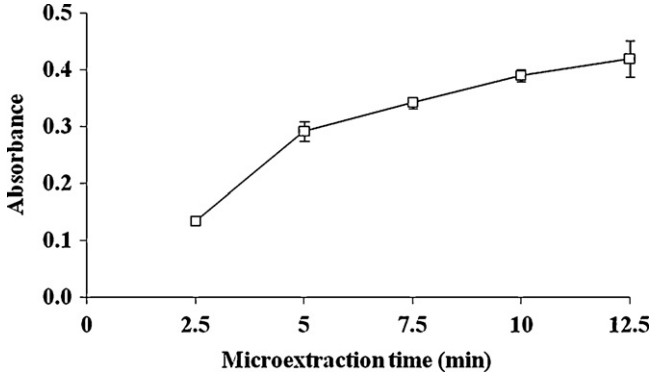

Fig. 3. Effect of microextraction time. DSDME conditions: Extractant phase, MIBK; extractant phase volume, 100 μL; stirring rate, 1200 rpm. Error bars represent the standard deviation for $N = 3$.

DSDME process, a DSDME time of 7.5 min was finally selected as a compromise between extractability and sample throughput [38]. Nevertheless, it must be highlighted here that a longer extraction time may be used with the aim of achieving enhanced sensitivity for phosphate determination at ultratrace levels.

3.1.5. Effect of NaCl addition

It is commonly assumed in LPME approaches that the addition of salt to the sample solution can give rise to two opposed effects: on the one hand, the increase in ionic strength favours the mass transfer of hydrophobic compounds into the extractant phase (salting-out effect) and, on the other hand, the salt dissolved in the sample solution may modify the physical properties of the Nernst diffusion film and slow down the extraction kinetics [34]. In this work, the effect of the NaCl added to the sample was evaluated in the range 0–10% (m/v). As shown in Fig. 4, the increase in NaCl concentration caused a negative effect over the extractability of the coloured ion pair in the whole range studied. On the basis of these results, further experiments were performed without addition of NaCl.

3.1.6. Effect of SDS

In a previous work, Huang and Zhang demonstrated that surfactants can act as sensitizers of the 12-molybdophosphate-malachite green method, SDS being one of the most suitable surfactants [9]. The effect of SDS on the extraction efficiency of the ion pair was evaluated in the range 0–10 mg L^{-1}. Extractability studies were not performed at larger SDS concentrations due to the unacceptable blank values obtained. A 0.25 μM phosphate aqueous standard was used in this study. In accordance with the results shown in Fig. 5,

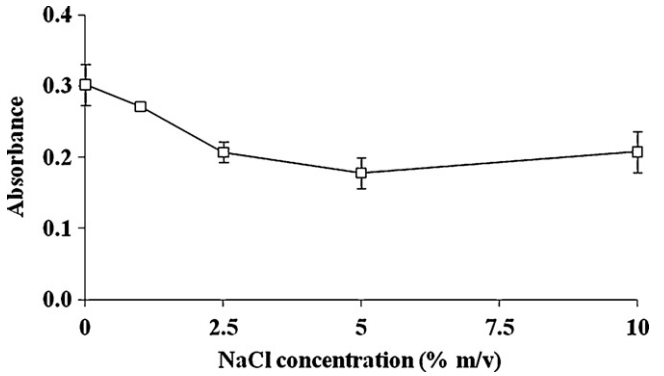

Fig. 4. Effect of NaCl addition. DSDME conditions: Extractant phase, MIBK; extractant phase volume, 100 μL; stirring rate, 1200 rpm; extraction time, 7.5 min. Error bars represent the standard deviation for $N = 3$.

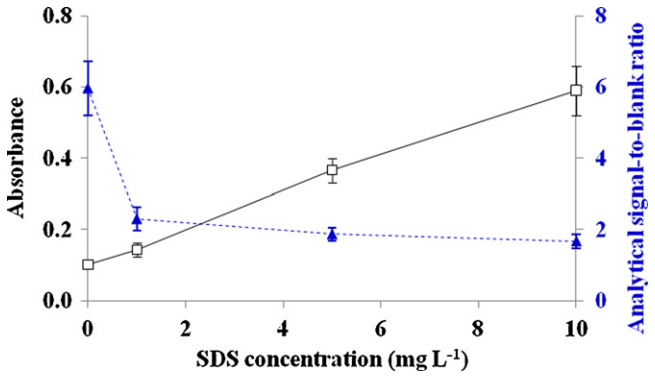

Fig. 5. Effect of the SDS addition. DSDME conditions: Extractant phase, MIBK; extractant phase volume, 100 μL; stirring rate, 1200 rpm; extraction time, 7.5 min. Error bars represent the standard deviation for $N = 3$.

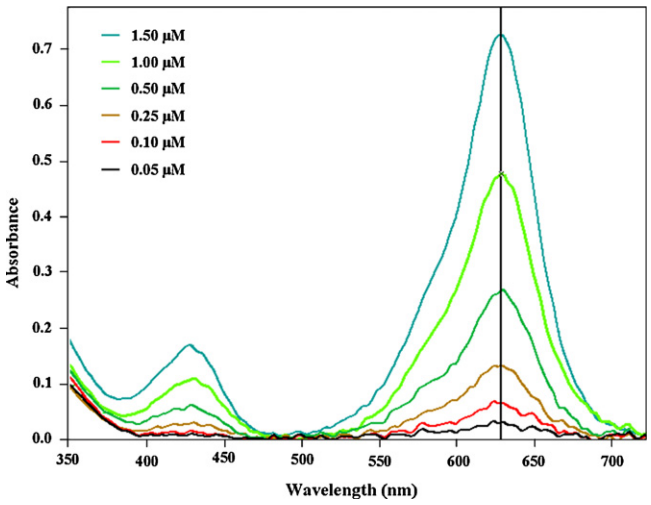

Fig. 6. Absorption spectra of fosfate (0.05–1.5 μM) obtained by DSDME-microvolume spectrophotometry. DSDME conditions: Extractant phase, MIBK; extractant phase volume, 100 μL; stirring rate, 1200 rpm; extraction time, 7.5 min.

the addition of SDS gives rise to an increase in the analytical signal of up to 6-fold as compared to that obtained without addition of the surfactant. These results reveal the possibility of using SDS when a larger sensitivity is required. However, it should be highlighted that the increase in SDS concentration is accompanied by an increase in the blank values, presumably as a result of the enhanced extractability of malachite green-SDS aggregates. In fact, the analytical signal-to-blank ratio worsened significantly with increasing SDS concentration (Fig. 5). Consequently, further studies were performed without SDS.

3.2. Method validation.

3.2.1. Analytical performance

The calibration graph was linear in the range 0.05–1.5 μM (number of calibration points, $N = 6$). The equation for the calibration line was: $Y = 0.4749[P] - 0.0007$, where $[P]$ is the concentration of phosphorus (μM). The regression coefficient was 0.9996. The absorption spectra obtained by using the proposed method at different phosphate concentrations are shown in Fig. 6.

The detection (LOD) and quantification limits (LOQ), calculated as $3sm^{-1}$ and $10sm^{-1}$ (s being the standard deviation of 10 blank measurements and m the slope of the calibration line) were 6.1 and 20.5 nM, respectively. The repeatability of the proposed method, expressed as relative standard deviation (RSD), was 2.7% for six replicate measurements of 0.5 μM phosphate.

The enrichment factor (EF) is defined as the ratio between the analyte concentration in the final extract and its initial concentration in the sample. Bearing on mind that a derivatization reaction takes place in the proposed method, the EF was calculated in this work by comparison of the slopes of the calibration lines obtained by DSDME and by conventional LLE, and was found to be 325.

The analytical characteristics of the proposed method, as well as a comparison with those provided by other spectrophotometric methods described in the literature for the determination of phosphorus in water samples, are shown in Table 1. It can be concluded that the proposed method allows achieving the highest EF (325), mainly as a result of the greatly reduced organic solvent-to-sample ratio. In spite of the loss of sensitivity due to the lower path length (1 mm) of the microvolume spectrophotometer used as compared to conventional photometric equipment, the LOD is comparable to that provided by other preconcentration techniques. It is also remarkable the low sample consumption of the proposed methodology.

3.2.2. Analysis of water samples and recovery study

The performance of the proposed DSDME-microvolume spectrophotometric method was tested by applying it to the determination of dissolved reactive phosphorus in four different mineral waters. Water samples were stored at 4 °C and analyzed after filtration through a Whatman cellulose acetate membrane (0.45 μm). All samples were analyzed in triplicate according to the proposed method. It should be highlighted here that tartaric acid is employed in the mixed reagent solution to alleviate the potential interference due to As(V), which gives rise to a positive interference due to the formation of molybdoarsenate-malachite green [5]. Analytical results are shown in Table 2. As can be observed, low contents of dissolved reactive phosphorus were found in the mineral water II (55.7 ± 5.5 nM), while in the rest of samples were found below the LOQ of the method.

Freshwater samples were spiked at two concentration levels of phosphate (300 and 600 nM) in order to check for matrix effects. The recovery values for the spiked water samples are also shown in Table 2. As can be seen, relative recoveries in the range 95–104%

Table 1
Comparison of the proposed DSDME method with other methodologies involving preconcentration and spectrophotometric determination of phosphate.

Analytical technique	EF	LOD (nM)	Working range (μM)	Precision (RSD %)	Sample volume (mL)	Ref.
CPE-UV–vis	20	16.1	0.032–4.032	1.4	10	[11]
CPE-UV–vis	n.r.	2600	2.6–31.2	1.2	10	[12]
Solid phase spectrometry	290	2.2	0.032–0.322	3–4	20	[39]
SPE-UV–vis	70	1.57	0.003–0.048	4.5	105	[40]
SPE-UV–vis	50	6.4	0.032–0.64	2.6–4.0	n.r.	[10]
Flow injection extraction-UV–vis	18	161	up to 64400	10–11	33	[41]
Ion imprinted polymer-UV–vis	147.9	1.3	0.006–0.051	0.38	100	[42]
Flotation-extraction-UV–vis	12.5	n.r.	up to 3220	<2	40	[43]
DSDME-microvolume UV–vis	325	6.1	0.05–1.5	2.7	5	This work

n.r.: Not reported.

Table 2
Analytical results for dissolved reactive phosphorus in freshwater samples.

Sample	Added concentration (nM)	Found concentration (nM)	Recovery (%)
Mineral water I (Fontecelta)	–	<LOQ[a]	
	300	304 ± 12	101 ± 4
	600	598 ± 20	100 ± 3
Mineral water II (Mondariz)	–	56 ± 5	
	300	351 ± 10	99 ± 3
	600	635 ± 32	97 ± 5
Mineral water III (Fontvella)			
	–	<LOQ	
	300	312 ± 12	104 ± 4
	600	589 ± 9	98 ± 2
Mineral water IV (Cabreiroá)	–	<LOQ	
	300	285 ± 21	95 ± 7
	600	618 ± 17	103 ± 3

[a] LOQ = 20.5 nM phosphate.

were obtained, with a mean value of 100% and RSDs ranging from 2 to 7%. These results demonstrate that the matrix had little effect on the DSDME of phosphate.

4. Conclusions

This paper describes a miniaturized spectrophotometric method for phosphate determination in water samples. The principle of the method lies in the DSDME of the 12-molybdophosphate-malachite green ion pair and subsequent detection using a state-of-the-art microvolume spectrophotometer. The use of such spectrometer avoids the dilution of the extract, hence keeping the high enrichment factor achieved during the DSDME process. The proposed method provides high sensitivity for phosphate determination along with low consumption of both sample and organic solvent.

Acknowledgements

Financial support from the Spanish Ministry of Science and Innovation (project CTQ2009-06956/BQU) and the University of Vigo (Contract for Reference Research Groups 09VIA08) are gratefully acknowledged.

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