

# Flame atomic absorption spectrometric determination of chromium(VI) by on-line preconcentration system using a PTFE packed column

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## Abstract

A new, sensitive and robust time-based flow injection (FI) method for on-line preconcentration and determination of ultra trace amounts of chromium(VI) by flame atomic absorption spectrometry (FAAS) has been elaborated. The sample is initially mixed on-line with ammonium pyrrolidine dithiocarbamate (APDC) and the Cr(VI)–PDC chelate is absorbed quantitatively on a mini-column packed with polytetrafluoroethylene (PTFE) turnings at a pH range 0.8–1.4. The complex is subsequently eluted with isobutyl methyl ketone (IBMK) and introduced directly into the nebulizer–burner system. The optimized system offered improved performance characteristics, with unlimited lifetime of the proposed column. The enhancement factor was 80, for a 3-min preconcentration time and the sample frequency was 18 h<sup>-1</sup>. The calibration curve was linear over the concentration range 1–40 µg l<sup>-1</sup> with a detection limit of  $c_L = 0.8 \mu\text{g l}^{-1}$  and a relative standard deviation of  $s_r = 3.2\%$ , at the 20 µg l<sup>-1</sup> level. The proposed method was evaluated by analyzing samples of certified and spiked water, and it was applied to the analysis of natural water samples and sediments. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Chromium; Flow injection preconcentration; Atomic absorption spectrometry; Polytetrafluoroethylene

## 1. Introduction

Chromium is usually found in natural media as hydrated chromium(III) species or as chromium(VI) (chromate) [1]. The last has a definitely toxic impact on living organisms and humans,

with mutagenic and potential carcinogenic properties [2]. Due to the constant interest for toxic elements monitoring, extended reviews about the analytical methodologies applied to chromium determination are recently published for liquid and solid matrices [3–5]. Flame atomic absorption spectrometry (FAAS) is one of the most extensively used techniques for various elements determination with significant precision and accuracy. Sample pre-treatment techniques which include analyte element separation and preconcentration

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are often required, in order to isolate the analyte from interfering matrix constituents and to bring its concentration into the dynamic measuring range of the detection system [6].

To develop reliable and robust systems for the above purpose, the flow injection (FI) technique with its inherent technical advantages and versatility presents itself as an obvious avenue of choice. FI on-line preconcentration procedures have been based predominantly on incorporation of column reactors packed with various polar or non-polar sorbent materials. Solid phase extraction (SPE) may be used as an alternative to solvent extraction, and the versatility of FI systems coupled with sorbent packed columns is widely approved. Chromium species are sorbed on these materials either directly [7,8] or after preliminary complexation with various chelating reagents like dithiocarbamates [9–16], or diphenylcarbazide (DPC) [17,18].

During the last decade, a number of methods have been reported to adapt FI on-line preconcentration with atomic absorption spectrometry, for the determination of chromium(VI). These methods usually make use of a column reactor packed with a suitable stationary phase like  $C_{18}$  [15], activated alumina [8], cellulose sorbent CellexT [7] etc. Alternatively, a polytetrafluoroethylene (PTFE) or polyether ether ketone (PEEK) knotted reactor (KR) can be used as a preconcentration unit [11–13]. In our previous work [19], a new preconcentration column packed with PTFE turnings as a sorbent material, constructed, elaborated and used for copper determination for the first time.

In this work, an attempt was made to develop a practical, suitable, robust and low cost, time-based FI procedure for on-line preconcentration and determination of ultra trace amounts of Cr(VI). For this propose, the APDC–isobutyl methyl ketone (IBMK) extraction batch-system [20] was combined with the above column reactor, and FAAS as a detector. The proposed method is applicable to various water and sediment samples, with very good analytical figures of merit, comparable to those obtained by using other more sophisticated and expensive systems.

## 2. Experimental

### 2.1. Instrumentation

A Perkin–Elmer model 5100 PC flame atomic absorption spectrometer equipped with a deuterium arc background corrector was used as a detector. A chromium hollow cathode lamp was used as light source operated at 25 mA. The wavelength was set at 357.9 nm resonance line and the slit at 0.7 nm. A time-constant of 0.2 s was used for peak height evaluation. The flame composition was optimized, as it is described below, to compensate for the effect of IBMK, which serves as additional fuel. A flow spoiler was used in the spray chamber for all measurements. An Orion EA 940 pH-meter was employed for the pH measurements.

The FI manifold and the column construction have been described in details in our previous work [19], and PTFE turnings were used as the sorbent material.

### 2.2. Reagents

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany) and doubly de-ionized water was used throughout for dilutions. All working standard solutions of chromium(VI) were prepared immediately before use, by stepwise dilution of a 1000 mg l<sup>-1</sup> stock standard solution (Merck) to the required µg l<sup>-1</sup> levels. The final working standards were made up to pH ≈ 1 with 0.1 mol l<sup>-1</sup> HNO<sub>3</sub>. The chelating reagent, 0.05% mV<sup>-1</sup> ammonium pyrrolidine dithiocarbamate (APDC) was prepared fresh daily by dissolving the appropriate amount of APDC (Merck) in de-ionized water. IBMK was used, after saturation with de-ionized water, without any other purification. Concentrated nitric, perchloric and hydrofluoric acids (Merck, pro analysi) were used for the wet digestion of the sediments. NIST CRM 1643b (Trace elements in water) standard reference material spiked with Cr(VI), was ap-

plied for verification of the accuracy of the proposed method.

### 2.3. Procedure

In the loading step, the injection valve was in the fill position; sample or standard and APDC streams propelled by pump 1, were merged together before passing through the column. The formed Cr(VI)–PDC complex was retained on the surface of the PTFE turnings in the column either for 60 or 180 s, depending on the calibration mode. During the elution step, pump 1 was stopped due to minimize the sample and reagent consumption; injection valve was in the injection position; IBMK is propelled through the column by activation pump 2 in order to elute the complex. Thus the eluted Cr(VI)–PDC complex is delivered to the FAAS nebulizer. The column was arranged in the manifold so that the IBMK flowed through it, in reverse direction to that of the sample and reagent, minimizing thus the dispersion of the analyte. The peak height of the signal was proportional to the chromium(VI) concentration and was used for all measurements. In order to ensure complete elution of the chromium complex, the elution time was fixed at 30 s. The recorded peaks were sharp and the baseline was stable. Five replicate measurements per sample were made in all instances.

Sub-samples (0.2 g each) of the sediments were precisely weighed into teflon crucibles and were wetted by nitric acid, followed by perchloric and hydrofluoric acids. The final acid mixture contained  $\text{HNO}_3$ – $\text{HClO}_4$ – $\text{HF}$  in a volume ratio of 3:2:1. A suitable concentration of Cr(VI) was added to the mixture in a number of sub-samples. The digestion was carried out under pressure at 130–140 °C, in a pressurized bomb. After cooling, the final digests were properly diluted with double de-ionized water and used for the recovery tests.

Water samples were filtered before analysis through 0.45  $\mu\text{m}$  filters and acidified to  $\text{pH} \approx 1$  with  $\text{HNO}_3$ , while the digests of the solid samples were adjusted close to this pH after proper dilution.

## 3. Results and discussion

### 3.1. Optimization of chemical and FI variables

It is well known that Cr(III) reacts with chelating agent APDC under mild conditions to give the complex tris[pyrrolidine-1-dithioato-*S,S'*]-Cr(III), denoted as Cr(III)–PDC [21]. The preconcentration or extraction of Cr(III) by APDC–IBMK system has been found to be inefficient, due to the difficulty of displacing the coordinated water from the strongly hydrated Cr(III) by APDC and formation of the Cr(III)–PDC complex [22]. On the other hand, Cr(VI) is reduced easily by APDC to Cr(III) and, then, produces two different complexes: the bis [pyrrolidine-1-dithioato-*S,S'*]-[pyrrolidine-1-peroxodithioato-*O,S*]-Cr(III) denoted as Cr(VI)–MP, which is the main product, and the by product tris-[pyrrolidine-1-dithioato-*S,S'*]-Cr(III), denoted as Cr(VI)–BP. Cr(VI)–BP complex was found to be identical with the Cr(III)–PDC [14]. In this study, the Cr(VI) complexes with APDC are abbreviated generally as Cr(VI)–PDC.

The chemical and FI variables of the manifold were optimized using a standard solution 40  $\mu\text{g l}^{-1}$  of Cr(VI). Varying the length of the column reactor in the range 3–5 cm, no effect to the signal had been obtained, thus a 3 cm column was used throughout.

Study of APDC concentration in the range of 0.01–0.1%  $\text{mV}^{-1}$  had no effect on the preconcentration efficiency. Finally, a 0.05%  $\text{mV}^{-1}$  solution of APDC in water was selected, and the flow rate of the APDC stream was fixed at 0.5  $\text{ml min}^{-1}$  for the optimization study. No detectable amounts of Cr(VI) could be retained in the packed column in the absence of the chelating reagent. When other metals which form strong M–PDC complexes are present at  $\text{mg l}^{-1}$  levels, a 0.1% solution and a 5 cm column could be used, to allow complete complexation and sorption of Cr(VI) species.

One of the critical variables for the formation of Cr(VI)–PDC complex, and its adsorption on the sorbent surface is the sample's acidity. The effect of the pH was studied over the range from –0.1 to 5.7 by adjusting with dilute nitric acid.

The results are illustrated in Fig. 1. The pH of the waste solution was similar to that of the sample, indicating that the APDC solution did not affect the acidity. The absorption signal is maximum and practically stable in a pH window between 0.8 and 1.4. This fact enables the use of the method directly in many aqueous samples after common preservation with nitric acid, without any laborious precise pH adjustment. The decrease of the efficiency at higher or lower pH values is probably due to non-complete complex formation and sorption, and not to the function of the column PTFE material, which is very resistant to any acidic or alkaline solution.

The effect of the sample flow rate during the loading step was studied in the range of 1.9–14.8 ml min<sup>-1</sup>. The absorption was linear up to 12.6 ml min<sup>-1</sup>, implying that the complexation is complete and the contact time is sufficient. This is a significant advantage of the proposed column preconcentration system because it enables more sample to be loaded during a given preconcentration time resulting in higher enhancement in sensitivity. At higher flow rates, between 12.6 and 14.8 ml min<sup>-1</sup> the signal is stable, indicating the beginning of the partial leaching of the analyte complex. Consequently, a flow rate of 12.6 ml min<sup>-1</sup> was selected as a compromise between high sensitivity and sufficient sampling frequency.

The influence of sample loading time was studied in the range 30–240 s. The absorption was increased linearly up to 180 s and practically up to 240 s. This fact proved that even at long loading times and prolonged sample flow, no negative effect is produced from partial leaching of the complex [23]. Finally, the performance of the system was checked for 60 and 180 s preconcentration time.

IBMK is considered to be a better eluent for FAAS, producing higher and sharper signals, because of more intensive enhancement of the flame atomization. On the other hand, IBMK is almost completely immiscible with water and less polar solvent, producing better elution characteristics and lower dispersion of the concentrated analyte, during the elution.

The effect of elution flow rate was studied in the range of 1.7–5.4 ml min<sup>-1</sup>. Changing the flow rate of IBMK caused significant changes to the flame composition, which is critical for the atomization of chromium. Thus, the elution rate was optimized for three different acetylene–air mixtures: 1.0–9.0 l min<sup>-1</sup>, 2.0–9.0 l min<sup>-1</sup>, 2.5–9.0 l min<sup>-1</sup> acetylene–air flow ratio. It was proved that the 2.0–9.0 l min<sup>-1</sup> flow ratio was better and the peak height goes through a maximum at IBMK flow rate of 2.9 ml min<sup>-1</sup>. Above this value, it slightly decreases, due mainly to the

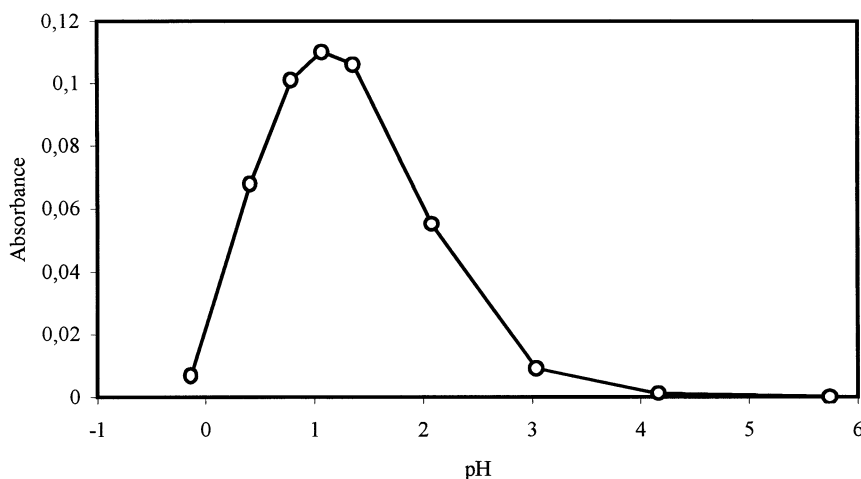


Fig. 1. Effect of the pH of sample solution on the peak height of 40 µg l<sup>-1</sup> Cr(VI).

Table 1  
Analytical performance of the FI on-line preconcentration FAAS method for Cr(VI) determination

Parameter	60 s preconcentration	180 s preconcentration
Sample volume	12.6 ml	37.8 ml
Loading time	60 s	180 s
Sampling frequency	40 h <sup>-1</sup>	18 h <sup>-1</sup>
Enhancement factor	50	80
Detection limit (3s)	$c_L = 1.9 \mu\text{g l}^{-1}$	$c_L = 0.8 \mu\text{g l}^{-1}$
Relative std deviation (20.0 $\mu\text{g l}^{-1}$ , $n = 11$ )	$s_r = 3.4\%$	$s_r = 3.2\%$
Linear range	2–120 $\mu\text{g l}^{-1}$	1–40 $\mu\text{g l}^{-1}$
Regression equation (14 standards, $n = 5$ )	$A = -0.001$ + 0.0018 [Cr <sup>VI</sup> ]	$A = -0.001$ + 0.0046 [Cr <sup>VI</sup> ]
Correlation coefficient	$r = 0.9992$	$r = 0.9995$

higher dispersion at these elution flow rates. Flow rates lower than 1.7 ml min<sup>-1</sup> caused abnormal signal shape and irreproducible peak height, due to gas bubbles formed in the system, because the nebulizer free uptake exceeded the elution rate. Thus, a 2.9 ml min<sup>-1</sup> elution flow rate and a 2.0–9.0 l min<sup>-1</sup> acetylene–air flow ratio for flame composition were chosen as optimal conditions.

### 3.2. Analytical performance of the on-line sorbent extraction FAAS system

The analytical performance of the method, under the optimum conditions described above, is given in Table 1. The calculations of regression analysis, precision and enhancement factors were based on the peak height absorption signals obtained by a series of working standards of Cr(VI). The detection limit was calculated by the 3s criterion. For a 180 s preconcentration time and a 18 h<sup>-1</sup> sampling rate, the enhancement factor was about 80. The detection limit was  $c_L = 0.8 \mu\text{g l}^{-1}$ , and the linear range of the method was found between 1 and 40  $\mu\text{g l}^{-1}$ . The precision of the method was  $s_r = 3.2\%$ , for a 20.0  $\mu\text{g l}^{-1}$  Cr(VI) standard.

For samples with higher Cr(VI) concentration, a shorter preconcentration time is sufficient, with a gain in sampling rate and expansion of the

linear range of the calibration curve. Thus, for a 60 s preconcentration time and a 40 h<sup>-1</sup> sampling rate, the enhancement factor was about 50. The detection limit was  $c_L = 1.9 \mu\text{g l}^{-1}$  and the linear range of the method was found between 2 and 120  $\mu\text{g l}^{-1}$ . The precision of the method was  $s_r = 3.4\%$ , for a 20.0  $\mu\text{g l}^{-1}$  Cr(VI) standard.

In Table 2, the figures of merit of this and other published on-line preconcentration methods, which make use of FAAS, ETAAS or UV as detectors, are summarized for comparative purpose. Only in methods with ETAAS as detector, is the detection limit one or two orders of magnitude lower. However, it should be taken into account that the proposed FI–FAAS method consists of much lower equipment and running costs. The detection limit and the precision of the proposed method are similar to others using FAAS as detector, but with much simpler apparatus and easier manipulation of the system. The analytical features of activated alumina [8] are also comparable to the proposed method but this sorbent material becomes exhausted after 80–100 loading–elution cycles [24]. PTFE turnings, on the other hand, were absolutely stable and effective even after more than 500 cycles.

### 3.3. Interference studies

With the proposed on-line system and 180 s preconcentration time, the interference of various elements was examined on the recovery of 10  $\mu\text{g l}^{-1}$  Cr(VI). Taking as a criterion for an interference the variation of the recovery more than  $\pm 5\%$ , Al(III) (10 mg l<sup>-1</sup>), Cd(II) (0.25 mg l<sup>-1</sup>), Ce(IV) (5.0 mg l<sup>-1</sup>), Co(II) (1.0 mg l<sup>-1</sup>), Cr(III) (10.0 mg l<sup>-1</sup>), Cu(II) (1.0 mg l<sup>-1</sup>), Fe(III) (10.0 mg l<sup>-1</sup>), Hg(II) (0.5 mg l<sup>-1</sup>), Mn(II) (10.0 mg l<sup>-1</sup>), Ni(II) (0.5 mg l<sup>-1</sup>), Pb(II) (1.0 mg l<sup>-1</sup>), Zn(II) (5.0 mg l<sup>-1</sup>) do not interfere. However, in case of waste waters or heavily polluted waters with high metal concentrations, the interference effects of Cd(II) and possibly of Pb(II), Hg(II), Cu(II) and Ni(II) could be minimized by using a longer (5 cm) packed column without significant changes in the performance characteristics. The pH adjustment for elimination of interference with small expense to sensitivity is also an efficient

Table 2  
Comparison of published methods for Cr(VI) determination by on-line preconcentration techniques

Reference	Technique	Chelating reagent	Sorbent material	Eluent	EF <sup>a</sup>	LT <sup>b</sup> (s)	SF <sup>c</sup> (h <sup>-1</sup> )	c <sub>L</sub> <sup>d</sup> (μg l <sup>-1</sup> )	s <sub>r</sub> <sup>e</sup> (%)
f	FI-FAAS	APDC	PTFE	IBMK	80	180	18	0.8	3.2
[12] <sup>g</sup>	FI-FAAS	APDC	KR (PEEK)	IBMK	–	60	–	0.54	2.9
[15] <sup>g</sup>	FI-FAAS	DDTC	C <sub>18</sub>	Methanol	500	300	10	0.02	3.5
[13]	FI-FAAS	APDC	KR (PEEK)	IBMK	65	60	30	2.0	2.1
[7] <sup>g</sup>	FI-FAAS	–	Cellex T	NaOH	–	150	–	1.4	4.5
[8] <sup>g</sup>	FI-FAAS	–	Activated alumina	NH <sub>4</sub> OH	25	35	55	0.8	1.1
[24] <sup>g</sup>	SIA-FAAS	–	Activated alumina	NH <sub>4</sub> OH	–	2	–	42	10
[9]	SIA-ETAAS	APDC	KR (PTFE)	IBMK	19	60	14	0.0067	0.29
[10]	FI-ETAAS	APDC	L/L extraction	IBMK	18	99	24	0.0033	0.83
[11]	FI-ETAAS	APDC	KR (PTFE)	Ethanol	19	60	21	0.0042	0.57
[14] <sup>g</sup>	HPLC-ETAAS	APDC	C <sub>18</sub>	Ethanol	–	522	–	0.6	2.2
[16] <sup>g</sup>	FI-ETAAS	DDTC	C <sub>18</sub>	Ethanol	12	60	22	0.016	9.1
[17]	SIA-UV	DPC	Wetting-extract ion	Octanol	25	56	17	2.0	2.8
[18]	FI-UV	DPC	Activated alumina	NH <sub>4</sub> OH	392	600	5	0.2	4.7

<sup>a</sup> A number of references report the enhancement factor, and the others the enrichment factor.

<sup>b</sup> Loading time.

<sup>c</sup> Sampling frequency.

<sup>d</sup> Detection limit.

<sup>e</sup> Precision, relative standard deviation.

<sup>f</sup> This work.

<sup>g</sup> Speciation of Cr.

APDC, ammonium pyrrolidine dithiocarbamate; DDTC, diethyl dithiocarbamate; DPC, diphenylcarbazide; KHP, potassium hydrogen phthalate.

approach, but till now only for copper is there the necessary data in literature [19].

Alkali and alkaline earth metals, which are usually found in high concentrations in natural waters, do not form complexes with APDC. However, the potential interference of them on the on-line sorption of the Cr(VI)–PDC complex was tested. Na(I) and K(I) up to 2000 mg l<sup>-1</sup> and Ca(II), Mg(II), Ba(II) up to 500 mg l<sup>-1</sup>, did not cause any significant interference.

A number of common anions like Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, SCN<sup>-</sup> and NO<sub>3</sub><sup>-</sup> were tested and found that they did not interfere at concentrations up to 2500 mg l<sup>-1</sup>. Also, the presence of SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> and CH<sub>3</sub>COO<sup>-</sup> up to 1000 mg l<sup>-1</sup> did not cause any significant variation to the signal.

Table 3  
Results of Cr(VI) determination in sediments (in dry weight basis)

Sediments	Added Cr(VI) (mg kg <sup>-1</sup> )	Found* (n = 3) [Cr(VI)] ± s (mg kg <sup>-1</sup> )
Coastal marine sediment	0	10.7 ± 0.8
	10.0	20 ± 1
River sediment	0	14.8 ± 0.7
	10.0	24 ± 2

\* Mean value ± standard deviation based on three replicate digestions and five determinations for each.

Table 4  
Results of Cr(VI) determination in water reference material and routine samples (in fresh weight basis)

Water samples	Certified <sup>a</sup> concentration (range) ( $\mu\text{g l}^{-1}$ )	Added Cr(VI) ( $\mu\text{g l}^{-1}$ )	Found ( $n = 5$ ) [Cr(VI)] $\pm s$ ( $\mu\text{g l}^{-1}$ )
CRM 1643b (water)	18.6 (18.2–19.0)	0	$< c_L$
		10.0	$9.8 \pm 0.4$
Tap water		0	$< c_L$
		20.0	$19.5 \pm 0.6$
Industrial wastewater		0	5.9
		20.0	$25 \pm 2$
River water (Axios)		0	$< c_L$
		20.0	$19.3 \pm 0.9$
Coastal seawater		0	$< c_L$
		20.0	$20.1 \pm 0.6$

<sup>a</sup> Value in certified reference material is referred to almost completely in Cr(III) form [8].

### 3.4. Applications

The proposed method was applied to the analysis of a certified water reference material and also to natural water, wastewater and coastal marine sediment samples collected from Northern Greece. The calibrations were performed by use of aqueous standard solutions. The certified values of the water reference materials are referred to total Cr, but the greatest part is Cr(III), as it was found by speciation studies [8], although ultra traces of Cr(VI) may exist [25]. The speciation of chromium in sediments has some basic difficulty arising from the possibility of oxidation state transformation between Cr(III) and Cr(VI) during the mineralization procedure. Therefore the mineralization of sediment of samples was done under mild oxidative conditions, as described above in the Procedure. The obtained results for sediments are expressed in dry weight basis and are presented in Table 3, and for waters in Table 4. The concentration of Cr(VI) in sediments samples refer to the value obtained after mineralization. It can be seen that the recoveries obtained from sediment and water analysis are sufficient, and the performance of the method is very good in all types of the examined samples. Finally the relative standard deviation for Cr(VI) determination in the real samples ranged between 3 and 6%.

### 4. Conclusions

The proposed method for Cr(VI) determination is convenient, low cost and has good performance characteristics, comparable to other more complicated on-line preconcentration FAAS methods reported in the literature. The system is flexible and easily mounted to FAAS with simple operation. The use of PTFE turnings as a sorbent material in the on-line adsorption preconcentration system was found to significantly improve the features of the determination. The column is effective, stable and reproducible with an unlimited lifetime. In addition, conditioning, activation or washing steps are not necessary. High preconcentration and enhancement factors were achieved due to the increased sample loading rates. The proposed method proved to be accurate and applicable to chromium determination in a variety of sediments and water samples with few interferences.

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