

US EPA Method 200.7 using the Thermo Scientific iCAP 7600 ICP-OES Duo

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Key Words

Environmental analysis, Method 200.7, US EPA, Drinking water

Goal

This note describes the use of the Thermo Scientific™ iCAP™ 7600 ICP-OES Duo for the analysis of water samples using the US EPA method 200.7.

Introduction

In 1970, the United States government established the Environmental Protection Agency (EPA) in response to growing public demand for cleaner water, air and land. The agency is responsible for researching and setting national standards for a variety of environmental programs and delegates the responsibility for issuing permits, monitoring and enforcing compliance to local government. Where national standards are not met, the EPA can issue sanctions and take other steps to assist local government in reaching the desired levels of environmental quality.

The Safe Drinking Water Act (SDWA) (last amended 1996) gave the US EPA power to set and regulate national standards for the quality of supplied drinking water and drinking water resources, such as ground waters. The EPA Office of Ground Water and Drinking Water (OGWDW) administers control under the Federal Regulation 40 CFR part 141 & 143. This regulation states that all supplied waters must comply with the Maximum Contaminant Levels (MCL) for the contaminants specified in the National Primary Drinking Water Regulations (NPDWR). Table 1 lists the MCL and Maximum Contaminant Level Goals (MCLG) that the EPA defines as the maximum level of an element in drinking water at which no known or anticipated adverse effect on the health of persons would occur. Further contaminants are given suggested maximum values in the National Secondary Drinking Water Regulations (NSDWR) as these elements will affect water properties such as taste and colour. The Unregulated Contaminant Monitoring Rule 3 (UCMR-3) requires that measurements are taken and recorded for two areas at every water treatment plant; the metals to be tested and their Maximum Reporting Limits (MRL) are shown in Table 1.



Table 1. MCLs for the National primary and secondary drinking water regulations and MRLs for UCMR-3

National Primary Drinking Water Regulations		
Contaminant	MCL (mg/l)	MCLG (mg/l)
Antimony	0.006	0.006
Arsenic	0.01	0
Barium	2.0	2.0
Beryllium	0.004	0.004
Cadmium	0.005	0.005
Chromium (Total)	0.1	0.1
Copper	1.3	1.3
Lead	0.015	0
Mercury	0.002	0.002
Selenium	0.05	0.05
Thallium	0.002	0.002
Uranium	0.03	0

National Secondary Drinking Water Regulations	
Contaminant	MCL (mg/l)
Aluminium	0.05 - 0.2
Copper	1
Iron	0.3
Manganese	0.05
Silver	0.1
Sulphate	250
Zinc	5

Unregulated Contaminant Monitoring Rule 3 (UCMR-3)	
Contaminant	MRL (mg/l)
Contaminant	MRL (mg/l)
Chromium (total)	0.0002
Cobalt	0.001
Molybdenum	0.001
Strontium	0.0003
Vanadium	0.0002

The approved ICP-OES method for the determination of metallic contaminants is the EPA Method 200.7, “Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry”. However, for some analytes, the required detection limit for compliance to the regulation is problematic with this technique, e.g. antimony, arsenic, mercury and thallium. Under the Arsenic Rule (part of 66 FR 6976, 2001) approval for ICP-OES methods for the determination of arsenic was withdrawn, since the typical detection limit of the technique is not routinely low enough to measure confidently at the MCL level of 10 µg/L. This leaves graphite furnace atomic absorption Spectrophotometry (GF-AAS), hydride generation atomic absorption Spectrophotometry (HG-AAS) and ICP-MS as the only available techniques for this analysis.

The ICP-OES method 200.7 is also used extensively for regulatory analysis of wastewater for compliance with the permits issued within the National Pollutant Discharge Elimination System (NPDES) under the Clean Water Act (CWA) (40 CFR part 136).

Large numbers of water samples are analysed using this method, including supplied waters, natural waters and waste waters. The method is commonly used in US States that require well water on private property to be analysed prior to the purchase of real estate. Method 200.7 is used globally as the basis of water analysis methods by ICP-OES, particularly in regions where environmental monitoring developed later than in the US.



Method 200.7 Summary

Method 200.7 describes the determination of 31 elements in water samples and suggests preferred wavelengths, calibration and quality control procedures in addition to specifying procedures for determining method performance characteristics, such as detection limits and linear ranges. A brief overview of the method procedures follows.

Method Detection Limit

The method provides a protocol for determining the Method Detection Limit (MDL). The instrument hardware and method are set up as intended for the analysis. A reagent blank solution spiked at 2-3 times the estimated instrument detection limit is subjected to seven replicate analyses. The Standard Deviation (SD) of the measured concentrations is determined and multiplied by 3.14 (the Student's t value for a 99% confidence interval for 6 degrees of freedom) to calculate the MDL. It is important that contamination is kept under control, especially for environmentally abundant elements such as Al and Zn, since any contamination will degrade the MDL. Interference corrections also affect the MDL, since they employ the monitoring of additional lines and propagate the measurement errors accordingly.

Linear Dynamic Range

The upper linear range limit of a calibration is termed the Linear Dynamic Range (LDR). Method 200.7 defines the upper LDR to be the highest concentration at which an observed signal deviates by less than 10% from that extrapolated from lower standards. Sample dilution can facilitate the measurement of high concentrations, but with additional effort, cost and error. Therefore, a wide LDR is desirable.

Quality Control

Method 200.7 specifies a variety of quality control (QC) standards. These are summarised in Table 2.

Check Name	Check Code	Purpose	Frequency	Limits
QCS	Quality Control Standard	Checks the accuracy of the calibration with a second source standard	Post Calibration	95-105% recovery
SIC	Spectral Interference Check Solution(s)	Checks for the presence of spectral interference and the effectiveness of inter-element corrections	Periodically	No specific requirements
IPC	Instrument Performance Check	A continuing check of accuracy and drift normally done by re-measuring a standard as a sample	Every 10 analyses and at the end of the run	95-105% recovery immediately following calibration; 90-110% recovery thereafter
Blank	Check Blank	A continuing check of the blank level by re-measuring the calibration blank as a sample	Every 10 analyses and at the end of the run	< IDL
LRB	Laboratory Reagent Blank	Checks the laboratory reagents and sample preparation process for contamination	1 per batch of 20 or fewer samples	< 2.2 x MDL
LFB	Laboratory Fortified Blank	Checks the recovery of analytes by spiking a known quantity into a blank	1 per batch of samples	85-115% recovery or within ± 3 standard deviations of the mean recovery
LFM	Laboratory Fortified Matrix	Checks the recovery of analytes in a matrix by spiking a known quantity into a batch sample	1 in 10 samples	85-115% recovery or within ± 3 standard deviations of the mean recovery

Instrumentation

A Thermo Scientific™ iCAP™ 7600 ICP-OES Duo was used for this analysis. The iCAP 7600 ICP-OES Duo contains a switching valve sample introduction system, which significantly reduces sample uptake and wash time, thereby minimising sample analysis time. In addition, the duo view plasma allows for elements expected at trace levels to be analysed axially, for best sensitivity and for elements expected at high concentrations to be measured radially, for best dynamic range. In conjunction with this instrument, a CETAC ASX-520 autosampler was used. An internal standard mixing kit was also used to introduce a 5 mg/l Yttrium internal standard solution online. Sample introduction details are given in Table 3.

Table 3. Sample introduction accessories

Nebulizer		Glass Concentric
Spray Chamber		Glass Cyclonic
Centre torch		2.0 mm ID
Sample Loop Size		4 ml
Pump Tubing	Sample	1.016 mm
	Waste	1.524 mm

Method

A LabBook was set up using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) for all 31 elements covered by method 200.7. Sulphur, which is not part of method 200.7 but is often required in this type of analysis, was also added to the method. Additionally Yttrium lines were added, to be used as an internal standard. The method modes and acquisition parameters used are shown in Table 4.

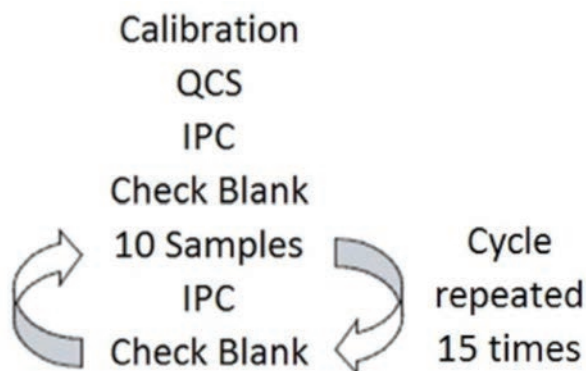
Table 4. Acquisition parameters

Analysis Mode		Speed
Exposure Time	Low	10 sec
	High	10 sec
# Repeats		3
Sample Flush Time		18 sec
Pump Rate		50 rpm
RF Power		1150 W
Coolant Gas Flow		12 l/min
Auxiliary Gas Flow		0.50 l/min
Nebulizer Gas Flow		0.65 l/min

All samples were preserved in 1% nitric acid, trace metal grade (Fisher Chemicals, Loughborough, UK). Calibration standards and QC solutions were prepared using 1000 mg/l standard solutions (Fisher Chemicals, Loughborough, UK); acid matched to the samples and made up to volume with ultra pure de-ionized water (≥ 18.2 mΩ).

Analytical Procedure

A linear dynamic range (LDR) and method detection limit (MDL) study was performed as described in method 200.7. The MDL study was performed with a reagent blank spiked with low concentrations of each element. An interference study was performed using single element SIC solutions as described in method 200.7. To demonstrate the performance of the iCAP 7600 ICP-OES Duo for typical routine analysis of a variety of water samples with method 200.7, a sequence was set up as follows:



The 10 samples analysed between each IPC and blank pair consisted of a variety of aqueous matrices. Three sample types were analysed, a drinking water, a river water and a waste water; each was spiked for analysis as a laboratory fortified matrix (LFM). The samples were analyzed multiple times throughout the process, replicating a run consisting of a total number of 150 samples (187 samples, including QC and calibration solutions).

Results

Table 5. Major interferences observed

Element and wavelength	SIC Solution	Contribution (mg/l)
Al 308.215nm	Mo	0.1644
Al 308.215nm	V	0.3268
B 249.678nm	Fe	-0.2712
Cr 284.325nm	Zr	-0.2605
Si 251.611nm	Mo	0.1816
Si 251.611nm	Sn	2.5110
Tl 190.856nm	V	-0.1782
Zn 213.856nm	Ni	0.0559

Table 6. Analytical wavelengths, plasma views used, LDR and MDL achieved

Element	Wavelength (nm)	Plasma view	LDR (mg/l)	MDL (µg/l)	Level of interest (µg/l)
Ag	328.608	Axial	>5	0.56	100
Al	308.215	Radial	>100	25	50-200
As	193.759	Axial	>50	4.4	10
B	249.678	Axial	>50	2.1	
Ba	455.403	Axial	>50	0.06	2000
Be	234.861	Axial	>50	0.10	4
Ca	315.887	Radial	>250	11	
Cd	226.502	Axial	>50	0.19	5
Co	228.616	Axial	>50	0.32	1*
Cr	284.325	Axial	>50	1.4	100 / 0.2*
Cu	224.700	Axial	>50	0.99	1300
Fe	259.940	Radial	>100	3.1	300
Hg	194.227	Axial	>5	1.3	2
K	766.490	Axial	>100	28	
Li	670.784	Axial	>50	0.05	
Mg	279.079	Radial	>200	26	
Mn	257.610	Axial	>50	0.28	50
Mo	203.844	Axial	>50	1.2	1*
Na	589.592	Radial	>100	8.0	
Ni	231.604	Axial	>50	1.1	
P	177.495	Axial	>50	4.9	
Pb	220.353	Axial	>50	3.2	15
S04	182.034	Axial	>300	19	250000
Sb	206.833	Axial	>50	4.5	5
Se	196.090	Axial	>50	7.3	50
Si02	251.611	Radial	>250	17	
Sn	189.989	Axial	>50	1.7	
Sr	421.552	Axial	>50	0.07	0.3*
Ti	334.941	Axial	>50	0.24	
Tl	190.856	Axial	>10	1.9	2
V	292.402	Axial	>50	0.52	0.2*
Zn	213.856	Axial	>50	0.20	5000
Zr	343.823	Axial	>50	0.29	

*Maximum report limit required for UMCR-3

Element	QCS			IPC (n=16)				
	Measured (mg/l)	Known (mg/l)	% Rec	Mean (mg/l)	Known (mg/l)	% Rec	SD	% RSD
Ag	0.496	0.5	99.3	0.190	0.2	94.8	0.004	2.0
Al	2.563	2.5	102.5	1.042	1.0	104.2	0.024	2.3
As	0.489	0.5	97.8	0.187	0.2	93.7	0.004	2.1
B	2.397	2.5	95.9	1.021	1.0	102.1	0.020	1.9
Ba	0.498	0.5	99.5	0.200	0.2	99.9	0.003	1.3
Be	0.489	0.5	97.7	0.205	0.2	102.7	0.003	1.4
Ca	4.970	5.0	99.4	2.088	2.0	104.4	0.062	3.0
Cd	0.494	0.5	98.8	0.192	0.2	95.9	0.003	1.6
Co	0.485	0.5	97.0	0.197	0.2	98.4	0.005	2.4
Cr	0.480	0.5	96.0	0.196	0.2	98.2	0.002	1.0
Cu	2.468	2.5	98.7	1.031	1.0	103.1	0.022	2.2
Fe	2.420	2.5	96.8	0.983	1.0	98.3	0.008	0.8
Hg	0.464	0.5	92.7	0.201	0.2	100.6	0.008	4.1
K	5.044	5.0	100.9	2.038	2.0	101.9	0.026	1.3
Li	0.475	0.5	95.0	0.198	0.2	99.1	0.003	1.5
Mg	5.248	5.0	105.0	2.052	2.0	102.6	0.074	3.6
Mn	2.446	2.5	97.8	1.014	0.2	507.2	0.026	2.5
Mo	0.475	0.5	95.1	0.197	0.2	98.4	0.004	2.2
Na	5.287	5.0	105.7	2.056	2.0	102.8	0.042	2.0
Ni	2.405	2.5	96.2	0.995	1.0	99.5	0.018	1.8
P	5.041	5.0	100.8	2.099	2.0	105.0	0.049	2.3
Pb	0.477	0.5	95.4	0.191	0.2	95.6	0.003	1.6
S04	14.920	15.0	99.5	6.265	6.0	104.4	0.199	3.2
Sb	0.518	0.5	103.6	0.203	0.2	101.7	0.005	2.6
Se	0.533	0.5	106.6	0.196	0.2	98.0	0.007	3.4
Si02	11.143	10.7	104.1	4.466	4.3	103.9	0.211	4.7
Sn	0.483	0.5	96.6	0.203	0.2	101.6	0.004	2.2
Sr	0.496	0.5	99.2	0.214	0.2	106.8	0.005	2.3
Tl	0.467	0.5	93.3	0.213	0.2	106.7	0.008	3.7
Ti	0.482	0.5	96.4	0.185	0.2	92.6	0.003	1.7
V	0.492	0.5	98.4	0.197	0.2	98.5	0.002	1.0
Zn	2.461	2.5	98.4	1.032	1.0	103.2	0.025	2.4
Zr	0.509	0.5	101.8	0.205	0.2	102.5	0.000	0.2

Table 8. Laboratory fortified matrix results

Element	Spike concentration (mg/l)	Drinking water			River water			Waste water		
		Unspiked (mg/l)	Spiked (mg/l)	% Rec	Unspiked (mg/l)	Spiked (mg/l)	% Rec	Unspiked (mg/l)	Spiked (mg/l)	% Rec
Ag	0.25	<MDL	0.252	100.8	<MDL	0.252	101.1	0.001	0.261	104.0
Al	1.00	<MDL	1.044	104.2	0.108	1.159	105.2	0.191	1.233	104.2
As	0.25	<MDL	0.240	94.6	0.003	0.230	91.0	0.022	0.289	107.1
B	1.00	0.019	1.046	102.7	0.048	0.963	91.5	0.136	1.151	101.5
Ba	0.25	0.058	0.300	96.9	0.047	0.282	93.9	0.108	0.372	105.6
Be	0.25	<MDL	0.236	94.4	<MDL	0.255	102.1	0.018	0.286	107.0
Ca	2.50	113.3	115.7	95.5	162.1	164.5	95.9	144.5	146.8	91.8
Cd	0.25	<MDL	0.241	96.3	<MDL	0.246	98.2	0.018	0.286	107.2
Co	0.25	<MDL	0.243	97.1	<MDL	0.241	96.5	0.019	0.261	97.1
Cr	0.25	<MDL	0.228	90.1	0.002	0.257	101.9	0.024	0.293	107.7
Cu	1.00	0.184	1.190	100.5	<MDL	1.031	102.4	0.150	1.200	105.0
Fe	1.00	<MDL	1.008	101.2	0.097	1.128	103.1	0.252	1.308	105.6
Hg	0.25	<MDL	0.254	101.3	<MDL	0.252	101.2	<MDL	0.255	101.4
K	2.50	1.94	4.45	100.5	5.33	7.90	102.8	6.58	9.29	108.4
Li	0.25	0.011	0.252	96.4	0.019	0.272	101.1	0.040	0.272	92.8
Mg	2.50	2.93	5.41	99.1	6.26	8.88	104.5	5.49	7.95	98.2
Mn	1.00	<MDL	0.967	96.7	0.011	0.969	95.7	0.082	1.089	100.7
Mo	0.25	<MDL	0.236	94.9	<MDL	0.227	91.1	0.018	0.281	105.3
Na	2.50	11.0	13.6	102.2	53.7	56.1	96.9	42.5	44.9	98.1
Ni	1.00	<MDL	0.933	93.2	0.002	1.070	106.8	0.071	1.060	98.9
P	2.50	1.12	3.69	102.8	0.48	2.97	99.5	2.84	5.43	103.3
Pb	0.25	<MDL	0.260	102.7	0.004	0.249	98.2	0.023	0.257	93.9
S04	7.50	28.6	36.2	100.6	82.9	90.3	98.5	64.1	71.5	98.3
Sb	0.25	<MDL	0.258	103.3	<MDL	0.237	95.0	0.019	0.278	103.6
Se	0.25	<MDL	0.242	98.0	<MDL	0.231	93.9	0.022	0.287	105.8
SiO2	5.36	14.4	19.6	98.0	13.6	18.8	97.1	15.9	21.4	102.7
Sn	0.25	0.084	0.325	96.5	<MDL	0.262	105.5	0.057	0.308	100.3
Sr	0.25	0.561	0.814	101.3	0.990	1.248	103.2	0.811	1.081	108.1
Tl	0.25	0.003	0.244	96.4	0.007	0.276	107.4	0.034	0.272	95.1
Ti	0.25	<MDL	0.240	96.3	<MDL	0.249	99.7	0.021	0.254	93.3
V	0.25	<MDL	0.256	102.5	0.001	0.242	96.7	0.019	0.284	105.9
Zn	1.00	0.005	1.012	100.7	0.008	1.025	101.7	0.104	1.115	101.1
Zr	0.25	<MDL	0.251	100.6	<MDL	0.253	101.3	0.002	0.263	104.3

Interference Study

Only eight significant interferences were found during the analysis of the SIC solutions, showing that the selected wavelengths are relatively interference free. The interferences observed (shown in table 5) can easily be corrected by using inter-element corrections when necessary.

LDR

The high standards analyzed for the linear dynamic range check showed little deviation from their expected values, indicating linearity up to at least the levels indicated in Table 6. These levels are normally more than sufficient for the analysis of typical water samples.

MDL

The method detection limits calculated from analysis of the MDL solution were generally in the low and sub ppb range for the majority of elements. All MDLs were sufficiently below the typical levels of interest for drinking water analysis, with the exception of antimony, arsenic, mercury, thallium, and aluminium. The MDLs for these elements were of the same magnitude as the level of interest. For this reason ICP-MS may be a more appropriate alternative for the regulatory drinking water measurements for these elements.

Accuracy, Precision and Stability

The iCAP 7600 ICP-OES produced consistently accurate results with minimal intensity drift, as shown by the results for the QCS and IPC solutions (see Table 7). The ongoing IPC results were consistently within the allowed range of 90-110% of the known value, as shown in Figures 1, 2 and 3. The precision of the 16 IPC measurements across the 150 sample run were also shown to be very good. Table 7 indicates that the relative standard deviations (RSDs) of these measurements were within 5% across the duration of the run (7 hours 14 minutes).

The accurate results for the LFM samples (shown in table 8) show that quantitative recovery can be achieved in a variety of real environmental matrices. All spike recoveries were well within the allowable range of 85-115%.

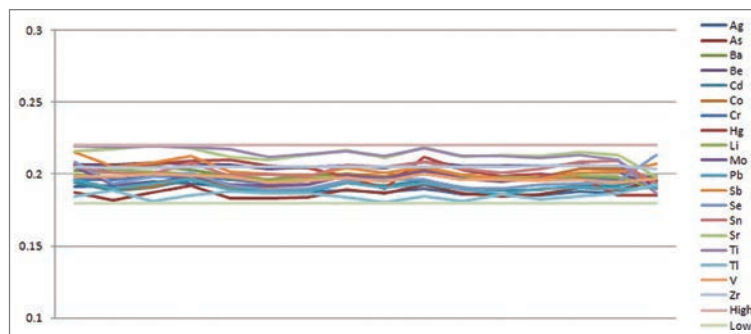


Figure 1. Stability of successive IPC measurements during the 150 sample analysis. Control limits are shown as high and low. Elemental results are shown for S and Si

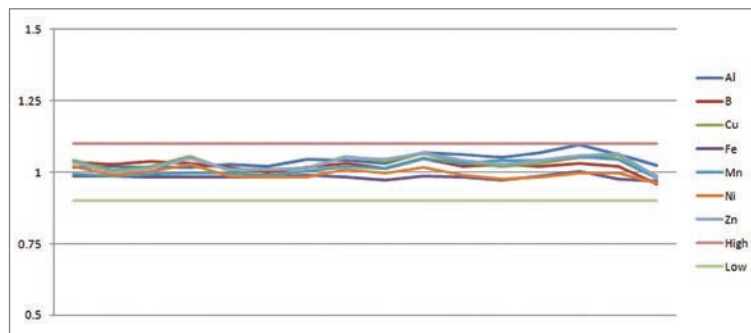


Figure 2.

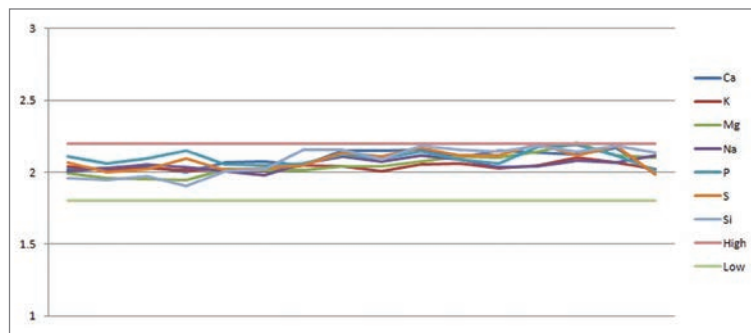


Figure 3.

Conclusions

The Thermo Scientific iCAP 7600 ICP-OES Duo demonstrated compliance with the requirements of EPA Method 200.7 for a wide range of water sample types. The instrument was successfully used to follow stringent AQC requirements of the method. A combination of specifically designed hardware and software tools enable and simplify compliant analysis.

Wavelength verification is quick and easy with the autopeak function, while method and instrument optimization are automatically performed with the built-in optimization procedures. These features combined with the high transmission optical design and sensitive CID86 detector, produce optimum performance, as indicated by the excellent method detection limits obtained. The lack of physical and spectral interference in environmental samples, demonstrated in the interference study, makes the iCAP 7600 Series ICP-OES ideal for analyzing waters and other environmental sample types.

Careful attention was paid to the thermal conductivity of the instrument components during the design phase, resulting in an extremely stable system that delivers accuracy over long periods of time or extended without frequent re-calibration, as demonstrated by the consistent IPC results.

Qtegra ISDS has a built-in QC checking capability that is designed to meet the requirements of EPA methods. The package also includes monitored uptake / washout features to maximize useful analytical time. The productivity tools of Qtegra ISDS combined with the speed of the iCAP 7600 ICP-OES and the loop filled sample introduction system drive rapid analysis times. Samples in this study were processed at a speed of 1 sample every 2 minutes and 22 seconds, or 25 samples per hour, making the iCAP 7600 ICP-OES the ultimate instrument for cost-effective elemental analysis.

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