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Study on the determination of $^{10}B/^{11}B$ isotope ratio in water samples by isotope dilution – inductively coupled plasma mass spectrometry (ID-ICPMS)

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Abstract: The determination of $^{10}B/^{11}B$ isotope ratio and boron concentration in various water samples using isotope dilution technique with inductively coupled plasma mass spectrometry (ICP-MS) was studied. The interferences on precision and accuracy in isotopic ratio determination by ICP-MS such as memory effects, dead time, spectral overlap of ^{12}C were investigated for the selection of optimum conditions. By the addition of certain amounts of enriched ^{10}B into samples, the $^{10}B/^{11}B$ ratio was determined through ICP-MS signal of ^{10}B and ^{11}B. The detection limit for ^{10}B and ^{11}B was experimentally obtained as 0.26 µg/L and 0.92 µg/L, respectively. The ratios of $^{10}B/^{11}B$ in measured water samples varied in the ranged between 0.1905 and 0.2484 for different matrices. This method has been then applied for the determination of boron isotopic ratio in VVER-1000 reactor-type simulated primary coolant water and in some environmental water samples.

Key words: *ICP-MS, Boron, $^{10}B/^{11}B$ ratios, Isotope dilution, water samples, VVER-1000*

I. INTRODUCTION

Boron (B) is a light element that has two natural isotopes ^{10}B and ^{11}B with 19.9 % and 80.1 % atomic abundances, respectively. Boron exists in solution in two forms-viz, trigonal boric acid $B(OH)_3$ and tetrahedral borate anion $B(OH)_4^-$. These two forms equilibrated in solution, and their relative proportions depend upon the pH of the solution, as given below:

$$B(OH)_3 + H_2O = B(OH)_4^- + H^+ \qquad (1)$$

At high pH values (pH > 11), $B(OH)_4$ dominates, while $B(OH)_3$ is the dominant form at pH < 7. An equilibrium isotope fractionation can, therefore, only be expected if the aquatic system has a pH between 7 and 11. Boron is stable in aqueous solutions as an oxo-anion and is not affected by oxidation-reduction reactions [1].

Trigonal $B(OH)_3$ is predominant in acidic media whereas the tetrahedral anionic form is mainly in basic solution. $B(OH)_3$ can be more enriched in ^{11}B, whereas $B(OH)_4^-$ is more enriched in ^{10}B as given below in exchange fraction.

$$^{10}B(OH)_3 + {}^{11}B(OH)_4^- = {}^{11}B(OH)_3 + {}^{10}B(OH)_4^- (2)$$

This could be observed in the adsorption of seawater by clay due to the differences in the vibrational frequencies of the two boron isotopes and the molecular coordination between boron species in different phases [2].

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It can thus be predicted that natural water from different matrices might vary the $^{10}B/^{11}B$ ratio.

Boric acid is an important compound of boron, which has been widely using in nuclear industry as strong thermal neutron absorbers [3]. The important role of boric acid in nuclear power plant was to control nuclear fission rate and thus to influence with the power generation [4].The investigated works on pressurized water reactors showed that enriched ^{10}B in coolant gave very strong absorption ability that absorption cross section of thermal neutron was five fold to natural boron abundance. During operation of nuclear reactor, the concentration of ^{10}B in coolant water should be reduced commensurably which required the regular determination of isotopic composition and concentration of boron. The determination of $^{10}B/^{11}B$ ratio could thus support the estimation of the B amount being absorbed by neutrons, and supply boric acid in time.

Nowadays, the advanced spectroscopic techniques such as: thermal ionization mass spectrometry (TIMS), secondary ion mass spectrometry (SIMS) and inductively coupled plasma source mass spectrometry (ICP-MS) were widely applied for the determination of $^{10}B/^{11}B$ isotope ratio. TIMS provided a high level of accuracy and precision for the determination of B isotopic composition [5-7]. However, TIMS required a purification steps [6] that caused the time consumption [8]. SIMS method could supply an advantage to analyse boron at relatively low concentration in a solid sample [9-11] but the volatile phase of boron caused the difficulty to get the high accuracy of analysis. The experiences from nuclear power plant utilities showed that ICP-MS was preferable to analyse the ^{10}B concentration in coolant system [12].

ICP-MS seemed to be a useful method to determine boron isotope ratios and boron concentration in a variety of matrices [13-17] though it required the sufficient sample treatment. The introduction of isotope dilution technique into this method resulted in the most precise approach in quantitative determinations [18].

ICP-MS combined with isotope dilution technique had been used for the determination of boron in high purity quartz [19], iron and steel [20-22], body fluids [23]. The isotope dilution technique was not interfered with the recovery of analyte and with the signal drift of measurement on ICP-MS. However, there were difficulties with the determination of trace boron in different sample matrices by ICP-MS due to the high memory effect, dead time effect and spectral overlap of ^{12}C (if there was) to ^{11}B. Memory effect could be minimized by the introduction of mannitol and ammonia [24] together with the sample just before the nebulizer [25], or by injection of ammonia gas into the spray chamber during the analysis [26, 27]. In our study, mannitol in nitric acid solution was applied for the enhancement of precision and accuracy measurement.

II. EXPERIMENTAL

A. Instruments

An ICP-MS instrument (7500a, Agilent) with quadrupole mass spectrometer was used in this study. The operating conditions of ICP-MS were optimized by using mass standard solution to obtain the ratios of oxide ions ($Ce^{+}O/Ce$) and doubly positive charged ions (Ce^{2+}/Ce^{+}) at the values of about 1.0 and 2.5 %, respectively. The operating conditions of ICP-MS system and the data acquisition parameters were summarized in Table I.

Table I. Operating parameters of ICP-MS system

Parameters	Value	Parameters	Value
RF power	1240W	Pressure for analysis	3.10^{-4}-2.10^{-3} Pa
Sample uptake	90 s	Coolant flow	2.2 $l.min^{-1}$
Sample flow	0.1 $ml.min^{-1}$	Coolant temp	2°C
Sample depth	6.4mm	Data Acquisition conditions	
Plasma gas flow	15 $l.min^{-1}$	Peak pattern	Full quant (3)
Carrier gas flow	1.2 $l.min^{-1}$	Integrations time	0.1s

B. Reagents and standard solutions

Standard solution of isotope enriched ^{10}B and that of ^{11}B (10mg/l) supplied by Inorganic Venture Company (USA). Standard stock solution of B 1000 mg/l was prepared in 0.3 M HNO_3 by dissolution of a certain amount of 99.99% H_3BO_3 (Merck, Germany). Other chemicals (HNO_3, mannitol, ammonia) were at analytical grade. All solutions were prepared in ultrapure water (Mili-Q with resistivity 18MΩcm^{-1}) and further diluted. Argon gas (Messer) with 99,999% purity was used.

C. Sample preparation

Water samples (mineral water, drinking water, pure water) could be stored in polyethylene bottles at 8°C, if necessary. Each portion of 5 to 7 ml of sample was transferred into five of 10 ml plastic volumetric flasks. 0.5 ml of 10% HNO_3, 0.5 ml of 2.5% D-mannitol solution and different amount of enriched ^{10}B standard solution was added then filled up with ultrapure water. A blank sample was prepared for background correction.

Water sample of simulated coolant water in the primary loop of a VVER 1000 unit was prepared according to the reference [28] from boric acid and potassium hydroxide. Boron concentration was taken in the range of 1000-2500 mg/l (simulated the operating cycle state). Total alkalinity was given by the concentration of potassium, lithium and sodium to equivalent potassium to be allowed as 20 ppm at maximum value. Lithium concentration varied during the operation cycles from 50 to 600 ppb with average values of 300-350 ppb, that of sodium from 30 to 350 ppb with average values of 200 – 250 ppb. Potassium / lithium ratio changed during the cycles from 10 - 100 ppm with average values in the range of 10-30 ppm.

In present study, a synthesized sample with the composition of 1400 mg/l B as H_3BO_3, 24 mg/l KOH and 5mg/l NH_3 to adjust pH_{25} in the range 7.0-7.2 was prepared in ultrapure water. This stock sample was then diluted proportionally into 10ml volumetric flask, where the enriched ^{10}B was spiked. These spiked sample solutions were measured using ICP-MS system under the identical condition. The signals (cps) at m/z =10 and m/z=11 for ^{10}B and ^{11}B were recorded, respectively.

D. Isotope dilution analysis

The isotope dilution (ID) technique is based on the addition of a known pure isotope to a sample containing the same element with variously isotopic abundance. The isotopic ratio between the added and the originally containing isotope in the mixed solution was measured on ICP-MS after the equilibration of the spike isotope with the analyte in the sample reached.

By adding other amounts of ^{10}B into samples, ^{10}B and ^{11}B signals on ICP-MS system were obtained and the correlation of ^{10}B and ^{11}B signals toward the added amount of enriched ^{10}B would show by an equation Y = A + BX. The ^{10}B/^{11}B isotope ratio is calculated by the following formula:

$$R = \frac{A_{10}}{A_{11}} \qquad (3)$$

Where: A_{10} denotes the coefficient of the plotted curve on the basic of dependency between ^{10}B signal and ^{10}B spike amounts;

A_{11} denotes the coefficient of the plotted curve on the basic of dependency between ^{11}B signal and ^{10}B spike amounts;

III. RESULTS AND DISCUSSIONS

A. Matrix effect

Matrix effects in ICP-MS are generally dependent on the mass due to the space charge effect [17]. Since boron is a light element, the matrix effect of any heavier element can be severe. Furthermore, the two isotopes ^{10}B and ^{11}B have different matrix effects, which could cause the deviation in the measured isotope ratios. On the other hand, the concentration of alkali and alkaline earth elements in environmental water might contribute to the matrix effect on the direct boron determination using ICP-MS but it would be negligible with the use of isotope dilution technique.

B. Memory effect and dead time effect

Boron is known to be one of the elements that are difficult to determine using ICP-MS due to a significant memory effect. Al-Ammar *et al.* [25, 26] reported that a primary source of the memory effect was the volatilization of boric acid droplets in the spray chamber. For the elimination of the memory effect, Vanderpool *et al.* [27] adjusted pH of sample solution to about 10 by addition of ammonium hydroxide solution or introducing a small amount of ammonia gas in the nebulizer gas flow [25, 26]. Sun *et al.*[24] added mannitol to the sample solutions to prevent B from binding to the spray chamber walls. In our work, 0.05% mannitol in 0.5% HNO_3 was added in sample solution and a dilute ammonia solution used for rinsing between measurements.

The dead time effect was automatically corrected with the instrument software. Besides the software correction, counting signals of the two isotopes were limited to between 100,000 and 2000000 to minimize the uncertainty from the dead time effect.

C. Effect of spectral ^{12}C onto ^{11}B and ^{10}B

The spectral interference of ^{12}C signals at ^{10}B and ^{11}B atomic masses was evaluated by the measurement of different concentrations of mannitol in the absence of boron. The results were shown in Fig1. It was seen that the signal of ^{10}B was not influenced with those of C while signal of ^{11}B enhanced with the increase of mannitol concentration. However, the ^{11}B signal was slightly increased in the range between 0 and 0.1% mannitol, and the interference would be controlled at the fixed mannitol concentration within this range. Furthermore, the addition of mannitol could reduce the memory effect [25] that would help the high recovery of each measurement and 0.05% mannitol was thus used for sample analysis in this work.

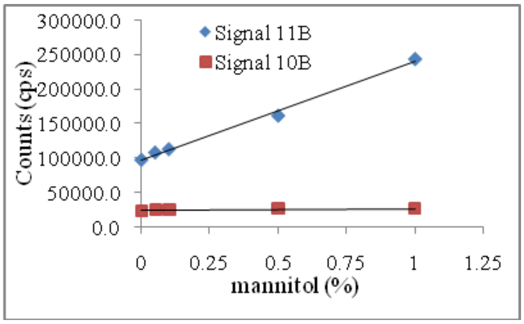

Fig.1 The dependence of apparent signal (counts/s) of ^{10}B and ^{11}B on mannitol concentration

D. Limit of detection, limit of quantitation

The limit of detection (LOD) of ICP-MS measurement for each isotope mainly depended upon the numbers of factors such as instrumental sensitivity, spectral interferences, memory effect, cleanliness of digestion vessels and blank level of analytical reagents. It is possible to define the lowest concentrations that can be reliably detected and quantified. The LOD and LOQ of ^{10}B and those of ^{11}B are determined by the calculation based on the following formula [29]:

$$LOD = \frac{3S.C_{STD}}{I_{std} - I_{blank}} \qquad LOQ = \frac{10S.C_{STD}}{I_{std} - I_{blank}} \quad (4)$$

Where: C_{STD} is concentration (µg/L) and I_{STD} is average intensity of the standard sample (cps);

S is standard deviation and I_{blank} is raw average intensity of the blank (cps);

Table II. Limit of detection and limit of quantitation

Isotope	Concentration (µg/L)	LOD (µg/L)	LOQ (µg/L)
^{10}B	100	0.26	0.86
^{11}B	100	0.92	3.04

Although B was a light element that was difficult to determine by ICP-MS but the results showed that this modern technique was capable of detection and quantification of boron at a trace amount.

E. Isotopic calibration curve

The experimental value of ^{10}B/^{11}B ratio measured on ICP-MS very much depended on instrument parameters such as plasma power, sample depth, fractionation of a light element, ect... A correction factor should be included in the calculation mentioned in formula (3), which could be obtained from the isotopic calibration curve for the improvement of the accuracy.

The isotopic calibration curve (Fig.2) was plotted by the Measured Isotopic Ratio - MIR10/11 values (the ratio of measured signals from boron solutions, in which ^{10}B/^{11}B ratio was changed while keeping constant total concentration) vs. MR10/11 values (Mass Ratio of corresponding composition between ^{10}B and ^{11}B in solutions). The result showed that high linearity correlation (R^2=1) from the linear regression equation (Y = 0.9936X - 0.0006).

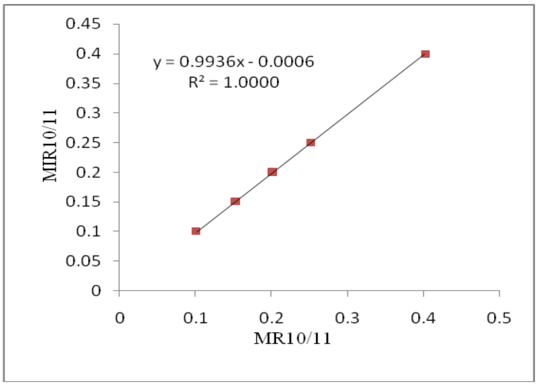

Fig.2. Calibration curve of B isotopic ratio

It is thus posible to correct the MIR 10/11 values of unknown samples using ID technique on the basic of isotopic ratios of spiked ^{10}B on ^{11}B samples.

F. Selection of ^{10}B spike added amount

Water sample containing 100µg/L B was prepared in a plastic flask. Two sets of ^{10}B spikes were then added into different flasks. Set I consisted of the following concentration: 2, 5,10, 15, 20 µg/L ^{10}B and the set II would contain respective 50, 100, 150, 200 µg/L ^{10}B. All sample solutions were measured on ICP-MS under the identical condition. The below figures showed the correlation of ^{10}B and ^{11}B signals toward the added amount of ^{10}B spikes. Within a narrow range of added amount of ^{10}B spikes in set I (Fig.3), the isotope ratio ^{10}B/^{11}B (R) was calculated by formula (3) to be 0.2271 with RSD = 0.35%, and the recovery of boron concentration was estimated as 100.33%.

The isotopic ratio ^{10}B/^{11}B (R) was calculated by formula (3) to be 0.2191 with RSD = 0.27% and the recovery of boron concentration was 106.32% for the added amount ^{10}B spikes in set II (Fig.4). These results showed that the isotopic ratio between added amount ^{10}B spikes in set I (range of 2-20 µg/L) and that in set II (range of 50-200µg/L) did not much change and the difference was within 1,3% error though the concentration of set II spike was much higher than that of set I. Therefore, the ^{10}B/^{11}B isotopic ratio value in the range of studied samples seemed not be affected by the added amount of ^{10}B spike. However, the enriched ^{10}B spike was tested for each sample batch and this added amount was often fixed within the researched sample series.

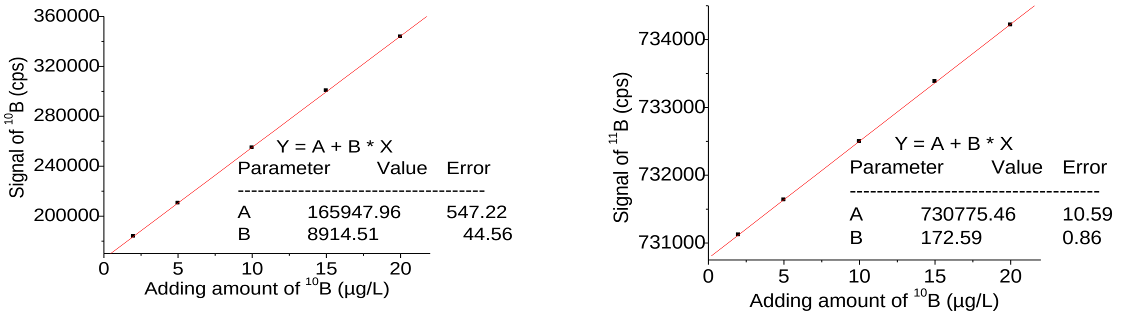

Fig.3 Correlation of ^{10}B and ^{11}B signals to added amount of ^{10}B spikes (Set I: 2-20µg/L)

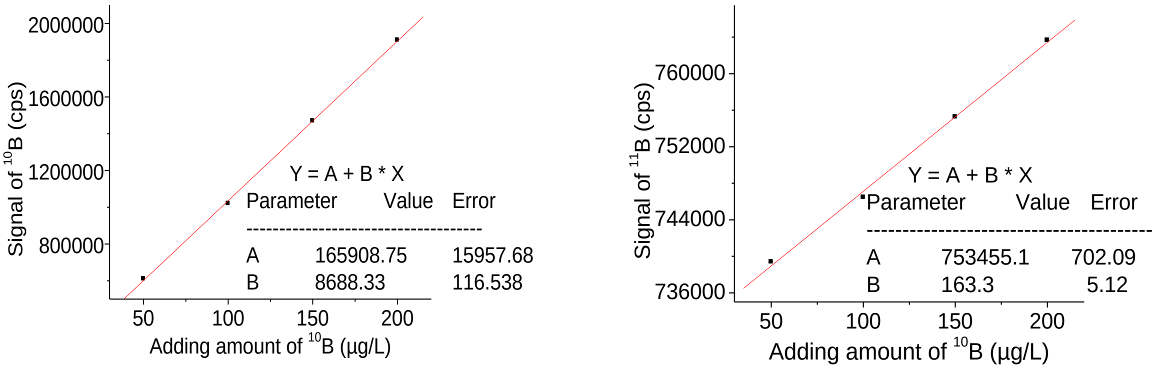

Fig.4 Correlation of ^{10}B and ^{11}B signals to added amount of ^{10}B spikes (Set II: 50-200µg/L)

G. Analysis of VVER 1000 - type simulated primary coolant water sample

The measurement of simulated primary coolant water samples was carried out under the identical conditions. The amount of ^{10}B was added in the range between 5 and 20 µg/L. The correlation between ^{10}B signal and ^{11}B signal with spiked amount of ^{10}B was showed in Fig.5.

The isotope ratio ^{10}B/^{11}B (R) was calculated by formula (3) to be 0.2164 with RSD = 0.29%. It was well agreed with the value of naturally isotopic boron compositions in boric acid (Merck Reagent, FR Germany made), which was confirmed within 19.9 to 22 % for natural boric acid (NBA) type by French researchers [12]. In order to learn further about boron isotopic ratio, several natural water samples were analyzed using this ID technique.

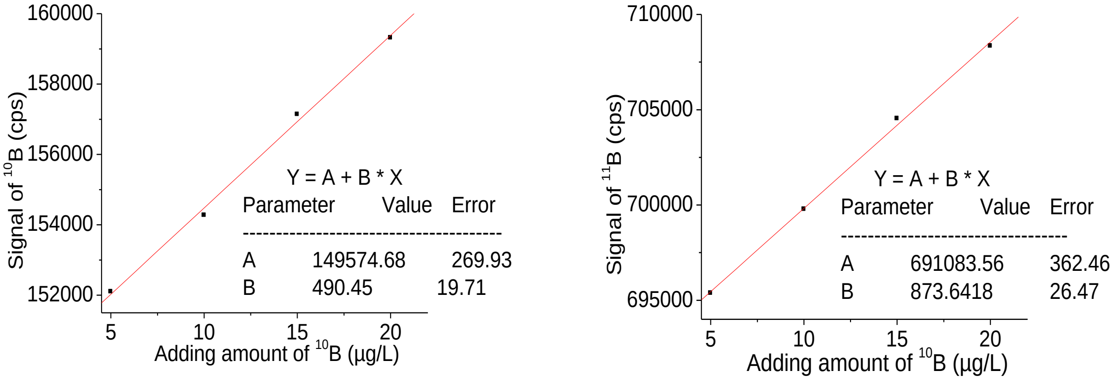

Fig 5. Correlation of ^{10}B and ^{11}B signal to ^{10}B spikes in simulated sample

H. Analysis of environmental water samples

The environmental water samples (drinking water, mineral water,..) were collected and stored as above described procedure. The different amount of enriched ^{10}B isotope was spiked. The isotopic ratio between ^{10}B and ^{11}B was calculated by formula (3). From that ratio ^{10}B and ^{11}B concentration in samples was determined and corrected by isotopic calibration. The results of $^{10}B/^{11}B$ were showed in table IV.

The $^{10}B/^{11}B$ isotopic ratio of the different water matrices seemed various (Table IV). The values obtained from spring water and bottled mineral water were similar to the natural boron abundance but these from tap water and from IAEA artificial mineral water gave higher than that of European boron isotopic ratio [12]. This difference could reflect the original source of water and it was also found to vary toward the region [30]. However, as an aspect of environmental water for human life, according to provisional guideline values for drinking water of WHO[31] (0.5 mg/L) and that of QCVN 01-2009 (Ministry of Health) [32] (0.3 mg/L), boron concentration should be lower than these limits in water for drinking usage. Moreover, boron concentration in human intake must not exceed 1mg/kg body weight/day [31], it should be safe for the consumption of approximately 2 litres water per day (about 0.064 mg boron intake per person), due to a very small fraction of the total amount of boron intake by drinking except for food.

Table IV. Analysis of environmental water samples

Sample name	$^{10}B/^{11}B$	^{10}B conc.(µg/L)	^{11}B conc. (µg/L)	Boron conc.(µg/L)
Mineral water (IAEA-V1)	0.2484±0.001	248.40±1.19	1000.0±4.07	1248.4±4.24
Spring Water (PacBo-CaoBang, VN)	0.1905±0.007	4.40±0.16	22.88±0.83	27.28±0.85
Bottled Mineral water (VN)	0.2040±0.009	2.69±0.11	13.18±0.58	15.87±0.59
Tap water – HN-1	0.2426±0.008	6.40±0.21	26.14±0.85	32.54±0.88
Tap water - HN-2	0.2530±0.005	6.60±0.12	25.86±0.51	32.46±0.52
Tap water - BN	0.2309 ±0.002	29.64±1.68	127.21±7.23	156.85±7.42
Mineral water BON-AQUA (Czech)	0.2045±0.003	41.34±0.62	200.01±2.93	115.20±2.99
Mineral water CRISTALINE (France)	0.2078±0.003	29.68±0.43	142.86±2.07	241.34±2.11
Mineral water ASAHI-Japan	0.2202±0.003	31.45±0.42	142.85±1.91	172.54±1.96
Mineral water TSUNAN- Japan	0.2252±0.003	29.25±0.39	129.88±1.73	174.3±1.77

II. CONCLUSIONS

The determination of $^{10}B/^{11}B$ ratio in water samples by ID-ICP-MS was studied and the analytical procedure would thus be established for the application in boron isotopic ratio investigation on pressurized water reactor (VVER1000 – type) simulated primary coolant samples and in environmental water samples. The $^{10}B/^{11}B$ ratio in measured water samples ranged from 0.1905 to 0.2484, which were very much dependent on the substance matrices. In addition to the conclusion, boron concentration in studied samples of drinking water varied from 15.87 to 32.54 µg/L, with an average value of 27.04 µg/L. The obtained values were below WHO-recommended limit of 0.5 mg/L that would be safe for drinking usage. The studied method was further expanded for the application in analysis of trace boron content in different sample matrix such as food, geology, biology.

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