Review

Review of Chloride Ion Detection Technology in Water

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Featured Application: Water is the source of life. It is both food for human beings and necessary for the existence of the whole ecological system. With the development of society, there are more and more water pollutants. Water detection technology needs modernization, intelligence, and speed. The chloride ion, an anion that is widespread in nature, will have harmful effects on industrial and agricultural production and ecology when its levels are too high. How to quickly and timely monitor chloride ions is an important question for industrial production, agricultural production, human activities, and ecological health.

Abstract: The chloride ion (Cl^-) is a type of anion which is commonly found in the environment and has important physiological functions and industrial uses. However, a high content of Cl^- in water will do harm to the ecological environment, human health and industrial production. It is of great significance to strictly monitor the Cl^- content in water. Following the recent development of society and industry, large amounts of domestic sewage and industrial sewage are discharged into the environment, which results in the water becoming seriously polluted by Cl^-. The detection of Cl^- has gradually become a research focus. This paper introduces the harm of Cl^- pollution in the environment and summarizes various Cl^- detection methods, including the volumetric method, spectrophotometry method, electrochemical method, ion chromatography, paper-based microfluidic technology, fluorescent molecular probe, and flow injection. The principle and application of each technology are described; their advantages, disadvantages, and applicability are discussed. To goal of this research is to find a more simple, rapid, environmental protection and strong anti-interference detection technology of Cl^-.

Keywords: chloride ion; detection; review; pollution; water

1. Sources and Hazards of Chloride Ion

Chloride ions (Cl^-) are widely distributed in nature. Almost all natural water contains Cl^-, mainly in the form of calcium, magnesium, and sodium salts. Natural water samples from different sources vary in Cl^- content. The Cl^- content in seawater can be as high as 19,000 mg/L, while the Cl^- content in general surface water and ground water is less than 50 mg/L. Although marine organisms have a relatively high tolerance towards Cl^-, the tolerance of terrestrial animals and plants is limited to a certain range. The Cl^- in natural water comes from natural strata, some salt deposits, and Cl^--containing sediments. With the development of society, human activities and industrial production have led to the increase in chlorine ions in the natural environment year by year. For example, road salt has been heavily used in many higher latitude countries in which it usually snows. It is reported that approximately 490,000 and 20,300,000 tons of salt were used in winter on roads in Poland and America, respectively [1], more than 6,000,000 tons of salt used in Canada [2], and 10,000,000 tons of salt used in France [3]. The concentrations

of Cl$^-$ induced by road salt infiltration have risen from 183 mg/L to 3568 mg/L near Azerailles, France and from 1243 mg/L to 12,086 mg/L in Poland [3,4]. One source of Cl$^-$ pollution is discharged water from domestic sewage and modern industries [5–7]. These industries include the soap industry, salt industry, alkali industry, leather- and fur-processing industry, pickled food industry, and so on. Another source of Cl$^-$ pollution is the development of new energy and new materials. For example, chloride ion batteries have high theoretical capacity and discharge platforms; they have been reported as one of the potential technologies which could replace lithium-ion batteries used in cars [8]. However, new chloride contamination may occur during battery recycling. Chloride is a compound widely used in industrial and agricultural production and human life, but excessive use will also put strain on the environment and ecology. Therefore, chlorine ion detection is particularly important. On the www.baiten.cn (accessed on 16 November 2021) patent website, a search with the keywords "Chloride ion detection" produces results that show that, in China, there are more than 30 related patents from 2007 to 2015, while there are more than 100 related patents from 2016 to now. It can be seen that people have gradually attached importance to the detection of Cl$^-$ pollution. China's national drinking water sanitation standard [9] stipulates that the Cl$^-$ content in drinking water should be less than 250 mg/L. If wastewater containing high levels of Cl$^-$ is directly discharged into the environment, the water quality will decrease, the aquatic organisms and plants in the ecological environment will be threatened, the life and health of terrestrial animals, plants, and human beings will be directly or indirectly affected, and industrial production will be seriously affected.

The main hazards of Cl$^-$ are as follows: (1) Soil, water, and air: Heavy content of Cl$^-$ influences the soil structure and decreases the retention capacity and the porewater pH of soil [10,11]. Cl$^-$ may reduce the self-purification process of water. Baker et al. found that a 1% increase in Cl$^-$ in impervious surfaces promoted an increase in conductivity by 15 μS/cm from 1986 to 2010 in 12 watersheds in Maryland's Upper Piedmont [12]. Kolesar et al. found that heavy Cl$^-$ influences air quality when it is aerosolized at not more than PM2.5 concentrations [13]. (2) Animals and plants: The increase in Cl$^-$ content in water reduces the self-purification processes of water and decreases the biodiversity of aquatic animals and plants [1]. Excessive potassium chloride in water will hinder the growth of tobacco, and even promote its death in serious cases [14]. High concentrations of Cl$^-$ have also deteriorated vegetation near the roads [15]. (3) Human health: High concentrations of Cl$^-$ can make water taste salty or bitter [16,17]. Excessive intake will cause diseases such as weakened immunity, hypertension, arteriosclerosis, cerebral infarction, etc. [18–20]. A severely reduced Cl$^-$ intake can have negative impacts such as chronic heart failure, chronic kidney disease, liver cirrhosis, and so on [21–24]. (4) Construction and building trades: Very elevated Cl$^-$ levels in cement raw materials will reduce the strength of concrete, corrode steel bars, affect the durability of the whole building, and severely affect project quality [25–27]. (5) Industrial equipment: In industrial production, Cl$^-$ will corrode stainless steel equipment (such as reinforced concrete, petroleum and chemical production equipment, power plants, and some high-purity water and gas systems), preferentially adsorb oxygen atoms on the metal surface, and form soluble metal Cl$^-$ with metal ions, leading to metal corrosion, causing economic losses, and even threatening the safety of operators [19,28]. (6) Chemical oxygen demand analysis: Cl$^-$ will disturb the chemical oxygen demand analysis [29].

Therefore, the detection of Cl$^-$ in water is very important and is of great significance for the prevention and control of environmental and ecological pollution. The technology used to determine levels of Cl$^-$ in water is also the basis for the detection of national standards of Cl$^-$ in food, feed, activated carbon, paper products, chemical products, fertilizer, air, soil, cement, and so on [30–38]. The detection of Cl$^-$ in the above items is finally achieved in the water detection phase. Only by introducing new detection and evaluation methods and putting forward preventive measures in time, can the quality

of soil, water, and air be guaranteed, the safety of life not be threatened, and industrial production and testing be carried out normally.

2. Traditional Methods and Advantages and Disadvantages

Traditional Cl⁻ analysis methods include the volumetric method, the electrochemical method, the photometric method, and chromatography. Different Cl⁻ detection methods have different applications, scopes and detection accuracies. Table 1 shows the summary of and comparison of relevant detection standards for Cl⁻ in water in China.

Table 1. Typical detection standards for chloride ion in water in China.

Detection Method	Name	Concentration Range (mg/L)	Applicable Objects	Standard Number
Volumetric Method	Mercury nitrate titration	2.5–500	Groundwater Surface water	HJ/T343 [39]
	Ammonium thiocyanate volumetric method	5–100 mg	Natural and clean water	GB/T29340 [40]
	Silver nitrate volumetric method	10,000–42,000	Seawater cooling water	GB/T33584.3 [41]
		>1.0	Domestic drinking water and source water	GB/T5750.5 [42]
	Mercuric nitrate volumetric method	>1.0	Domestic drinking water and source water	GB/T5750.5 [42]
	Silver nitrate titration	10–500	Natural water	GB/T11896 [43]
Electrochemical Method	Potentiometric titration	5–1000	Industrial circulating cooling water and boiler water	GB/T15453 [44]
Spectrophotometry Method	Coprecipitation enrichment photometric method	10–100	Industrial circulating cooling water and boiler water	GB/T15453 [44]
	Ferric photometric method of mercury thiocyanate	0.4–6.0	Meteoric water	GB/T13580.9 [45]
Chromatography Method	Ion chromatography	0.1–500	Clean water	GB/T14642 [46]
		0.15–2.5	Domestic drinking water and source water	GB/T5750.5 [42]

The common detection method of Cl⁻ is the volumetric method, and the silver nitrate titration method is suitable for neutral to slightly alkaline water. The end point of this method is not sensitive, the operation requirements are strict, and the anti-interference ability is weaker than that of the ammonium thiocyanate volumetric method. The end discoloration of mercuric nitrate titration is more acute than that of silver nitrate titration, but it is more affected by the acidity of the tested sample. Th electrochemical method, which can be used for colored and turbidized water samples, mainly determines the endpoint through the potential jump. However, the electrode has a photosensitive effect, and the precipitation easily stains the electrode, so it should be cleaned promptly. The spectrophotometry method is more sensitive and faster than the volumetric method and has a higher accuracy for the low-concentration chloride test, but the use of the mercury reagent is harmful to the environment. Ion chromatography has high sensitivity and selectivity, and its accuracy is higher than other methods, but the analysis cost is high. The chromatography column easily adsorbs impurities, especially benzene organic matter; this permanent adsorption will lead to a reduction in the separation column's adsorption capacity, and so this method is not suitable for mass test liquid determination and is difficult to popularize.

3. The Development of Detection Technology

With the development of industry and agriculture, there are more and more pollutants in the water. There will be more unknown components to interfere with Cl⁻ determination. The accuracy of Cl⁻ detection is becoming more and more important. If the traditional methods are not improved, it is more and more difficult to adapt to the detection requirements of the new environment. Therefore, optimized versions of various traditional methods and new detection technologies are constantly emerging.

3.1. Advances in Volumetric Method

The volumetric method is widely used in the detection of chloride in most bodies of water, because of its good repeatability and wide detection range. However, the end point of titration is not sensitive enough, so many scholars have explored and improved it. Liu used the volumetric method to compare the end points of titration of different water qualities (pure water, mineral water, and tap water), and took the values measured by ion chromatography as reference. The study found that among the three end points of titration colors (light orange, orange, and orange-red), orange-red had the lowest absolute and relative errors [47]. In the ammonium thiocyanate volumetric method, silver thiocyanate precipitation easily adsorbs excess silver ions in the solution, resulting in an advance of the end point. The results show that adding nitrobenzene, dibutyl phthalate, and other organic matter before titration can reduce the adsorption of ions by precipitation and make the end point more accurate. Barra et al. [48] improved the method by replacing toxic nitrobenzene with soybean oil, and the recovery rate was equal to or better than that of titration with nitrobenzene, and the Cl^- content in different samples such as salt and brine was tested with good results. Wanda et al. [49] used thermostatic semi-automatic devices to measure Cl^-. The standard solution of silver nitrate was used as the titration agent, titration was carried out in a burette equipped with a controllable electronic valve, and self-made software was used to fit the mathematical model to indicate the end point of titration.

3.2. Advances in Electrochemical Method

The optimization of the electrochemical method lies mainly in the optimization and improvement of electrodes, the improvement of detection efficiency, and the development of automatic detection equipment. Many scholars have studied sensitive film materials on electrodes, such as silver thiocyanate, tripod fluorides, graphene-based selective film electrodes, metal oxide sensors, etc. [50–54]. Jiang et al. [55] disclosed a photochemical method for the detection of Cl^- concentration in water by using a three-electrode system, which was mainly constructed by a bismuth-based compound thin-film working electrode, auxiliary electrode, and reference electrode. The bismuth-based electrode material generates bismuth hypochlorite in liquid and forms a heterostructure with the raw material. The formation of the heterostructure could promote the separation of carriers and improve the photoelectric response of the material. The change in the photoelectric signal had a good linear relationship with the Cl^- concentration in the range of 0.1~10 μmol/L. Venancio et al. [56] used $ZnPc (Tos)_8$ to prepare electrode sensor coating for continuous monitoring of Cl^- concentration in water, but this sensor had the highest selectivity to sulfate, and the detection was interfered with by bicarb, bromide, and sulfide. Generally, the concentration of bromide and sulfide in water was low, which was not enough to cause strong interference with the chloride test. Bicarbonate needed to be pretreated before testing. The concentration of Cl^- in the method was between 2.018×10^{-5} mol/L and 2.514×10^{-3} mol/L, and the detection limit was 50 μmol/L. The precision of this method was slightly lower than the titration method, but its simplicity was much higher than the titration method.

3.3. Advances in Spectral Method

Spectral methods include ultraviolet- and visible-spectrophotometer spectroscopy, resonance light scattering, Raman spectroscopy, atomic absorption spectroscopy, near-infrared spectroscopy, etc.

Compared with the volumetric method, the cyanomercuric sulfate photometric method has the characteristics of higher sensitivity and efficiency, but the interference of halogen elements is high, and the test uses mercury-containing reagents, which is not friendly to the environment. Therefore, many scholars have studied silver nitrate turbidimetry, which uses the positive correlation between the absorbance value of the suspension generated by the reaction of Cl^- and silver nitrate to determine Cl^- concentration [57–59]. However,

the silver chloride precipitation is unstable, and stabilizers such as polyethylene glycol, glycerin, macrodextrin, and Twean-80 are usually added to the reaction to stabilize the suspension; the precipitation generation is greatly affected by temperature, so controlling a certain reaction temperature is also key [60].

Cao and Wu [61] found that silver chloride aggregates produce strong resonance-scattering light, and the resonance-scattering light intensity with a maximum peak of 571 nm had a linear relationship with Cl^- concentration in the range of 1.42–8.52 ng/mL; the detection limit was 0.71 ng/mL. Zhang et al. [62] established a detection method combining Raman spectroscopy and silver nitrate turbidimetry. Under acidic conditions, a silver chloride colloid was obtained by reaction with acetone as stabilizer, and then the Raman spectra of silver chloride colloid were collected by a small Raman spectrometer. The Gaussian fitting peaks of the Raman spectrum at 1050 and 1635 cm^{-1} had a good linear relationship with Cl^- concentration. The detection range was 0.10–4.00 mg/L, and the detection limit was 0.015 mg/L. This method has been successfully applied to the detection of Cl^- in sulfur-containing sewage. Atomic absorption spectrometry was an indirect method for the determination of Cl^-. After the known amount of silver ions reacted with the Cl^- in the sample, the silver chloride was filtered to obtain the supernatant, and the remaining silver ions in the supernatant were measured to obtain the content of Cl^- indirectly. Wang et al. [63] indirectly measured the Cl^- content in the dry base of molecular sieve powder using an atomic absorption spectrometer. By using a nitric acid digestion sample, the Cl^- recovery rate was more than 95%, and the minimum detection limit was 0.024 mg/L. Laser-induced breakdown spectroscopy has been reported to be used in the detection of Cl^- concentration on steel surfaces [64]. Due to the high ionization energy of Cl^-, the sensitivity of direct laser-induced breakdown spectroscopy to Cl^- element detection was poor. Ma et al. [65] proposed a new technique of indirect laser-induced breakdown spectroscopy to improve detection sensitivity. The method indirectly detected the excess silver after the precipitation reaction of silver ions and Cl^- to detect Cl^- in water, and the limit of quantification was 5 mg/L. Near-infrared spectroscopy had the advantages of simple sample pretreatment and environmental friendliness. Watanabe et al. [66] used NIR spectroscopy to non-destructively detect the content of Cl^- in cement paste. The near-infrared spectra of different cement pastes containing different Cl^- concentrations (ordinary Portland cement, high fast-setting cement, b-type slag cement) were compared. It was found that there was a correlation between Cl^- concentration and NIR absorption value in cement, and the correlation between NIR absorption intensity and the measured value of Cl^- content in ordinary Portland cement was the best. Therefore, this method is more suitable for the detection of Cl^- in ordinary Portland cement.

3.4. Advances in Ion Chromatography Method

The detection method of ion chromatography has high sensitivity and selectivity, but it requires high water quality and is only suitable for testing clean water samples. If ion chromatography is combined with combustion, steam distillation, ultrasonic, and other suitable pretreatment processes, it can be applied to the detection of Cl^- in water quality, blood, soil, cosmetics, iron ore, and other fields [67,68]. Tetiana et al. [69] combined an ultraviolet detector and a conductivity detector to effectively improve the sensitivity of Cl^- detection. Shen et al. [70] used ion chromatography to determine the Cl^- levels in serum, diluted the serum sample 500 times, and eluted it by ion chromatography gradient with a potassium hydroxide eluent generator. The concentration of Cl^- had a good linear relationship with its peak area. The lower limits for detection and quantification were 9.87×10^{-5} mmol/L and 3.27×10^{-4} mmol/L, respectively.

3.5. Advances in Paper-Based Microfluidic Method

Paper-based microfluidic technology is a fast detection method with a low cost and real-time detection. The method is mainly used to judge the concentration of the measured substance by colorimetric analysis. Generally, color changes can be judged or read by the

naked eye, camera, smart phone, or special chromatic meter. At present, there are four types of paper-based microfluidic technology reported, which are nano gold paper-based, nano silver paper-based, silver nitrate paper-based, and electrode silver paper-based.

Xu et al. [71] developed a gold nanoparticles test paper for the detection of Cl^-. The film was placed into the gold nanoparticles solution with an ultrasonic load, and the gold nanoparticles were dried to obtain the gold nanoparticle test paper. The working principle of the paper was that Cl^- could etch gold nanoparticles in nitric acid solution, and the concentration of Cl^- would be correlated with the etch effect. The quantitative detection of Cl^- could be realized by optical analysis of the reacted gold nanoparticles through image software, and the minimum detection limit could reach 0.01%. Mbambo et al. [72] developed an instrument for the determination of sodium chloride concentration in seawater and estuary water based on the color change in gold nanoparticles. The instrument analyzed the color change with Colorgrab application and CIELab color management and could accurately predict the Cl^- level in water samples.

Yakoh et al. [73] prepared a simple, highly sensitive and highly accurate paper-based colorimetric sensor using nano-silver, which could obtain Cl^- content within 5 min. In the range of 10–1000 mg/L, the paper changed from dark purple to red with the increase in Cl^- content, and the degree of color change had a good linear correlation with Cl^- concentration; the detection limit was 1.3 mg/L. The method had a strong anti-interference ability towards common ions in natural water, but weak anti-interference ability towards halogen ions, especially bromine ions. However, the content of these chlorides in natural water was not high.

Gorbunova et al. [74] used potassium permanganate to oxidize Cl^- to generate chlorine gas, and then reacted with the nano-silver test paper after extraction. The nano-silver test paper changed color from gray to white. The degree of color change was linearly related to the content of Cl^-. This method could be used for the determination of Cl^- in pharmaceutical preparations, river water, tomato juice, etc., with high selectivity and no sample pretreatment; the detection range was 0.1–1.5 mg/L.

Rahbar et al. [75] transformed the traditional molar precipitation titration method into paper-based microfluidic diagnostic equipment, which only required 5 µL of samples for determination. A trapezoidal channel was used to create a paper reaction surface. Firstly, silver nitrate solution was deposited on the channel at a certain speed. After drying, chromate was deposited on the channel and red precipitate formed. When the paper encountered Cl^-, the silver chromate reacted with Cl^- to produce silver chloride, and a white band appeared. The length of the band was correlated with the concentration of Cl^-; Cl^- content could be obtained by measuring the length of the white band.

Cinti et al. [76] reported an electrochemical detection technology using silver electrode filter paper. The paper-based electrochemical detector was used for the detection of Cl^- in serum and sweat samples, with a detection range of 1–200 mmol/L and a sample dosage of only 10 µL. The recoveries were between 93% and 108%.

3.6. Advances in Fluorescent Molecular Probe Method

When a fluorescent molecule is irradiated by ultraviolet or visible light, it can excite fluorescence, and the fluorescence properties, such as excitation/emission wavelength, intensity, and polarization, can change with the environment, so as to realize the detection of samples. Ma [77] synthesized fluorescent probes for Cl^- detection, which were named "M2" and "MY". M2, a derivative of 6-methoxyquinoline, had a high relative fluorescence quantum yield and could be quantitatively detected at pH = 7.4. MY was synthesized with M2 as a recognition group and naphthalimide as a reference group. As a ratio fluorescent probe, MY had excellent selectivity and anti-interference and could detect Cl^- in actual water samples and biological samples. Kronfeld et al. [78] introduced fluorescein into polyacrylamide hydrogel particles to make a fluorescence sensor, and the detection time was 5–7 min. When the sensor encountered Cl^-, fluorescence quenching was induced. The fluorescence signal of the sensor followed the Stern–Volmer equation and showed a

negative linear relationship with the concentration of Cl^- in the range of 0–130 mmol/L. The sensor had good reproducibility and reversibility. Pineda et al. [79] studied the ruthenium complex of bis (benzimidazole-2-ethyl) sulfide as a fluorescence sensor for the recognition of Cl^-. The sensor selectively combined with Cl^- to stimulate fluorescence at 365 nm, and the detection limit of Cl^- was up to 0.44 μmol/L by measuring fluorescence intensity at 453 nm. It has a good anti-interference ability with common ions such as F^-, Br^-, I^-, NO^{3-}, and SO_4^{2-} plasma. Graphitized carbon nitride (PCN) is a new conjugated polymer semiconductor. The adsorption of Cl^- in the PCN gap will cause the fluorescence attenuation of the semiconductor, so the material has potential value for the detection of Cl^-. Zhang et al. [58] used silver to modify PCN to obtain silver-modified carbon nitrite nanosheets. This material had high porosity and coordination function and was more likely to adsorb Cl^- in water compared with the single PCN, thus improving fluorescence detection performance. Cl^- could be quantitatively detected within the concentration range of 0.5–100 mmol/L. It had strong practical application.

3.7. Advances in Flow Injection Analysis Combined Method

Flow injection analysis is an automated analytical method developed in recent years and has been widely used in many fields. This method mainly automates sampling, reagent addition, reaction determination, and other experimental steps [80,81]. Flow injection technology is generally combined with the electrode method, turbidimetric method, photometric method, and other technologies, which greatly increases the speed and convenience of Cl^- detection.

Chen et al. [82] combined the flow injection method and the electrode method to determine Cl^- in milk. Xing et al. [83] combined the flow injection technology with mercury thiocyanate spectrophotometry for the detection of trace Cl^- in industrial water. When the concentration flow of water sample was 1 mL/min and the concentration time was 20 min, the detected Cl^- concentration had a good linear relationship within the range of 1.0–50.0 μg/L. Galvis-Sánches et al. [84] combined the flow injection method with silver nitrate turbidimetry for the detection of sodium chloride content in food. Polyvinyl alcohol and gelatin were used as silver chloride precipitation protective agents, and the detection range was 50–600 mg/L. Flow injection analysis technology can realize remote monitoring and cleaning, and is one of the development directions of continuous Cl^- monitoring in the future.

4. Conclusions

With the continuous development of technology, chloride ion detection methods are also developing. On the one hand, traditional detection techniques, including the volumetric method, the photometric method, the electrochemical method, and ion chromatography, have been improved and optimized; on the other hand, new detection techniques are emerging. In different backgrounds and fields, the recommended national methods for Cl^- determination are all different, and each technology has its own advantages, disadvantages, and applicability, including timeliness, operation complexity, reagent environmental protection requirements, automation requirements, etc. The complexity of natural water samples, especially some sewage water samples, leads to the unpredictability of some interfering substances, which limits the accuracy of different Cl^- detection techniques. Therefore, more convenient, rapid, environmentally friendly, and strong anti-interference detection technology is the focus of research concerning Cl^- detection. The development of paper microfluidic technology and the flow injection method have made the determination of Cl^- faster and more convenient. The development of a fluorescent molecular probe and new spectrometric method has provided more selectivity for the determination of Cl^-. However, the repeatability, anti-interference ability, and accuracy of the new technology need to be further optimized in the actual testing process.

The analysis technology of Cl^- in water plays an important role. It is the basis for the detection of Cl^- in food, feed, activated carbon, paper products, chemical products,

fertilizer, air, soil, cement, and so on. The monitor of Cl^- is of concern to quality of soil, water, and air, the survival of animals and plants, human health, the safety and security of construction and building, the prediction of the corrosion of industrial equipment, industrial process control, the accuracy of chemical oxygen demand analysis, and so on. Therefore, the detection of Cl^- in water is very important. The development of Cl^- detection technology will promote the ecological environment, social development, and human health. With the development of detection technology with high sensitivity, high throughput, and high anti-interference ability, the quality of soil, water, and air can be guaranteed, the survival of animals and plants can be guaranteed, life safety will not be threatened, and industrial production and testing can be carried out normally.

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Abbreviations

Cl^-	Chloride ion
CIELab	Lab color space defined by International Commission on Illumination
PCN	Graphitized carbon nitride
ZnPc (Tos)8	Zinc (II) 2,3,9,10,16,17,23,24-Octatosylaminophthalocyanine

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