Recent Progresses on Detection of Mercury Ions for Protecting Vegetable Products Safety

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Abstract. In vegetable industry, heavy metal pollution is a serious problem, which possesses a serious impact on the human health, hinder the development of vegetable industry. It is valid to promote the detection of mercury ions for protecting food safety, especially, vegetable is a sensitive kind of agriculture product for it need amount of water to irrigate, which would bring exogenous mercury ion into it. Among them, mercury ion (Hg\textsuperscript{2+}) is the most poison substance. Detection of mercury ion includes atomic absorption spectroscopy, atomic fluorescence spectroscopy, inductively coupled plasma mass spectrometry, although they have high detection sensitivity, but no information compared their differences for pointing which one is more suitable for detection of mercury ions in vegetable processing industry. Thus, we reviewed the advanced detection skills in analysis of Hg\textsuperscript{2+}, and pointed that anisotropic characteristics of gold nanorods to achieve differential imaging under polarized light microscopy is the suitable method to analysis Hg\textsuperscript{2+}. As well as, we gave a prospective for the future of this detection skill.

1. Introduction

Mercury and its compounds are harmful to human health. If they exist in natural waters, they will pose a threat to a wide range of people. Vegetables, which need amount of water to irrigate, could be significantly influenced by mercury and its compounds.

It can accumulate in organisms and transfer to the human body through vegetables. The accumulation of Trace Mercury in human body could not be excreted by its own metabolism, which will directly lead to heart, liver and thyroid diseases, like chronic mercury poisoning, and even malignant tumors, as well as cause disorders in nervous system.

Dissolved Hg\textsuperscript{2+} is the main form of mercury pollutants discharged into natural waters because of its high chemical activity. Its compounds have high water solubility and are also the hub of various forms of mercury transformation [1].

Therefore, the analysis and determination of mercury in aquatic environment is a subject of great concern. In the past 20 years, researchers have designed and developed a series of mercury ion detection technologies. This paper mainly focuses on these research and development [2].

The development trend of mercury ion detection technology is summarized and introduced, and the development direction of mercury ion detection technology is preliminarily discussed.
2. Methods and characters

2.1. Atomic Emission Spectrometry

Atomic emission spectrometry is based on the gaseous atoms of the substance to be measured. Measurement of Wavelength and Intensity of Characteristic Linear Spectrum emitted by Excitation, an analytical technique for the composition and content of material elements.

The method has the following characteristics:
① Better selectivity can be obtained under different excitation sources.
② Examination forms with the same sensitivity, such as arc light source and spark light source
③ Atoms under Inductively Coupled High Frequency Plasma Source (ICP)

Emission spectroscopy, this detection method possess ng/g detection limit and pole Small matrix effect, high measurement accuracy and wide measurement range [3]. Combination plasma atomic emission spectrometry (ICP-AES) can be used for qualitative and quantitative analysis of mercury ions in a wide concentration range, especially for the detection of Trace Mercury in vegetable processing industry. For example, Hydride generation ICP-AES was used to determine mercury in purified water. The detection limit was 0.1ug/L, the precision was 2.85%, and the recovery was 90%~113%. Quinine as derivative reagent and loaded it on cation exchange resin to make quinine loaded resin [4]. After adsorbing mercury complex anion, the content of mercury ion was determined by ICP-AES. It was found that the detection limit of this method could reach 1.4ng/mL, and it could be applied to the determination of Trace Mercury in Lake water. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) for the determination of mercury ion is simple in sample preparation, but it requires a higher instrument and accuracy, expensive in cost, and can not be measured in real time. At the same time, due to the need to vaporize the test sample, the sample is required to have low thermal sensitivity, clarification of the reaction solution, less suspended impurities, and higher requirements for the sample [5].

2.2. Spectrophotometry

Spectrophotometry is based on the selective absorption of light by different substances. The experimental equipment of this method is simple and the instrument is manufactured. Because of its low price, convenient detection and high detection sensitivity, it can be used as a tool for the detection of bacteria. Therefore, It is widely used in the analysis and detection of mercury [5].

Among them, dithizone method has been widely used in the colorimetric analysis of mercury, and has become one of the national standard methods for the determination of mercury. When testing, the water solution with pH 0~13 and the organic solution containing dithizone were shaken together. The complex salt formed by the reaction of Hg$^{2+}$ and dithizone completely entered the organic phase. According to the absorption value of the complex salt at the maximum absorption wavelength of 490 nm, the detection of mercury ion can be realized [6]. In order to solve the problems of rigorous test conditions, poor selectivity, low sensitivity and the need for organic solvents in dithizone method, and to realize the rapid and sensitive determination of mercury in water environment, a series of chromogenic reagents have been developed for the spectrophotometric determination of mercury ions [7]. It was found that Rhodamine B could form a multicomponent ion association complex with mercury complex anion. The mercury ion was determined by Spectrophotometry in the presence of polyvinyl alcohol.

Chromogenic agents, like 1-(4-nitrophenyl)-3-(5-chloropyridine), 1-azobenzene 3-(6-methoxy-2-benzothiazole) -triazene, has been identified as the effective agents, besides, N-m-toluene-N-(sodium p-aminobenzene sulfonate), Thiourea (MMPI) system, chlorosulfophenol azo thiordanin (HSCT), O-carboxyphenyl diazo-aminobenzene are also observed as the valuable agents for detection of mercury.

Further study also found that sensitization of micelles can effectively improve the sensitivity of Spectrophotometric Determination of mercury ions. Using Tween-80 as sensitized micelle system and
meso-tetra (3-chloro-4-methoxyphenyl) porphyrin as chromogenic reagent, the concentration of mercury ion was determined by second derivative spectrophotometry.

Although the sensitivity of Spectrophotometric Determination of mercury ion is high, how to reduce the reaction time and achieve real-time measurement, how to design and prepare mercury ion-specific chromogenic agents [8], and how to prevent misreading in the presence of heavy metal ions with similar chemical properties of mercury ion are needed in the selection of chromogenic agents.

2.3. Atomic Absorption Spectrometry

Atomic Absorption Spectrometry (AAS) is a method based on the absorption ability of gaseous atoms to the characteristic spectral radiation emitted by the same kind of atoms.

AAS is currently the most commonly used method for mercury detection. In China's mercury monitoring standards, this method is basically used for mercury detection. Cold Atomic Absorption Spectrometry (CVAAS) is the most popular method for the determination of mercury and has become a national standard method. During the test, the sample was dissolved by appropriate method, so that all the mercury contained in the sample was converted into Hg²⁺. Then Hg²⁺ was reduced to mercury vapor with reductant, which was imported into the mercury analyzer for determination [9].

This method is widely used in mercury monitoring standards in China. Cold Atomic Absorption Spectrometry (CVAAS) is the most popular method for the determination of mercury and has become a national standard method. Samples are dissolved by appropriate methods to convert all mercury into Hg²⁺, and then reductant is used [10].

A method for the determination of trace inorganic mercury in environmental water samples by cold atomic absorption spectrophotometry (CAAS) with acid-base insoluble cross-linked chitosan and EDTA as complexing agent was developed. The linear range of the method is 30-500ng/L and the enrichment factor is 100 times. For the analysis of actual water samples, the recovery is 94%~98%, the detection limit is 7.8ng/L, and the relative standard deviation is less than 6% [11].

The water samples were oxidized by Potassium Permanganate under acidic conditions to convert mercury into mercury ions, then reduced by stannous chloride to elemental mercury. The elemental mercury was transported into the mercury analyzer by carrier gas, and the mercury vapor had the maximum absorption effect on the ultraviolet 253.7nm wavelength. This method [12] improves digestion by improving the digestion of samples. In order to improve the accuracy of detection, the probability of sample loss due to boiling phenomenon is reduced.

Under neutral and weak alkaline conditions, appropriate amounts of Bi³ + and Na₂S were added to the water sample to form a co-precipitation of sulfide [13] (HgS and Bi₂S₃) with Bi³ + in the water sample. The precipitate was dissolved in hot dilute nitric acid and its content was determined by cold atomic absorption spectrometry.

The experimental results show that the method of adding alum to accelerate the precipitation and condensation of sulfides and then to absorb supernatant is a very simple and practical method for the detection of mercury ions.

2.4. Hydride Generation-Atomic Fluorescence Spectrometry

The principle of hydride generation-atomic fluorescence spectrometry for mercury analysis is that in acidic medium, mercury ions in the sample are reduced to atomic mercury, and then carried into the atomizer by carrier gas. Under the irradiation of mercury hollow cathode lamp, ground state mercury atoms are excited to high energy state, and fluorescence of characteristic wavelength is emitted during deactivation and return to ground state. The fluorescence intensity of light is proportional to the mercury content. Hydride generation atomic fluorescence spectrometry has the advantages of economy, simple spectral line, high sensitivity, less interference and low detection limit.

A method for the determination of Trace Mercury in water samples by using potassium borohydride as reducing agent. The minimum detection concentration was 0.0158ug/L and the relative standard deviation was 0.31% [13].
Trace mercury in terrestrial water was determined by Hydride Generation-Atomic Fluorescence Spectrometry with SnCl2 as reducing agent in nitric acid system. The detection conditions and interference of coexisting elements were studied. The results showed that 500mg/L Fe, Pb, Mn, Cu, Ca, Na, K and Mg did not affect the determination of Hg. The detection limit of mercury is 0.001ug/L and the accuracy is 1.73%. The method can be used for the determination of Trace Mercury in fruits and vegetables.

Based on the combination of atomic fluorescence and hydride technology, samples were injected intermittently. Compared with other injection methods, this method has the advantages of good stability and high precision [14]. Atomic fluorescence spectrometry is simple, rapid, sensitive and has less loss of mercury. It has been widely used in geology, metallurgy, biology, commodity inspection, food and other fields.

2.5. Polarized light microscope based on gold nanomaterials deformation

Gold nanomaterials have been widely used in many fields, such as catalysis, electronics, optoelectronics, chemical sensing and imaging, information storage, pharmaceuticals, due to their high chemical stability, strong oxidation resistance and biocompatibility.

Gold nanomaterials [15] with different morphologies often have different properties and functions. Therefore, the morphology of gold nanomaterials can be adjusted by controlling synthesis, and materials with different properties and functions can be obtained.

Due to the different synthesis methods, gold nanomaterials with different structures, properties and functions can be obtained. Common gold nanomaterials include gold nanoparticles, gold nanorods and gold nanostars.

The anisotropic characteristics of gold nanorods to achieve differential imaging under polarized light microscopy. The anisotropic-based gold nanorods are transformed into spherical gold nanoparticles in the presence of mercury ions, which produced changes in the light intensity. It realized highly sensitive and highly selective detection of mercury ions, in addition, the macroscopic sample water and microscopic sample plant cells were tested by this method, which proved that our method is feasible, with unique advantages, high sensitivity and spatial resolution.

2.5.1. Gold nanoparticles. Gold nanoparticle [16] are one of the most widely used and simplest synthesized gold nanomaterials. The synthesis method of gold nanoparticles is mainly the reduction synthesis of trisodium citrate. In the solution containing chlorauric acid, AuCl4- ion is reduced to Au atom by adding reduction reagent. When more and more Au atoms are produced, the solution becomes supersaturated, resulting in the precipitation of Au atoms in the form of subnanoparticles and further growth. In order to prevent the nuclei from gathering together, stabilizers need to be added to the surface of Au. With the improvement of synthesis methods, the size of gold nanoparticles can be precisely controlled, and gold nanoparticles with different particle sizes of 2-200 nm can be obtained. With the increase of particle size, the color of gold nanoparticles in aqueous solution changed from bright red to wine red and then to purple red and purple.

At the same time, the surface plasmon resonance absorption peak will gradually shift red, and the surface enhanced Raman scattering effect will also change [17].

2.5.2. Gold nanorod. Unlike gold nanoparticles, gold nanorods have anisotropy, and their longitudinal localized surface plasmon resonance absorption peaks.

Localized Surface Plasmon Resonance (LSPR) changed obviously with the change of aspect ratio. In the past decade, the synthesis of gold nanorods has been the hottest research field. Many synthetic methods have been developed and can accurately control the aspect ratio of gold nanorods. The seed growth method was first proposed by Murphy and her colleagues.

Seed growth includes two steps: seed synthesis and growth of gold nanorods in the presence of surfactant cetyltrimethylammonium bromide (CTAB). Among them, gold seeds need to be reduced by strong reductant sodium borohydride, and the growth of gold nanorods needs ascorbic acid and silver
nitrate reagents. By controlling the amount of silver nitrate, gold nanorods with a aspect ratio of 1 to 10 can be obtained [18].

![Figure 1. Analysis Hg²⁺ through Gold nanorod.](image)

2.5.3. Gold nanostar. AuNS [19] is also a common gold nanomaterial. The surface plasmon resonance absorption peaks of gold nanostars are in the near infrared region, and their structures contain a large number of sharp branches, which, like lightning rods, can greatly improve the local electromagnetic field.

At present, there are many methods [20] to synthesize gold nanostars, among which the seed growth method is simple, time-consuming, reaction conditions are not harsh and easy to control. Seeds were synthesized by simple sodium citrate reduction method. Chlorogluoric acid, silver nitrate and ascorbic acid were added in the process of growth, and the pH value was controlled at about 5 [21]. Different number of branches can be obtained by adjusting the amount of silver nitrate added.

3. Prospective
In our review, we concluded that the detection of Hg²⁺ included atomic emission spectrometry, spectrophotometry, atomic absorption spectrometry, hydride generation-atomic fluorescence spectrometry, polarized light microscope based on gold nanorod deformation, the most effective method is the gold nanomaterials, furthermore, gold nanoparticles is lower sensitive than gold nanorod, as well as, gold nanostar is not easy to control.

Therefore, we concluded gold nanorod is the most suitable detection method which needs to do more detailed test.

However, gold nanorod is necessary to alter its signal amplification effect, which could to promote through surface-enhanced Raman scattering and plasma chiral sensors, for the assistant of high specificity recognition of adapters.

4. Conclusion
In the exploration and development of simple and sensitive mercury ion analysis and detection methods, biosensor detection technology has become a new way with great advantages.

In recent years, a lot of theoretical and experimental foundations have been accumulated in the design and synthesis of biosensors, paving the way for further improvement and innovation, and
becoming one of the development directions of mercury ion detection in aquatic environment. However, improving the stability and sensitization of biosensors is still an unsolved problem. According to our analysis, gold nanorod is the most suitable research direction to promote, it is hoped that through the introduction of this paper, more researchers will be interested in the practical significance of mercury ion detection in vegetable industry, in order to achieve a perfect and better, rapid and simple detection of mercury ion.

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