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REVIEW

Recent Developments in Analytical Methods for Inorganic Elements in Foods

Yang Hong-Ben*, Yang Fan, Hu Zeng-Bin, Bai Xiang

Yunnan Institute of Product Quality Supervision and Inspection, Kunming 650223, China

*** Corresponding author:** Yang Hong-Ben, ynyhb6269@163.com

ABSTRACT

Inorganic elements play a crucial role in both nutrition and health safety. Analyzing these elements in food helps assess its nutritional value, prevent the consumption of toxic or harmful substances, and understand the extent of contamination to identify and control pollution sources. Additionally, it aids in the production and development of fortified foods, enhances food processing technologies, and improves overall food quality. Therefore, monitoring and detecting inorganic elements during food production is essential. This paper reviews the main methods and characteristics of inorganic element analysis in food, both domestically and internationally, highlighting trends in analytical techniques, including traditional chemical and physical methods, as well as recent advances in nanotechnology and biotechnology. It also summarizes the practical applications of these analytical methods in recent years.

Keywords: inorganic elements; analysis methods; chemical methods; physical methods, nanotechnology methods; biotechnology methods

1. Introduction

There are more than 50 kinds of inorganic elements in food, which can be divided into essential elements according to their effects on human body. Nonessential elements and toxic elements fall into three categories[1]. The intake and absorption of inorganic elements play a vital role in human nutrition, health and safety, including cadmium. Lead. Arsenic. Mercury and other inorganic elements are toxic to human body. A very small dose can inhibit the activity of human chemical reaction enzymes and poison human cytoplasm. The purpose of the detection and control of inorganic elements in food is to evaluate the nutritional value of food and avoid toxic and harmful food; understand the situation and extent of food contamination in order to identify and control the source of pollution; it is beneficial to guide the production and development of nutrition fortified food; it is conducive to the improvement of food processing technology and food quality.

There are mature analytical methods for the analysis and detection of inorganic elements in food at home and abroad, such as ultraviolet spectrophotometry, Atomic absorption spectrometry (AAS), Atomic fluorescence spectroscopy (AFS), Inductively coupled plasma atomic emission spectrometry (ICP-AES), X-ray fluorescence spectroscopy (XFS), Inductively coupled plasma mass spectrometry (ICP-MS), Hydride generation atomic fluorescence spectrometry. Electrochemical polarography, etc.[2–5]. This paper summarizes

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the main methods of inorganic element analysis in food at present. The development trend aims to provide some reference for researchers and practitioners in the analysis and detection of inorganic elements in food.

2. Analytical chemical methods of inorganic elements

2.1. Dithizone colorimetry

Dithizone, also known as Diphenylthiocarbazone. Dithizone colorimetry, also known as dithizone colorimetry, is a conventional method for detecting and analyzing the content of metal elements in food. The principle of dithizone colorimetry is a method of qualitative and quantitative determination of metal ions by spectrophotometry, in which some metal ions form colored complexes with Dithizone under a certain pH environment after digestion of samples.

Dithizone colorimetry only needs spectrophotometer, and does not need special instruments and equipment. It is still a common method used in grass-roots laboratories to determine metal elements in food. The biggest disadvantage of dithizone spectrophotometry is that the operation is cumbersome, the sensitivity is low, and the repeatability is poor. Poor selectivity. A little improper operation is easy to cause the deviation of experimental results, and the reagent cost is high, and the types of detection elements are limited; in addition, dithizone colorimetry also has some disadvantages, such as no obvious jump in the color change process of the indicator, and it is difficult to accurately control the optimal pH range[6,7].

Kai[8] established a method for the determination of trace lead in popcorn by Dithizone spectrophotometry. Using dithizone as the developer, controlling the pH of the solution to 8.5, measuring the absorbance at 513 nm wavelength, and using the standard curve to calculate the lead content; the pH of the solution was also discussed. Reaction time. The determination results show that the lead content in the sample is 5.0 mg/kg, which is significantly higher than the national standard of 0.5 mg/kg.

Dong[9] used dithizone as the chromogenic agent to determine trace zinc in tea by cloud point extraction spectrophotometry. In the acetic acid sodium acetate buffer solution with pH 4.6, zinc formed a stable complex with dithizone λ_{max} = 528 nm, the linear range of the method is 0.2–1.0 μg/mL, the recovery is 96.50%–102.50%. The results show that the method can be used for the determination of Trace Zinc in tea.

Lu[10] discussed the reliability and applicability of dithizone aqueous phase spectrophotometry for the determination of zinc content in water. Dithizone aqueous phase spectrophotometry was used to determine zinc synthetic water samples, and the comparison experiment was carried out with the national standard method GB 5750-2006 drinking water inspection method. The results showed that the precision and accuracy of dithizone aqueous phase spectrophotometry met the requirements, and there was no significant difference compared with the national standard method for spiked water samples ($P > 0.05$). Therefore, dithizone aqueous phase spectrophotometry can accurately determine water samples and zinc reference materials, which is a more simple operation. Quick. Accurate. Environment protectionlow cost new method.

Wang[11] studied the rapid determination of trace lead in Chinese Cabbage by Dithizone visual colorimetry in order to provide a simple and convenient method. Accurately detect vegetables. Food. Method for trace lead in feed, etc. After sample digestion, masking agent is added by controlling the acidity of the solution to eliminate the interference of coexisting ions. In the trichloromethane solution with Dithizone added, because lead and dithizone form a red complex in the slightly alkaline solution, its color depth in the organic solvent is directly proportional to the lead content within a certain range. The lead content in the sample can be quickly determined by visual colorimetry. The improved method not only retains the advantages of the original Dithizone photometric method to eliminate interfering ions, but also does not use any optical instruments and does not need to draw standard curves. There is no need to prepare a standard series of color scales, which

greatly simplifies the detection conditions and operation steps, and has a fast. Accurate. Advantages of saving time. The relative deviation of the improved method is less than 5%, and its relative standard deviation (RSD) is less than 2.5%, which can fully meet the limit requirements of the national standard. It is a fast method. Sensitive. An efficient method for the determination of trace lead.

2.2. Electrochemical analysis

The electrochemical methods used for the analysis of inorganic elements in food mainly include cyclic voltammetry. Polarography. Ion selective electrode potential analysis. Stripping voltammetry and flow injection combined with electroanalysis. Among these electrochemical analyses, ion selective electrode method and polarography are the common inorganic element analysis methods. Ion selective electrode method is an electrochemical method that uses the indicator electrode to change the concentration of the measured substance into the electrode potential value, and then calculates the amount of the measured substance according to Nernst equation. Ion selective electrode method has simple instrument. It is light, easy to operate, easy to be used for flow monitoring and automatic detection, fast, without damaging the test solution system, and suitable for some samples that are not suitable for analysis by other methods. Polarography is a kind of electrochemical analysis method, which determines the concentration of the measured substance in the solution by measuring the current potential (or potential time) curve of the polarized electrode obtained in the electrolysis process, and has high accuracy. High sensitivity. It has a wide range of applications. Fast analysis.Good selectivity.Continuous measurement can be realized.Simple equipment and other advantages[12].

Wang Qingru established a polarographic method for the determination of selenium in food[13]. The study shows that the selenium concentration has a linear relationship with the peak current in the range of 0.0005–0.008 mg/kg, the standard coefficient is 0.9990, and the detection limit is 0.0005 g/kg. The experiment proved that when the food amount was 0.040 g, the selenium concentration had a good linear relationship in the range of 0.10–1.0 mg/kg. Ten parallel experiments were carried out on samples containing 0.32 mg/kg selenium, the relative deviation was 2.35%, and the recovery was 94.5%–97.2%. This method is simple to operate. High sensitivity.

At present, stripping voltammetry is a more advanced electrochemical analysis method in the elemental analysis of food samples. The principle of stripping voltammetry is to take the liquid or solid electrode whose surface cannot be renewed (such as hanging mercury electrode or mercury film electrode) as the working electrode, enrich the components to be measured on the working electrode by controlling potential electrolysis, gradually change the potential of the electrode (apply voltage in the opposite direction), so that the substances enriched on the working electrode can be dissolved again and enter the solution, Quantitative analysis is carried out according to the linear relationship between the peak height (or peak area) of the voltammetric curve at the time of dissolution and the change of metal ion concentration. Stripping voltammetry has high sensitivity (it can analyze 10^{-10}–10^{-11} mol/L heavy metal elements). With the advantages of good selectivity and diversity of working electrodes, it is widely suitable for the speciation analysis of heavy metal elements and superheavy metal elements. It is the fastest developing method in recent years.

Xi et al.[14] used graphene to modify glassy carbon electrodes by optimizing the supporting electrolyte and pH value. Modifier dosage. According to the measurement conditions such as enrichment potential and time, a linear scanning anodic stripping voltammetry method for the determination of cadmium in bean paste was established. In the NaAc-HAc buffer at pH 4.2, after enrichment for 5 min, the dissolution peak current has a good linear relationship with the cadmium concentration in the range of 1.0×10^{-8}–5.0×10^{-5} mol/L, and the detection limit is 3.0×10^{-9} mol/L. The relative standard deviation (RSD) of 5.0×10^{-6} mol/L cadmium solution was measured 10 times in parallel, and the relative standard deviation (RSD) was 2.8%. The method

was applied to the determination of cadmium in bean paste, and the average recovery was in the range of 96.7%–105.0%, and the results were satisfactory. The method has high sensitivity. Good choice. Electrodes are easy to make. Good reproducibility. Simple and reliable.

Wang and Sun[15] established a new method for the determination of lead in vegetables by differential pulse anodic stripping voltammetry with Nafion mercury film modified electrode. Using 0.1 mol/L NH_4NO_3 as supporting electrolyte, the enrichment time is 420 s, the stirring speed is 300 r/min, and the volume of Nafion modification is 10 μ. The interference of coexisting ions was investigated under L condition. The linearity of lead was good in the range of 0.01–14.0 μg/L, the detection limit was 0.2 μg/L, and the recovery was 89.5%–106%. The determination results of vegetable samples near the lead-acid battery factory are consistent with those of graphite furnace atomic absorption spectrometry, and the performance of the electrode is stable after continuous use for one month.

The apparatus of electrochemical element analysis method is simple. Easy to operate. Easy to automate and continuous analysis, rapid determination. The sensitivity and accuracy are high, and the measured concentration can be as low as 10^{-29} g/L (metal ions). Electrochemical elemental analysis method with its unique advantages to adapt to modern analysis is simple and fast. High sensitivity is required, and the required instruments are cheap. It is especially suitable for on-site real-time detection and grass-roots health and epidemic prevention. Commodity inspection. It is used by medical and health departments and small and medium-sized food production enterprises. Due to the rapid development of computer technology and exchange polarography. Square wave polarography. With the emergence of modern analytical methods such as pulse polarography and linear scanning polarography, electrical analysis methods will play a more important role in the field of elemental analysis in food.

3. Physical methods of inorganic element analysis

3.1. Atomic absorption spectrophotometry

Atomic absorption spectrometry (AAS) is a method for quantitative analysis of elements based on the absorption intensity of atomic resonance radiation of the ground state atoms of the tested elements in the vapor phase. Atomic absorption spectrometry has high sensitivity. High accuracy. Good selectivity. Fast analysis. There are many kinds of elements.The reagent used has the advantages of low cost. As the preferred method for the determination of trace metal elements, atomic absorption spectrometry has been widely used in the analysis and detection of inorganic elements in food in recent years. However, atomic absorption spectrometry has shortcomings: most non-metallic elements cannot be determined at the same time, different element lamps need to be changed to determine different elements, and the determination efficiency of multiple elements is not high; the linear range of the standard working curve is narrow (generally within an order of magnitude). For complex samples, the interference is serious, the operation is complex, and the instrument is expensive. The general detection limit of flame atomic absorption spectrometry can reach 10^{-9} g/L, and that of graphite furnace atomic absorption spectrometry can reach 10^{-10}–10^{-14} g/L.

Sa et al.[16] used flame atomic absorption spectrometry to determine and analyze the contents of 9 trace elements Cu, Na, Fe, K, Sr, Mg, Ca, Mn, Zn in pepper and pepper food. The research shows that the standard curve correlation coefficients of Cu, Na, Fe, K, Sr, Mg, Ca, Mn, Zn are: 0.9999, 0.9820, 0.9997, 0.9927, 0.9982, 0.9965, 0.9991, 1.0000 and 0.9985.

Tai and Xing[17] used mixed acid to digest the sample, magnesium nitrate as matrix modifier, and graphite furnace atomic absorption spectrometry to determine the content of aluminum in flour food. The detection limit is 4.8 under the best experimental conditions μg/L, the recovery is between 88.8% and 105.5%, and the relative standard deviation (RSD) is between 0.136% and 0.188%.

Atomic absorption spectrometry is simple to operate, but its analytical sensitivity is low, so it is complex in the analysis of matrix. For samples with extremely low content of target elements, certain separation and enrichment techniques should be supplemented before determination. Qin et al.[18] studied the use of sodium diethyldithiocarbamate as chelating agent. Determination of Trace Copper by cloud point extraction system flame atomic absorption spectrometry with non-ionic surfactant Triton X-114 as extractant. The pH was investigated. DDTC concentration. Triton X-114 dosage. A new method for the determination of Trace Copper in samples by Cloud Point Extraction Flame atomic absorption spectrometry was established, with a linear range of 0–250 μg/kg, and the method was successfully applied to tea. Determination of Trace Copper in milk powder and mineral water. With the improvement of economic and technological level, the accuracy of analytical instruments has been improved. The requirements for accuracy are getting higher and higher, and a single atomic absorption spectrometer can not meet the needs of all aspects of testing. In recent years, relevant experts have done a lot of research work on the combination technology of atomic absorption spectrometry and other instruments, and made some progress. For example, the combination of atomic absorption spectrometry and electrochemistry has greatly improved the sensitivity of atomic absorption spectrometry. Chromatography can effectively separate metal elements in samples, and carry out qualitative or quantitative analysis of elements to be measured. The combination of atomic absorption spectrometry and chromatography gives full play to the advantages of high detection sensitivity of atomic absorption spectrometry and good separation effect of liquid chromatography.

Zhang et al.[19] established a new suction elution method for the determination of trace lead in preserved eggs by flow injection on-line preconcentration and flame atomic absorption spectrometry. The experiment shows that the concentration coefficient is increased from 3.7 to 11.6, and the detection limit is 3.91μg/L, the relative standard deviation (n = 11) is 1.8%. The elution process depends on the suction rather than the thrust of the peristaltic pump, which can significantly reduce the dispersion of the analyte in the elution process, improve the peak value and concentration coefficient of the atomic absorption signal, increase the emptying steps of the remaining sample solution, and ensure the accuracy and repeatability of each experiment, which is of great significance for the accurate determination of samples.

Liu et al.[20] used their own designed interface to realize the combination of high performance liquid chromatography (HPLC) and AAS. By analyzing the elemental forms of common arsenic, the performance of the interface of high performance liquid chromatography Ultraviolet online digestion hydride generation atomic absorption spectrometry was investigated, and the optimal analysis conditions of the instrument were studied. Determined fast. Direct. Continuous. Online elemental speciation analysis method. After separation, the macromolecules that cannot be directly used for hydride generation are “online” digested into small arsenic compounds by UV.

With the deepening of theoretical research and the development and progress of technology, atomic absorption spectrometry analysis technology and equipment are improving day by day, especially with the expansion of the combination with other instruments, atomic absorption spectrometry will play a more active role in the detection of inorganic elements in food.

3.2. Atomic Fluorescence Spectrometry

Atomic fluorescence spectrometry (AFS) is a quantitative analysis method based on the fact that the fluorescence intensity emitted by gaseous atoms is directly proportional to the atomic concentration of analytes after they are irradiated by a light source with a certain characteristic wavelength. The instrument usually used is the atomic fluorescence photometer. Atomic fluorescence spectrometry has high sensitivity. Strong selectivity. Little interference. Wide linear range. Several elements can be determined at the same time. Less samples. The method is simple. The reagent used is less toxic. Easy to operate. Strong practicality and other characteristics. However, AFS also has some shortcomings, the scope of application is not wide enough, and there is fluorescence quenching effect. Scattered light interference. Atomic fluorescence spectrometry is widely used in the determination of mercury in food. Arsenic. Lead. Selenium. Antimony. Tin. Cadmium and other trace inorganic metals.

Arsenic is one of the inorganic elements harmful to human body. Long term ingestion of arsenic containing food will cause cell poisoning and even induce malignant tumors. Inorganic arsenic is a carcinogen of skin cancer and lung cancer. Atomic fluorescence spectrometry is a general method for the detection of arsenic content in food in China. The content of different forms of arsenic in food can be determined by Liquid Chromatography Atomic Fluorescence Spectrometry[21].

Liang et al.[22] established that the samples were digested by microwave in HNO_3+HCl or HNO_3+HCl+H_2O_2 system, and thiourea-ascorbic acid mixture was used as pre-reducing agent, and hydride atomic fluorescence spectrometry was used to determine the content of tin in canned food. method. The results showed that the linear relationship was good in the range of 0–100 μg/L tin concentration, the minimum detection limit of the method was 0.067 mg/kg, and the recovery rate of standard addition was between 99.7% and 108.3%. The method has high accuracy. Sensitive and fast. With the advantages of good precision, safety and environmental protection, it is suitable for the determination of tin in canned food. In the national standard method for food testing, the detection of arsenic and mercury must be digested by different methods. Arsenic was digested by wet digestion or dry ashing, and mercury was digested by microwave.

The disadvantage of this standard method is that the amount of digestion reagents is large, it is easy to introduce pollution, it is easy to cause the loss of arsenic at high temperature, and the process is complicated and time-consuming and labor-intensive. Zhai et al.[23] simultaneously measured arsenic and mercury in food by using micro-acid microwave digestion technology and high-sensitivity atomic fluorescence spectrometry. This method does not need to drive acid. After directly adding a pre-reducing agent to reduce pentavalent as to trivalent, the same digestion solution is used to simultaneously measure arsenic and mercury. The method is simple and fast, and can meet the detection of arsenic and mercury in various foods.

Zhang and Han[24] digested the sample with nitric acid under high pressure and added 100 g/L potassium thiocyanate. 100 g/L oxalic acid is used as interference inhibitor, potassium dichromate potassium ferricyanide is used as oxidant, and the analytical solution with hcl as medium is mixed for oxidation reaction to produce lead alkane. Lead is determined by hydride generation atomic fluorescence spectrometry. The linear range of this method is 0–80 μg/L, detection limit is 0.35 μg/L, relative standard deviation (RSD) < 2.7%. When applied to the detection of actual samples, the spiked recovery is 98.0%–103.0%, and the precision is 1.8%–3.6%.

3.3. Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is an atomic emission spectrometry analysis method that uses the light source of high-frequency inductively coupled plasma discharge as the excitation light source. It can carry out the simultaneous determination of multiple elements. It is a new excitation light source with excellent performance and wide application. Compared with other methods, ICP-

AES has faster analysis speed. The time distribution is stable. Low interference. It can read out the characteristic spectra of many measured elements at one time. The advantages of wide linear range and simultaneous qualitative and quantitative analysis of multiple elements. The disadvantage of ICP-AES is that the equipment is expensive and the operation cost is high, and the detection advantage of some elements is not obvious.

Maohong et al.[25] established microwave digestion inductively coupled plasma mass spectrometry (ICP-AES) for the simultaneous determination of lead in more than 30 kinds of food. Cadmium. Copper and other trace elements. The results show that the linear correlation coefficients are all greater than 0.999, and the precision of the method is less than 8.0%. The national standard materials: wheat flour (GBW08503b), poplar leaves (GBW08513), and mussels (GBW08571) are all within the standard value range, and the measured values are within the range of the standard values. The results of absorption spectrophotometry were in good agreement. ICP-MS method can analyze more than 30 elements at the same time, with strong anti-interference, but the cost of instruments and reagents is high; atomic absorption spectrophotometry requires the determination of elements separately, which has great interference, especially the determination of high salt samples after dilution. The determination cycle is long, but the instrument cost is low and the popularity is high.

Chen et al.[26] used microwave digestion to process samples, and ICP-AES was used to determine seven inorganic elements of zinc, iron, manganese, copper, cadmium, chromium, and arsenic in vegetables, tea, seafood and other foods. The experimental results showed that the relative standard deviation was less than 6%, the recovery was 92.6%–106%, and the detection limit was the range of 0.764–1.537 μg/L. This method is simple and fast. Element loss is small. The amount of oxidant is small.Microwave digestion is complete.Digestion time is short.Simultaneous determination of multiple elements.High sensitivity.High stability. High precision and good accuracy. The method is suitable for the determination of heavy metals in food and is timely. Effective food testing and management to provide strong technical support.

Tea is rich in many elements, and its element content is closely related to the growth environment. Therefore, the determination of element content in tea by ICP-AES is of great significance for tea quality identification and origin identification. Moreda et al.[27] used ICP-AES to determine the content of 17 inorganic elements in 85 tea samples from Asia and Africa, combined with linear discriminant analysis (LDA) and soft independent modeling of class analysis (SIMCA), to classify the geographical origin of tea. Using principal component analysis (PCA) and component analysis (CA) as exploratory techniques and LDA and SIMCA as classification means, it is concluded that at the significance level of 5%, the accuracy of LDA and SIMCA in the classification of African tea leaves is 100%, and that of Asian tea leaves is 94.4% and 91.7%, respectively.

McKenzie et al.[28] determined white tea by ICP-AES. Green Tea.black tea. The content of 14 inorganic elements in Oolong tea and Pu'er tea, the classification model constructed by combining linear discriminant analysis and probabilistic neural network, the recognition rates of 5 kinds of tea are 81% and 97% respectively. As a mature analytical method, inductively coupled plasma atomic emission spectrometry has been successfully applied to liquid. The detection of metal elements in solid foods and the sampling system will still be the focus of future research. In addition, the use of new detectors and the application research of the combined technology of analytical instruments will promote the intellectualization of ICP-AES. Miniaturization is suitable for the development of instruments for field analysis.

3.4. Inductively coupled plasma mass spectrometry

In recent ten years, inductively coupled plasma mass spectrometry (ICP-MS) has been one of the key directions in the research and application of trace inorganic elements. ICP-MS is an advanced method that can be used in trace amounts. Trace and ultra trace. And it can realize the method of simultaneous determination of multiple elements, which has the advantages of low detection limit, high sensitivity, wide analytical element range, fast analysis speed, wide linear range and high accuracy[29,30].

Tang et al.[31] used microwave digestion technology and inductively coupled plasma mass spectrometry to detect 32 inorganic elements in 22 steamed green tea leaves from different regions of Chongqing. The results showed that the contents of rare earth elements in fresh tea leaves in Chongqing varied greatly with different regions, and the contents of the other 17 elements ranged in dozens μ from g/kg to several thousand mg/kg, the content of rare earth elements plays an important role in the identification of origin, and the characteristic elements of each region are different. Therefore, it is feasible to distinguish different tea producing areas with inorganic elements as indicators.

Li et al.[32] used hydrogen peroxide-nitric acid as solvent, used closed microwave digestion of samples, and used inductively coupled plasma mass spectrometry to simultaneously determine boron, cadmium, copper, cobalt, chromium, molybdenum, lithium, nickel, lead in plant samples , lanthanum, germanium and other 11 elements. The optimum working parameters of microwave digestion instrument and plasma mass spectrometer were studied, the interference of organic residues and coexisting ions was effectively solved, the determination isotopes of various elements were selected, and the matrix effect was compensated by 45Sc and 103rh double internal standards, and the sample determination method was established. The method is applicable to the fruit of plants. Root. Stem. Determination of various trace elements in different types of samples such as leaves.

Rare earth elements are non essential elements for human body. Due to the wide application of rare earth elements in industry and agriculture and the enrichment of organisms, eating some plant derived foods will inevitably lead to an increase in the content of rare earth elements in human body. People are generally concerned about the impact of rare earth elements on human health. The national standard GB 2762-2012 limits of pollutants in food has clearly stipulated the limits of rare earth elements in vegetable foods. At present, the detection of rare earth elements in plant derived foods has attracted widespread attention. Because ICP-MS has unique advantages in the detection of rare earth elements, the application of ICP-MS in rare earth analysis is becoming more and more popular. For example, the national standard GB 5009.94-2012 stipulates the ICP-MS determination method of rare earth elements in plant foods.

Wang et al.[33] used inductively coupled plasma mass spectrometry to determine 15 rare earth elements in drinking water, and adopted internal standard correction method, using RH, Re, Bi is the internal standard, combined with optimizing instrument conditions and interference correction equation to eliminate interference. The method has less interference. The detection limit is low. Good precision. It has the advantages of high accuracy, simple sample pretreatment process, and realizes the simultaneous measurement of multiple trace elements, which can provide a fast way for the ecological environment investigation of drinking water source. Accurate monitoring data.

Compared with other methods, ICP-MS has manythe anylysis characteristic, such as advantages of low detection limit, high accuracy, wide dynamic range, less interference, high analytical precision, fast analysis speed, simultaneous determination of multiple elements, and accurate isotopic, ect. However, the cost of this instrument is very high. So far, the application of ICP-MS is only limited to the research field.

3.5. X-ray fluorescence spectrometry

X-ray fluorescence spectroscopy (XFS) is a method that uses primary x-ray photons or other micro particles to excite the sample to be tested, and the x-rays emitted by the sample after excitation change with the change of element composition and element content in the sample to analyze the material composition and study the chemical state. Its detection limit can reach μg/g. XFS has fast analysis. Easy to operate. A wide range of analyzable elements. The spectral line is simple. Less spectral interference. Low cost. The sample will not be damaged during excitation. The strength measurement has the advantages of good reproducibility and convenient for nondestructive analysis. At present, it is widely used in nondestructive testing of food.

Wang et al.[34] established a relatively simple method for the detection of calcium in milk powder by energy dispersive X-ray fluorescence spectrometry. The samples do not need to be digested and measured directly by pressing tablets. The measurement time of each sample is 160 s. The results show that the accuracy, precision and relative standard deviation of the method are basically consistent with those measured by the national standard flame atomic absorption method. Because energy dispersive X-ray fluorescence spectroscopy can directly measure solid samples, no harmful gas is generated during the experiment, saving manpower, material resources, and time, so it can be used as a convenient, fast, and effective method to detect calcium in milk powder.

Zhang et al.[35] used X-ray fluorescence spectroscopy to determine the types and contents of elements in spirulina and donkey-hide gelatin samples. The results showed that the two medicinal materials contained K, Ca, Fe, Mg, Zn, Mn, S and other elements, which provided a certain scientific basis for further research on the efficacy and function of Spirulina and Ejiao.

4. Methods of detecting metal elements in food by nanotechnology

After the 1980s, nanotechnology has developed rapidly. Nanotechnology has the ability to create new production processes. Because of the great potential of new substances and products, nanotechnology has aroused widespread interest of scientists all over the world. Nanotechnology has a broad application prospect in detecting the concentration of heavy metal ions. Number of surface atoms of nanoparticles. The surface area and surface binding energy increase rapidly with the decrease of particle size. Nanoparticles have large specific surface area and insufficient coordination of surface atoms. Compared with bulk materials of the same material, they have strong adsorption capacity. The surface atoms of nanoparticles lack adjacent atoms, which are unsaturated and easy to combine with other atoms through electrostatic interaction[36]. Therefore, nanoparticles are ideal separation and enrichment materials for trace element analysis, which improves the sensitivity and selectivity of analysis, and can be used to improve and improve the technical performance of metal element determination or speciation analysis in food. Liu and Zhou[37] studied the adsorption performance of nano tio_2 for manganese and determined the best conditions for adsorption and desorption. The method was applied to the separation and enrichment of manganese in food samples and the determination of manganese by graphite furnace atomic absorption spectrometry. The recovery was 93.3%–105.5%, RSD was 3.18%–5.21%.

Because nanoparticles are easy to condense in aqueous solution, it is limited to enrich heavy metal ions only by electrostatic attraction on the surface of nanoparticles. Therefore, surface modification of nanoparticles to improve stability and selectivity will be the main research direction in the future. However, most methods of enrichment and analysis of metal ions using nanoparticles still need centrifugation. Complex operations such as filtration and large analytical instruments. In recent years, studies have found that modifying fluorescent probes on the surface of nanoparticles can achieve rapid and on-site analysis of metal ions with the naked eye[38]. The detection of heavy metals in food by nanoparticles with fluorescent switching function is still a topic of concern.

At the same time, the surface modified magnetic nanoparticles have both magnetism and surface active groups, which can further interact with metal ions. Cells. Enzymes. Protein. Antibody and nucleic acid coupling[39,40]. Under the action of external magnetic field, magnetic particles can be easily separated and enriched, which has the advantages of simple operation and high separation efficiency. In addition, magnetic microspheres have large specific surface area, which provides the basis for modifying a variety of high-density molecular probes, and show broad application prospects in the fields of metal ion separation and detection[41].

Fe_3O_4@SiO_2 Composite nanoparticles have large specific surface area. Greater specific surface energy. Large adsorption capacity for heavy metal ions. Easy to separate.It has been widely used in many fields due to its advantages of being reusable. Fe_3O_4@SiO_2 Composite nanoparticles have both the unique magnetic response of magnetic Fe_3O_4 nanoparticles and the small size effect of ultrafine particles. Silica has good biocompatibility and stability. The silica layer on the surface of Fe_3O_4 nanoparticles improves the oxidation resistance of Fe_3O_4 nanoparticles and improves the dispersion of nanoparticles in solution. Xu et al.[42] adopted Fe_3O_4@SiO_2 Composite nanoparticles as detection. A new base material for enriching and eliminating heavy metal ions. With Fe_3O_4@SiO_2 Nanoparticles as the matrix, based on molecular design and tailoring, according to the interaction between reactive groups in the molecular structure of ligands and the functional groups on the surface of nanoparticles, chemical covalent coupling method is used in Fe_3O_4@SiO_2 The surface of nanoparticles is modified with organic ligand molecules or biological macromolecules that have selective effects on heavy metal ions to realize the characteristics of molecular diversity and adjustability of surface modification of nanoparticles, and it is applied to the selective detection of heavy metal ions. Enrichment and elimination.

Rhodamine derivatives maintain fluorescence quenching due to the effect of photo induced electron transfer (PET) in the spiro state. After the ring opening is induced by a certain metal ion, the pet effect is blocked, showing changes in color or fluorescence intensity, showing an “off-on” fluorescent signal, which can play the role of detecting this kind of metal ion. Hexamethylene diisocyanate (HDI) was grafted to Fe_3O_4@SiO_2 Surface of nanoparticles, synthetic isocyanate surface modified Fe_3O_4@SiO_2 Nanoparticles, recorded as Fe_3O_4@SiO_2-NCO, the synthetic rhodamine 6G derivative (Rho6G-EDA) and Fe_3O_4@SiO_2-NCO Reaction, and finally prepared functional nano materials, recorded as Fe_3O_4@SiO_2-Rho. After being induced by Hg^{2+}, the nano sensor shows orange fluorescence changes that can be recognized by the naked eye, while there is no change after the addition of other heavy metal ions, so the functionalized nano material can be used as a sensor for selective detection of Hg^{2+}[43]. Also Fe_3O_4@SiO_2-Rho The nano sensor has good adsorption capacity for Hg^{2+} (the adsorption rate is as high as 85.44%).

Rhodamine B hydrazide reacts with 2-hydroxy^{-1}-naphthalene formaldehyde to produce rhodamine B derivatives (rhob EN) containing phenolic hydroxyl groups Fe_3O_4@SiO_2-NCO The surface isocyanate active functional group grafts rhob en onto the surface of nanoparticles to synthesize a nanosensor of zinc ions[44]. The functionalized nanoparticles have a good selective detection effect on Zn^{2+}, and show pink fluorescence changes under the excitation of 365 nm ultraviolet light. Fe_3O_4@SiO_2-Rho can also be used as an adsorbent for zinc ions. When the initial concentration of zinc ions is 50 ppm, the removal rate of zinc ions by 10 mg functionalized nanoparticles is as high as 87.34%.

The fluorescence quenching effect of quinoline derivatives on copper ions and the fluorescence enhancement effect on zinc ions were used to detect Zn^{2+} and Cu^{2+}. 8-aminoquinoline reacts with chloroacetamide to produce 8-chloroacetylaminoquinoline (CAAQ), which is grafted into amino modified Fe_3O_4@SiO_2 Nanoparticles(Fe_3O_4@SiO_2-APTES)Surface, synthesis of functional nano materials Fe_3O_4@SiO_2-CAAQ, which is used for selective detection of Zn^{2+} and Cu^{2+}[45]. Fe_3O_4@SiO_2-CAAQ. The composite has good adsorption capacity for Zn^{2+} and Cu^{2+}, and its adsorption rates are 92.37% and 91.65%

respectively.

The application of nano materials in the detection and analysis of metal elements in food is a new field. Exploring and synthesizing new nanocomposites and applying them to the detection and analysis of metal elements in food has become a hot spot in the field of inorganic element detection.

5. Methods for detecting metal elements in food by Biotechnology

5.1. Immune detection technology

Immunoassay is a highly specific technique. High sensitivity. Economics. Large amount of screening. According to the types of antibodies, it can be divided into monoclonal antibody immunoassay and polyclonal antibody immunoassay. Monoclonal antibody immunoassay has indirect competitive ELISA one-step immunoassay. Since Reardan et al.[46] first prepared monoclonal antibodies against indium and established immunoassay methods in 1985, the research on immune detection technology of metal elements at home and abroad has been very active.

To analyze heavy metal ions with immune detection technology, first of all, appropriate compounds should be selected to combine with metal ions to obtain a certain spatial structure, so as to produce reactivity; the second is to connect the compounds bound with metal ions to the carrier protein to produce immunogenicity. Among them, the selection of compounds that bind to metal ions is the key to the preparation of specific antibodies.

In recent years, the immune detection technology of cadmium pollution in food has made great progress and has been widely used; Khosraviani et al.[47] Established an indirect competitive ELISA method for the detection of cadmium in water samples, with a detection range of 7–500 nmol/L and a detection limit of 7 nmol/L. It has a strong cross reaction with mercury and a small cross reaction with other metal ions.

Colloidal gold immunochromatography is a simple and rapid method combining colloidal gold labeling technology with chromatography technology. This method has many advantages: (1) the detection speed is fast, and the detection result can be determined in only a few minutes; (2) Low cost, no need for any instruments and equipment. Less reagents are needed, which are readable with naked eyes; (3) Easy to detect on site; (4) Stable, colloidal gold can be preserved stably and is less affected by the outside world[48,49]. Xiang et al.[50] used the immune competition method to coat the anti Cd^{2+}-EDTA monoclonal antibody colloidal gold complex on the colloidal gold binding pad, and coated the synthetic Cd-iEDTA-BSA detection antigen on the surface of nitrocellulose film to prepare a colloidal gold immunochromatographic rapid detection strip for detecting cadmium ion residues in water samples. The detection limit of the prepared test strip for cadmium ion is 100 ng/mL, but it has a cross reaction with Hg^{2+} ion, and it has a cross reaction with Fe^{3+}, Pb^{2+}, Cu^{2+} plasma has no cross reaction, the test strip has good stability after being placed at room temperature for 8 weeks, and the test results of standard water samples are consistent with those of ICP-AES. Colloidal gold immunochromatography can be used as an effective means for on-site detection and monitoring of cadmium ion residues in water samples.

The immune detection technology of metal ions is faster than traditional detection methods. High sensitivity. Strong specificity. With the advantages of low cost, it can be used as a method for rapid detection of metal elements, but it is only an auxiliary method and cannot replace the traditional method. In recent years, the progress of recombinant monoclonal antibody construction technology provides a broad application prospect for immune detection technology. Screening new compounds with good specificity. Monoclonal antibodies will be the development direction in the future. This is of great significance for the detection of metal ions in food.

5.2. Enzyme sensor

Metal ions can quantitatively inhibit the activity of enzymes, which can quickly detect the concentration of metals in food. At present, the national standard method used to detect metal elements has high sensitivity. It has strong specificity but complicated operation. High cost of instruments. Liu et al.[51] selected glucose oxidase (GOD)-horse radish peroxidase (POD) catalytic system to establish a fast, simple, colorimetric enzyme inhibition method for the determination of cadmium, tin and lead. The effects of cadmium, tin, lead and other metal ions on the activity of glucose oxidase were determined by the inhibitory effect of metal ions on the enzyme activity. The detection limits of this method were 1.3, 0.4 and 1.4 μg/mL for cadmium, tin and lead, respectively. The recoveries of standard additions were 92.7%–105.7%, and the standard deviation was ≤1.0%. Li et al.[52] used the inhibitory effect of Hg^{2+} on horseradish peroxidase to detect Hg^{2+}, the determination range was 1.0–5.0 mg/L, and the detection limit was 0.58 mg/L. Kou[53] made a potentiometric biosensor based on urease inhibition by covalently coupling urease to a nylon mesh and covering it on a pH composite electrode, 8 and 30 μg/L. The interference effects of metal ions such as Zn^{2+}, Ni^{2+} and Mn^{2+} can be eliminated by using masking agents. The sensor has good stability, high reproducibility and high precision, can be reused several times after regeneration, and can detect multiple samples at the same time, and the time can be greatly shortened. Therefore, this method can be used as a sensitive, rapid and reliable method for the detection of heavy metal ion residues in the environment.

The advantages of enzyme sensor detection method make it have the potential to meet these conditions at the same time. The development of enzyme sensor should improve its performance as much as possible by using various new technologies to overcome the great influence of environmental factors on materials. It is not easy to preserve and other shortcomings, and give full play to its advantages of easy automation and miniaturization to develop a special detection instrument with strong practicality.

6. Conclusion and outlook

To sum up, there are many methods for the detection of inorganic elements in food. In addition to the above methods, there are isotope dilution methods. Neutron activation analysis, etc., but its practical application is less. At present, these methods are also simplifying the pretreatment operation from the traditional chemical analysis means. Lower energy consumption costs. Breakthrough and development in the elimination of background interference. It is believed that with the continuous improvement of people's consumption level and the increasing attention to the requirements of dietary health, trace elements and pollution required by the human body in food. Hazardous heavy metal elements. The detection methods of inorganic elements are also moving towards fast. Safety. It will play an increasingly critical role in standardizing and improving the quality and safety of food and agricultural products.

Conflict of interest

The authors declare no conflict of interest.

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