A Review on Spectrometer of Pb(II) in Water

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Abstract. Heavy metals have many characteristics such as susceptible to bio-accumulation, ecological amplification effect, and high toxicity and so on. Heavy metal pollution in water not only destroys the ecological environment, but also threat to human health and life seriously. Pb (II) enters the body through the enrichment of animals and plants in water, and damage to the reproductive ability, nervous system and body function of human. Source controlling is the key to the prevention of heavy metal pollution, so we urgently need to apply a plenty of heavy metal fast-detection instrument. we know that the research and development of heavy metal fast-detection instrument is becoming more and more important. However, the existing methods of detection of heavy metals have many problems like its procedure is too complicated, its equipment is expensive and operation process is not suitable for site test. The detection instruments are also numerous and varied, but the classified papers about heavy metal rapid-detecting instrument based on different principle seldom appear. In this paper, the current situation of existing heavy metals rapid-detection instrument based on different principles was reviewed, and the development direction of rapid-detection instrument was pointed out.

Keywords: Rapid, detection equipment, Pb (II), portable.

1 Introduction

There are some heavy metals entered our body through food disrupting the body's normal physiological function and harming our health, and they are known as toxic heavy metals mainly including Hg, Cd, Cr, As, Pb, etc [1].Water environment mainly includes rivers, lakes, reservoirs, marine and industrial water by human processing, discharge water and drinking water etc [2].Heavy metal pollution of water environment refers to the heavy metals discharged into water exceeding the self-purification ability of water. It makes the composition and properties of the water

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change, the biological growth conditions in water environment deterioration, and bad influence to human life and health. Since the heavy metals in the water environment have some characteristics of multi-source, strong concealment, slight transport property, high toxicity, complex chemical behavior and ecological effect, non-biodegradable, biological accumulation effect, its low concentration have larger toxicity and so on, they become important pollutants in the water environment [3-5]. If they are absorbed by the food chain of aquatic plants, they will harm humans and animals.

Pb (II) pollution is defined as the most harmful environmental pollution to humans by WHO, and Pb (II) in food comes mostly from the enrichment of animals and plants in the water or soil [2]. Pb (II) to the nervous system especially the child's nervous system is extremely sensitive toxins. Infant exposed to high concentrations of Pb (II) is easy to cause poison, and then lead to toxic encephalitic. The main symptoms are excitement or sleepy, gastrointestinal discomfort, movement disorder, headache suffering, and it even can lead to coma when serious. If the children exposure to the low concentration of lead by long-term, it can cause changes in behavior functions, the analog learning ability decreased, movement disorders, inattention, impulsiveness, hyperactivity, and IQ decline [5-9]. In addition, lead pollution can affect reproductive ability, sexual function and nervous system, and cause high blood pressure .

To protect the water environment, control the water pollution, maintain ecological balance and protect human health, china has formulated a series of standards and methods corresponding to the evaluation of water quality [7]. The Indicators of Heavy Metal Pollution of Water Environment: "GB 3838-2002 Surface Water Environmental Quality Standard", "GB/T 14848-93 Groundwater Quality Standards", "GB 5749-2006 Life Drinking Water Health Standards "," GB 3097-1997 Water Quality Standards "," GB/T 11607-1989 Fishery Water Quality Standards ".

2 Methods for Heavy Metal Pb (II) Detection

The most usually used traditional indeterminacy of heavy metals is chemical analysis methods, such as Atomic Fluorescence Spectroscopy (AFS), Atomic Absorption Spectroscopy (AAS), Plasma Emission Spectroscopy (ICP), Reagent Colorimetric etc. With the advances of material science, information technology and sensing detection, the progress of a new indeterminacy based on mufti-disciplinary promoted the development of rapid-detection technology of heavy metals. Common methods for fast-detection include Electrochemical methods, UV-visible Spectrophotometry (UV), X-ray Fluorescence Spectrometry (XRF), Near Infrared Spectroscopy, Immunology Detection, Enzyme Inhibition and Bio-sensor Technology [10-26].

2.1 Traditional Indeterminacy of Heavy Metals

Atomic fluorescence spectrometry (AFS) is a analytical method of measuring the target element atomic vapor fluorescence emission intensity excited by the radiation to measure the target element [27]. The limit of detection of Atomic fluorescence spectrometry is less than that of atomic absorption spectrometry, and Atomic fluorescence spectrometry has simple lines and less interference, wide linear range, but the application of finite elements.

Atomic absorption spectrometry (AAS).In the method of ample vapor phase, the ground state atoms of the measured element create resonance absorption which is response for the characteristic of the atomic narrowband radiation emitted by the light source or hollow cathode lamps , outer electrons from the ground state to an excited state to produce atomic absorption spectrometry. Within certain limits, the absorbance is proportional to the concentration of the measured elements of the ground state atoms in a vapor phase, the quantitative relationship can be expressed Lambert-Beer's law [28]. The downside is that it requires a specific element corresponding hollow cathode lamp as a light source, cannot be achieved at the same time multi-element determination.

Inductively coupled plasma mass spectrometry (ICP-MS). The inductively coupled plasma mass spectrometry high temperature ionization combined with the advantages of sensitive fast scanning, mainly used for inorganic elemental and isotopic analysis test [29]. Excitation light source is inductively coupled plasma torch, and the test substance is ionized and then is separated by charge-to-mass ratio. Measure the spectral peak intensity to determine the ion concentration. The analysis method is highly sensitive, fast, little interference and can be completed within a few minutes while quantitatively determine dozens of elements, but easy to appear some of the ion background interference in ICP high temperature environment in the process of some elements determination.

2.2 Methods for Fast-Detection of Heavy Metals

Electrochemical analysis method based on the electrochemical properties established by the substances in solution and on the pole [31]. The electrical signals of power, potential, current and conductivity can be measured directly in the electrochemical analysis method, and do not need to signal conversion. The electrochemical analysis method is recognized as the trace and ultra trace analysis method of accurate, rapid and sensitive in the chemical composition analysis, and its concentration can be measured as low as 10~12g/L (metal ion). The electrochemical detection of heavy metals mainly includes potentiometry, polarography, conductometry, voltammetry etc.

UV visible spectrophotometry is a qualitative, quantitative and structural analysis method according to the absorption characteristics of the electromagnetic wave in the range of 200~760nm of the material molecular [32]. Its detection principle is some heavy metals make complexion reaction with one chromogenic agent in solution, and react with a colored complex, and its color depth is proportional to the concentration of the solution. Then make the spectral scanning in certain wavelength of ultraviolet visible light wave band to realize the detection of heavy metal content.

X-ray fluorescence spectrometry is also a qualitative, quantitative analysis method using the sample absorption characteristics to X-ray, which changes with the ingredients and concentration of the samples [33]. The method is simple, rapid, less spectral interference, small destructive and its elemental analysis range is wide, spectral line is simple. This method has low detection limit and high accuracy, but the X-ray fluorescence spectrometry need to train the operation staff before the experiment, so operation is more trouble and not suitable for on-site detection.

Near infrared spectroscopy can simultaneity determine a variety of data only through one time near infrared spectrum scanning of the samples in a short time, and this method need a small amount of sample, without damage and pollution, with the advantages of high efficiency, fast, low cost and environmental protection. [34]Near infrared light is mainly for the multiplier frequency and sum frequency absorption of the vibration of hydrogen groups. Different organic contains different groups, and different groups have different energy levels, so the absorption wavelength of the near infrared to all groups in different physical and chemical environment has significant difference. While the composition of aquaculture water is complicated, we cannot realize the direct detection of heavy metals using near infrared light needing the combination with other methods.

Biosensor method's principle is fixing specific protein on the electrode material, making the metal ion combined with the specific protein, and then the protein structure will change and transfer the signal to the capacitance sensor, and make the quantitative detection of heavy metals by using the change of capacitance signal sensitivity [35]. In recent years, such as the specific protein biosensor is developed for the determination of toxic compounds in aqueous solution. But the lifetime of the biological sensor mainly depends on the biological activity; the organisms generally live for a short time, which restrict the application and development of biological sensors. The principle of enzyme inhibition method is the heavy metal ions combining with the active center of the enzyme of methyl sulfhydryl or sulfhydryl, and then the enzyme changes its structure and properties and its activity decreased, making the color, conductivity and absorbance of the chromogenic agent changed [36]. We build the relationship between heavy metal concentration and enzyme system change through the photoelectric signal obtained. This method is used for qualitative measurement of heavy metal in environmental, food, water and vegetables. The enzyme inhibition method has advantages of fast, convenient and economic, which can be used in field and rapid detection, but compared with the traditional detection technology, its sensitivity and accuracy is low. Immunological analysis method has a high specificity, but its sensitivity is also high. We classified this method according to the immunoassay method of the type of antibody to heavy metal ions [37].We must finish the work in two aspects before analyzing the heavy metal ions in the use of immunoassay, the first step is to select a suitable complexes connecting with metal ion, guaranteed a certain spatial structure, so as to produce original reaction. The second step is to the combined metal ion compounds attached to a carrier protein, producing an immunogenic. The choice of compounds is the key to prepare specific antibody.

3 Instruments of Heavy Metal Pb (II) Detection

The research and development level of scientific instruments represents the scientific prowess of countries and overall national strength to some extent. The research and development of corresponding instrument based on the above traditional or rapid heavy metal detection method has become the focus of current research. The traditional instruments of heavy metal detection have high accuracy and good precision, but the body of that is too large and the price is expensive, the pre-processing and detection process is complicated, the detection time is too longer. The concrete function and price of those is shown in table 1:

Table 1. Traditional instrumental analysis methods of function and price

Analysis methods of function and price detection limit(g/L)	Atomic fluorescence spectrometry (AFS)10^{-9}	Atomic absorption spectrometry Flame 10^{-7}	Atomic absorption spectrometry Grahite funace10^{-9}	Inductively coupled plasmamass spectrum ICPP-AES10^{-9}	Inductively coupled plasmamass spectrum ICP-MS10^{-10}
Range of linearity	3-5order of magnitude	narrow		wide	
accuracy	high	high		high	
Multielement analysis at the same time	yes	no		yes	
Element valence state analysis	yes	no		yes	
Number of metal elements	More than twenty	More than seventy		More than eighty	
Instrument price/ten thousand yuan	10-99	1-99		10-999	

As for the rapid detection technology of heavy metal, the corresponding instruments have the characteristics of high sensitivity, good accuracy and timeliness strong. The research focus at home and abroad is mainly reflected in the development of the products of rapid detector of heavy metals. The key research direction is to implement the instrument which is low cost, small and portable, whose detection is suitable for field detection combining equalization with quantitation [10-12]. According to the characteristics of existing portable rapid-detector of heavy metal, we generally divide them into two classes of physicochemical instruments and biological instruments.

3.1 Portable Instruments Based on Physicochemical

Physicochemical instrument refers to which are designed and developed on the basis of spectrophotometry and electrochemical technology, through the material innovation and the small simple design including the instruments based on electrochemical method, UV Vis spectrophotometry (UV), near infrared spectroscopy and X-ray fluorescence spectrometry (XRF). These kinds of product have a lower price and wide detection range, its pre-treatment and operation process has improved than the precision instruments, but they still complicated.

3.1.1 Portable Instruments Based on Physicochemical

The electrochemical methods work with electrochemical sensor, and its performance is mainly limited by the range of potential scanning. The potential of the anode direction is determined by the materials of working electrode of electrochemical sensor. The oxidation potential in the electrolyte is different with electrode material. The potential of the cathode direction is determined by the over potential of hydrogen which depends on the influence of support electrolyte solution [11-13]. The electrochemical detection of heavy metals mainly includes ion-selective electrodes, polarography and voltammetry. The instrument using Anodic Stripping Voltammetry has developed rapidly in recent years, and Anodic Stripping Voltammetry is an electrochemical analysis method based on the theory of the classical polarography and combined with constant potential electrolysis enrichment and voltammetry determination. China has promulgated a national standard of Anodic Stripping Voltammetry which is suitable for the determination of metal impurities in chemical reagents. The Anodic Stripping Voltammetry method can determine varieties of metal ions in one time continuously, and it has the common advantages of electrochemical method that is low detection limit, high sensitivity, simple instrument and convenient operations [11-14].

The detecting instrument of electrochemical in foreign develop fast. As early 2007, Japan University of Tsukuba and Chemical Industrial Co. Ltd. have developed a model of the THMA-101 analyzer jointly. This instrument weights 4.2kg working with the theory of Anodic Stripping Voltammetry, which can detect Pb, Cd, Hg, Sb, Sn and some other heavy metals continuously. Its detection limit is l01-10mol/l and the analysis time is less than 5min [15] .The Company of wagtech in UK has developed a series of upgrades named HM1000-HM5000 based on the theory of Anodic Stripping Voltammetry. One of the latest products is HM5000 portable detectors of heavy metal, whose power supplied by rechargeable battery. Its weight reduces to 3.5kg, and the fastest sample detection time is 3min, and the detection limit is less than 1ppb [16]. Domestic electrochemical detection instrument is also quite mature. Skyray Instrument Company in JiangSu province of China combined the method of Anodic Stripping Voltammetry which have high sensitivity and recognized authority with National Standard Methods "Colorimetric method" which have fast detection rapid and good immunity, and developed a series of HM products. The resolution of the latest product of HM5000P is 0.01ppb, the detection time is less than 5 minutes, and the fastest detection time is less than 30 seconds [17-18]. The analysis of heavy metals based on the theory of Differential Pulse Stripping Voltammetry was developed by Cai Wei, and measured four kinds of heavy metal ions using the methods of pre-plating with mercury film. He puts forward the test method with different background of pure water solution and sea solution. The detection accuracy of background with pure water solutions is high, the precision of which can reach about 5%. It can also effectively determine with the seawater background solution, the precision of that is controlled within 15%, and its detection limit is 0.1-0.3ng/L. The above electrochemical detector all have the characters of low detection limit, high sensitivity and convenient operation, but the cost is relatively high.

3.1.2 Instruments Based on Spectrophotometry

The theories of spectrum instruments include ultraviolet visible spectrophotometry (UV), near infrared spectroscopy and X-ray fluorescence spectrometry (XRF). The three methods are a kind of analysis about qualitative, quantitative and structural based on the absorption properties of substance molecule on different wavelength range of the electromagnetic wave [20-22]. The detection theory in aspects of heavy metals is the organic compounds of chromogenic agent making complexion reaction with heavy metal, generating colored molecular group or producing fluorescence. The depth of color or the intensity of fluorescence is proportional to concentration. So we can detect the heavy metals under the specific wavelengths using the corresponding method. The amount of the sample to be detected of the spectral method is little. There is no damage and no pollution in the process of detection. So these methods have the advantages of efficient, fast, low cost and environmental protection etc. [10-22]. The above portable instruments at home and abroad based on the theory of UV-visible spectrophotometry (UV), near infrared spectroscopy are rarely reported, but the instruments based on X-ray fluorescence spectroscopy (XRF) technology have developed more mature.

The Checkboy Soil analyzer developed jointly by central Science Japan and Research Institute of resources and Environmental System. There is a built-in and small portable spectrophotometer and it powered by battery. It is suitable for on-site analysis the content of heavy metals in soil and water. It can also be simultaneous to determine nitrogen, phosphorus, COD and other indicators. Ten samples can be detected per hour. This instrument has been used for the rapid screening of environmental pollution source in Tokyo [25].

America Thermo Fisher Scientific Company launched the NITON-XL3t-600 portable instrument whose accuracy and precision is high, and the testing time of the sample is only 120s-200s. Seiko yingsi Electronic Technology Co., Ltd. specifically launched the SEA1100 of X-ray fluorescence spectrometer for the detection of heavy metals in soil; it also can be used in soil laboratory rapid for the detection for heavy metals. The instruments named X-MET 5000 analyzer developed by British Oxford using the Oxford high-energy, long-life and miniature X-ray tube. It can rapid analyze the content of heavy metals of Cd, Cr, Hg, Pb, Cu, Zn, Sn, Sb in the soil and environment in a few seconds [11]. Wang Jihua published a portable soil heavy metal analyzer specifically for rapid detection of heavy metals in soil, and developed a portable detector of XRF-7 which can test heavy metals in the soil. But the drawbacks of this kind of instrument are the high cost, and the detection limit of some heavy metals is not enough low [24-25].

3.2 Portable Instruments Based on Biological and Others

Biological instrument primarily based on the theories of heavy metals immunological or enzyme inhibition, using the development of biological specificity and sensor technology to achieve. Including the instruments based on immunological test, enzyme inhibition and biosensor technology. As early 1985, Reardan through a antigens of metal chelating agent isolated single antibody for the first time, making the immunological detection technology began to be used in heavy metal detection [26] .Subsequently, the complex antibody of metal chelates agent of the heavy metal ions of Hg2+, Cd2+, Pb2+ had successfully developed [27-29]. Enzyme inhibition technology is determining the content of heavy metals using the inhibitory effect of enzyme to metals. Biological Sensor Technology is fixing the specific protein, enzyme and its composite system on the electrode or biofilm and realizing the corresponding rapid detection of the heavy metals. The detection accuracy and sensitivity of such instruments used biological specificity principle is affected by antibody or enzyme specificity, which belongs to the indirect detection instruments [20-22].

Blake [39] initially developed an instrument named KinExA based on the theory of heavy metals immunological of ELISA. This instrument can make a rapid detection to heavy metal ions, which is expected to realize the field detection. There are few reports about this kind of instrument at domestic. This kind of instrument although can overcome the shortcomings of traditional instruments such as time-consuming and laborious, expensive, needing for lots of samples pretreatment, and the detection must be carried out in a large indoor laboratory. At the worse, the screening of heavy metals for small molecule specific monoclonal antibody is more difficult, it needs a long cycle time, its development cost is expensive, and its pH detection range is narrow.

Beijing Agricultural Product Quality Detection and Farmland Environment Monitoring Technology Research Center and South Korea Makar Heath Co. Ltd. jointly developed the "fruit and vegetable pollutant three in one portable detecting instrument", in which the effective range of detection based on enzyme inhibition technique of heavy metal lead is between0.5mg/mL and 4.0mg/mL [40]. Lehmann [41] using fermented glutinous rice recombinant yeast strains as biological components, developed a current type microbial biosensor for special measuring copper ion, the biosensor can detect the CuSO4 solution in the concentration range of 0.5 m/mol to 2m/mol. Karlen [42] the use of basophilic bacteria into the biological sensor, and used for the measurement of the concentration and bioavailability of Zn2+ in sewage , the concentration in the range of 0mg/l to 10mg/l, its shortcoming is the determination is single.

4 Portable Instruments Based on Colorimetry

Near infrared spectrum technology has been developing rapidly, It has many advantages, such as fast analysis, no needing for sample preparation and no environment pollution, so it is getting more and more attention. Since the 1980s, china agricultural university introduced the Fourier transform infrared spectrometer to carry out the research on agricultural products quality analysis, combined with the chemometrics methods, and established data analysis model. In the early years, the key technology of portable near infrared spectrometer was almost mastered by foreign, and our country can only rely on imports using a similar system. In 2006, Chongqing University began to develop a portable near infrared spectrometer, breaking through the key technologies of the structure design and products can be applied on the pesticide composition and content of vegetable base on-site rapid detection. Beijing Ying Xian has now successfully commercialized portable near infrared spectrometer. The reduction of volume and quality of series of products, fast analysis, high precision measurement, give the way to implement of low cost, low detection limit, detection a variety of metal detector.

5 Summaries

In conclusion, at this stage, portable rapid detection of heavy metals is lack of detector which is low cost, low detection limit, early simple treatment and suitable for a variety of heavy metals. The near-infrared spectroscopy and reagent colorimetric method, can be simplify the complex pretreatment of colorimetry. The tested object converses to a measured compound to build detection model, and the model is applied to a portable near-infrared spectrometer to achieve the detection of heavy metals. The portable detector of heavy metals will become low cost, low detection limit, early simple treatment and be suitable for many heavy metals detection equipment.

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