

Application of Liquid Phase-Mass Spectrometry in Water Quality Detection

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Abstract:

The paper is based on the High Performance Liquid Chromatography (HPLC) and Liquid Chromatography-Mass Spectrometry, (LC-MS) Basic principles and characteristics of joint use, the application of HPLC with LC-MS in various water quality testing programs, clarify the treatment method, specificity, sensitivity and other related information in water pesticide residue detection, industrial pollutant detection, antibiotic detection, elemental pollutant detection, biological toxin detection. It further confirms the application advantages of HPLC and LC-MS in water quality testing in order to provide useful reference for water quality testing.

Keywords:

High-performance Liquid Chromatography, Liquid Phase-Mass Spectrometry, Water Quality Detection

1. Introduction

HPLC is a chromatographic system with a liquid as a mobile phase , High-pressure infusion pump pressurization can be used to improve the detection efficiency, which is often used in the detection of organic compounds. Mass spectrometry (MS) refers to the detection method of separating various components in the sample into ions with different charge ratio, and then generating an ion beam under the action of an external electric field, and measuring the chemical structure, molecular mass and other parameters of the sample by the mass analyzer. LC-MS detection can fully realize the high qualitative performance of MS and can achieve efficient quantitative and qualitative detection.

As an important resource for human survival, water quality has an extremely important impact on human health, production and life. With the acceleration of industrialization and urbanization, water pollution has attracted wide attention. The number of deaths caused by drinking water safety problems is increasing worldwide, the spread of disease is also directly related to water sources, and water pollution has become one of the factors threatening human life safety. The continuous progress of

science and technology makes the water quality detection technology more diverse, and different water quality detection technology has great differences in sensitivity, accuracy and other aspects, among which HPLC and LC-MS are the most commonly used water quality detection technology. Based on this, on the basis of clarifying the basic principles and characteristics of HPLC and LC-MS, the treatment methods and sensitivity of HPLC and LC-MS in water quality testing are analyzed from five aspects, in order to provide reference for water quality testing.

2. HPLC in Pesticide Residues in Water

Pesticide pollution in water has long been widely concerned, and HPLC and LC-MS have been widely used in the detection of pesticides, herbicides and pesticide residues in water. In previous studies, solid phase extraction technology (Solid Phase Extraction, SPE) was usually used as a pretreatment method to remove other disturbances in the water quality, and then HPLC was used to detect the residual pesticide content in the water. For example, in the determination of furan and menol residues in drinking water, HPLC combined post-column derivation technology in drinking water. The resulting test results have extremely high sensitivity, confirming that the sensitivity of this test method is 10 times [1] higher than that of the same type.

In recent years, with the deepening of water quality detection research, HPLC and LC-MS technology gradually applied to water pesticide residue detection, the detection method tends to use tandem mass spectrometry, in the detection process need to apply two quality analysis filter, compared to pure LC-MS detection means, the detection means of qualitative effect is stronger. For example, Zhang Ji [2] used HPLC and LC-MS to detect the residues of 8 kinds of organophosphorus pesticides in water at the same time. After testing, it was proved that HPLC and LC-MS had the characteristics of high precision and good accuracy, and the recovery rate could reach between 87.99% and 102.96%, with the standard deviation between 3.08% and 7.73%, which could effectively detect the 8 kinds of organophosphorus pesticide residues contained in the water. Wu Chunying [3] et al. used HPLC and LC-MS combined technology to detect 26 organophosphorus pesticide residues in water, Pre-sample processing using the Oasis HLB solid-phase extraction column, Acetone: dichloromethane = 8 : 2 as elution, 1% 0.1 methyl formate: 0.1% formate acetate: 0.1% ammonium formate acetate 5:5 as mobile phase, Organophosphorus pesticide residue detection in water based on the optimal conditions, The results showed that the target recovery rate of HPLC combined with LC-MS was between 80.5% and 119.8%, Standard deviation is between 5.9% and 11.5%, Confirming that this method has the advantages of low detection limit, high recovery rate and high accuracy, It is suitable for detecting 26 kinds of organophosphorus pesticide residues in water. In general, previous studies have confirmed that HPLC and LC-MS are used in the detection of pesticide residues in water without complex pretreatment means, and can detect a variety of pesticide residues at the same time, which has the advantages of good detection efficiency and high accuracy. But in the detection process often need to introduce advanced processing instruments, the cost of use is relatively high.

3. HPLC Was Used in Conjunction with LC-MS for the Detection of Industrial Pollutants in the Water

HPLC and LC-MS can also be used in pollutant detection in water, and this method can effectively determine phthalate, acrylamide and bisphenol A in water.

Phthalate is a typical industrial pollutant. Under specific conditions, the decomposition of this pollutant into water will seriously disrupt the human endocrine system, and then cause a variety of diseases. In their study, Wang [4] et al. used HPLC and LC-MS to detect the content of two phthalate compounds in water, separated by C18 column, gradient elution with methanol-0.1% methyl acid water, and analyzed the samples by positive ionic multiple reaction monitoring (SRM) method. The results showed that the recovery rate of the target in water was 86.3%-102.% and the standard deviation was 4.4% -4.5%. It is considered that the combination of HPLC and LC-MS has the advantages of high efficiency and high accuracy in the detection of phthalate compounds in water.

Acrylamide is usually used as a coagulant for water treatment treatment, but acrylamide has been listed as a class 2A carcinogen, which can cause some damage to the human body. Zou Kangbing et al. used HPLC and LC-MS to detect the acrylamide content in water. With the help of tetrafoethene needle filter, the samples were quantitatively analyzed by positive ion injection source (ESI ~ +) and multi-response monitoring (MRM). The results showed that when the concentration of acrylamide in the water sample was 0.04-10.00 µg/L, the correlation coefficient was the best, the target recovery was between 85.7% -106.6%, and the standard deviation was 3.2% -8.10%, confirming that HPLC and LC-MS can effectively detect the acrylamide content in water, which has the characteristics of high reproducibility and high sensitivity.

Bisphenol A is also A more common industrial raw material, which is widely used and easy to degrade in water, and can be detected in drinking water. Wang Heng [6] et al applied solid-phase extract-HPLC with LC-MS to determine bisphenol A in water, purified and enriched samples with C18 solid-phase extract column, then separated samples with XR-ODS(2.0mm 100mm, 2.2 µ m), and finally detected by MRM anion mode. The results showed that the target recovery rate was between 90% and 111%, and the standard deviation was 7%, which confirmed that the detection of bisphenol A content in water has high accuracy. Overall, previous studies have confirmed that HPLC and LC-MS have high sensitivity in the detection of industrial pollutants in water.

4. HPLC for the Detection of Antibiotics in Water Combined with LC-MS

The misuse of antibiotics is a relatively serious international problem. International reports that antibiotics such as erythromycin and roxithromycin were detected in American water samples; erythromycin was detected in British surface water samples. Quinolone antibiotics, tetracycline, oxytetracycline and roxithromycin were also detected in domestic water sources. In previous studies, HPLC is often used to detect the antibiotic content in water. However, in recent years, research and development, the content of antibiotics in drinking water is relatively low, and it is often necessary to reach ng/L level. HPLC detection alone cannot reach this level, which has low sensitivity.

In order to improve the sensitivity of the antibiotic detection in water, the combination of HPLC and LC-MS was gradually used in the antibiotic detection in water. In their study, [7] et al. used HPLC and LC-MS to determine five quinolone antibiotics (ciprofloxacin, ofloxacin, enrofloxacin, lomefloxacin, norfloxacin) in the sample, After optimizing the pretreatment and separation conditions, Found that the

analysis of five target compounds in water can be performed within 6.5min by using HPLC and LC-MS combined technology, Target compound recovery rates between 81.5% – 116%, Standard deviation is between 6% and 14.1%, Confirm that the combination of HPLC with LC-MS can be used for determining quinolone antibiotics in water, It has the characteristics of high sensitivity level. In their study, [8] et al. also used solid-phase extraction-HPLC and LC-MS to determine the residue of tetracycline, roxithromycin and other compounds in water. When formic acid solution and acetonitrile were used as liquid phase, it was found that the determination of tetracycline and roxithromycin in water could be completed within 5min. The detection limit was 0.08ng/L-0.35ng/L, the recovery rate was 82.5% -114%, and the standard deviation was 1.4% -5.6%, which proved that this method has high sensitivity in the detection of antibiotics such as tetracycline in water. ABUIN [9] is the internal standard, which quickly and accurately measured multiple macrolide antibiotics in water samples by HPLC and LC-MS, and its precision and detection limit were about 10 times that of MS alone. In general, all domestic and foreign studies have confirmed that HPLC and LC-MS have high sensitivity in antibiotic detection in water.

5. HPLC and LC-MS Were Used in the Detection of Elemental Pollutants in Water

Related literature shows that HPLC and LC-MS can also be used to detect elemental pollutants in water. In their study, Zhao Yanhui [10] et al. reviewed the detection of HPLC / ICP-MS combined technology in the trace morphology of the elements, and found that the technology could effectively detect the elemental pollutants contained in the water. Using the combination technique of HPLC with LC-MS in the study, Li Fei [11] et al, By optimizing chromatographic conditions such as mobile phase, concentration and pH, Finally, using 20mm.mol l⁻¹ ammonium acetate and 2mm.mol l⁻¹ ethylenediaminetetraacetic acid (EDTA) as mobile phases, Regulation of pH by tributyl ammonium hydroxide (TBAH) (pH=7.5), Cr (III), Cr (VI) detection, Limit of detection of > 1.0 μg.L⁻¹, The average recovery rate of Cr (III) and Cr (VI) in actual water analysis is 85.0% -101%. It proves that this method has high sensitivity in detecting elemental pollutants in water. Li Changping [12] et al. also use similar technology, With arsenite (As (III)), dimethyl arsenic (DMA), monomethyl arsenic (MMA), arsenate (As (V)) as the research subjects, Using the phosphate buffer solution as the mobile phase, With potassium borohydride as a reducing agent, Preliminary analysis of As (III), DMA, MMA, As (V) in the samples, The results show that the detection can be completed within 7min, As (III), DMA, MMA, As (V) all have a very good linearity, The limit of detection is 0.06 μg/L, 0.12 μg/L, 0.09 μg/L, 0.15 μg/L, Compared with the actual water samples, the results show that, This method has a relatively high sensitivity and accuracy. In general, the HPLC and LC-MS combination can greatly improve the detection rate of elemental pollutants in water.

6. HPLC in Conjunction with LC-MS to Detect Biotoxins in Water

When algae pollution occurs in the water, biological toxins will be produced. The detection of algae toxins in the water is included in the national standard. ODSC18 pillars is used to develop enrichment treatment for samples to be tested, which can effectively detect biological toxicity in the water. However, combined with the

existing studies, the effectiveness and sensitivity of HPLC and LC-MS in biological toxins in water have not been confirmed, and more thorough such studies are needed.

7. Conclusions

In conclusion, the combination of HPLC and LC-MS is widely used in the detection of pesticide residues, industrial pollutants, antibiotics and elemental pollutants in water, but the application of biological toxins in water still needs to be further confirmed. Admittedly, the combination of HPLC and LC-MS has high sensitivity and effectiveness in water quality detection, and has high application value.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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