Magnetic Solid-Phase Extraction Based on Different Modified Materials for the Determination of Lead in Environmental, Food and Biological Samples

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Abstract. Lead is one of the most important trace heavy metals, which is damaged to human beings and environment. Hence, the determination of lead in environmental, food and biological samples is extremely important to guarantee the public health and safety. This paper summarized and compared the magnetic solid-phase extraction based on different modified materials for the determination of lead in environmental, food and biological samples.

1. Introduction

Lead Pb(II) is one of the most toxic elements that is widely used in chemical and plastic industries, battery manufacturing, smelting, printing industries and mining [1]. Exposure to lead can result in significant health issues [2, 3], such as kidney, brain, liver, bones, hematological damage, and even result in death [4, 5]. However, the amounts of lead ions in real samples are usually lower than the detection limits of most analytical methods. Besides, the direct determination of trace lead is not recommended due to the matrix effects occurring in real samples [6]. Therefore, separation and preconcentration steps are usually required to achieve accurate quantification.

Several extraction and preconcentration procedures have been reported for trace lead, such as coprecipitation [7, 8], cloud point extraction (CPE) [9], liquid liquid extraction [10], solid phase extraction (SPE) [11, 12]. Among these techniques, SPE is the most popular one due to high enrichment factor, simple operation and low cost [3, 13]. However, SPE has its limitations such as being time-consuming, large amounts of organic solvents, low sensitivity and selectivity [14].

As a novel SPE procedure, magnetic solid-phase extraction (MSPE) based on the separation of target analytes from the sample solution by using magnetic sorbents and an external magnetic field, has attracted much interest and attained wide applications [15]. In MSPE, the phase separation of the solid magnetic sorbent from a liquid sample can be separated easily and quickly using the external magnetic field without centrifugation and filtration [16]. Therefore, it is obvious the choice of appropriate magnetic-based sorbents is a key factor for effective extraction of lead. To date, different sorbents such as carbon nanotubes [17], graphene oxide [18-21], metal organic frameworks [22], molecular...
imprinted materials [23], polymeric materials [15, 24] and biosorbents [25] have been employed for the preconcentration of lead in MSPE.

This paper summarized MSPE based on various modified materials for determination of lead in environmental, food and biological samples, and compared the difference between different sorbents for determination of lead in different samples.

2. Different materials for determination of lead in environmental samples
The monitoring of lead in environmental samples is of great importance to ensure the quality of human health. Recently, lots of modified magnetic nanoparticles have been widely applied for determination of lead in environmental samples, including inorganic materials (Mg-NiFe2O4), carbonaceous materials (MBT-MMWCNTs) and molecular imprinted materials (MIIPs). Suo et al. [18] synthesized silica-coated magnetic graphene oxide nanocomposite (Fe3O4-GO@SiO2) coupled with ICP-MS to determine lead. Gugushe et al. [26] and Gu et al. [27] applied magnetic multi-walled carbon nanotubes/zeolite nanocomposite (MWCNT-Fe3O4@Zeo) and graphene-grafted silica-coated Fe3O4 nanoparticles (Fe3O4-SiO2-G) combined with ICP-OES for determination of lead, respectively. Zadeh et al. [28] utilized magnesium (II)-doped nickel ferrite (Mg-NiFe2O4) nanoparticles coupled with FAAS for analysis of lead. As shown in Table 1, most of the determination of lead in environmental samples were coupled with FAAS and the detection limits were found to be very low.

Table 1. Different materials for determination of lead in environmental samples.

| Analyte | Application | Materials | Technique | LOD       | References |
|---------|-------------|-----------|-----------|-----------|------------|
| Lead    | Bottled mineral water | Fe3O4-GO@SiO2 | ICP-MS    | 3.641 ng/L | [18]       |
|         | Industrial wastewater | MWCNT-Fe3O4@Zeo | ICP-OES  | 23.0 ng/L | [26]       |
|         | Lake water | Fe3O4-SiO2-G | ICP-OES  | 0.922 ng/L | [27]       |
|         | Industrial wastewater and acidic lead battery water | Mg-NiFe2O4 | FAAS     | 0.2 ng/mL | [28]       |
|         | River, drinking, sea, well and springwater | MBT-MMWCNTs | FAAS     | 0.21 ng/mL | [29]       |
|         | Tap, well and mineral water | MWCNTs and 1,10-diaza-18-crown-6 NPs | FAAS     | 1.1 ng/mL | [30]       |
|         | Well and aqueduct water | MIIPs | GFAAS   | 2.4 ng/L | [31]       |
|         | Lake, tap and waste water | Nitroso-R salt impregnated magnetic Ambersorb 563 | FAAS     | 1.5 ng/mL | [32]       |

3. Different materials for determination of lead in food samples
Food samples are very complex, often containing proteins, fat, salts, acids, bases and numerous food additives. Hence, the determination of lead ions in food samples require higher demand. Recently, a large number of highly sensitivity and selective magnetic sorbents have been applied in pretreating food samples. Yavuz et al. [33] synthesized a nanosized spongelike Mn3O4 combined with FAAS for determination of lead in various food (strawberry, potato, black cumin, lettuce, lentil, ginger, nettle, artichoke, cress, and squash). Akkaya et al. [34] utilized cobalt magnetic particles (Co-MPs) coupled with FAAS to determine lead. Mehdinia et al. [35] took advantage of Fe3O4@graphene oxide@polyimide nanocomposite (Fe3O4@GO@PI) combined with FAAS to determine lead ions. Besides, Fe3O4 nanoparticles coated with 3-(trimethoxysilyl)-1-propanethiol and modified with ethylene glycol bis-mercaptopoacetate (EGBMA-MSPT-MNPs) combined with ICP-OES were used to determine lead ions [36]. Table 2 clearly demonstrates the potential of MSPE based on different modified materials as a powerful sample preparation tool in analysis of lead in complex food samples.
Table 2. Different materials for determination of lead in food samples.

| Analyte                              | Application                              | Materials                        | Technique | LOD (ng/mL) | References |
|--------------------------------------|------------------------------------------|----------------------------------|-----------|-------------|------------|
| Lead                                 | Various food                             | Nanosized spongelike Mn₃O₄       | FAAS      | 3.0         | [33]       |
|                                      | Black tea samples                        | Co-MPs                           | FAAS      | 7.77        | [34]       |
|                                      | Fish and mollusk samples                 | Fe₃O₄@GO@PI                      | FAAS      | 0.25        | [35]       |
|                                      | Rice, canned tuna fish, and tea leaves   | EGBMA-MSPT-MNPs                  | ICP-OES   | 0.08        | [36]       |
|                                      | Drinking samples                         | LDH-based hydrogel               | FAAS      | 0.39        | [3]        |
|                                      | Milk, indian rice and red tea            | MWCNTs-Fe₃O₄ MNP                 | ICP-AES   | 0.6         | [37]       |

4. Different materials for determination of lead in biological samples

Nowadays, most of the reported methods were applied to simple matrix samples, such as environmental water [13, 14, 38-41]. The determination of lead ions in biological samples is a great challenge because the high complexity of real sample matrix and effects of interfering species. Thus, the determination of lead ions in biological samples requires higher selectivity and higher adsorption capacity of the adsorbent material with higher sensitivity and accuracy instrumentals. Sun et al. [42] synthesized magnetic graphene oxide nanocomposite (Fe₃O₄/GO) coupled with ICP-MS to determine lead in human urine and plasma samples. Ramandi et al. [43] utilized 1-(2-pyridylazo)-2-naphthol modified Fe₃O₄/TiO₂ combined with FAAS for determination of lead ions in human urine and blood plasma samples. Besides, γ-mercaptopropyltrimethoxysilane (γ-MPTS) modified silica-coated magnetic nanoparticles were synthesized and combined with electrothermal vaporization-inductively coupled plasma mass spectrometry (ETV-ICP-MS) for lead determination in cells [44], as shown in Table 3.

Table 3. Different materials for determination of lead in biological samples.

| Analyte                              | Application                              | Materials                        | Technique | LOD References |
|--------------------------------------|------------------------------------------|----------------------------------|-----------|----------------|
| Lead                                 | Human urine and plasma samples           | Fe₃O₄/GO                         | ICP-MS    | 0.157 mg/mL    | [42]       |
|                                      | Human urine, and blood plasma samples    | 1-(2-pyridylazo)-2-naphthol      | FAAS      | 1.21 mg/mL     | [43]       |
|                                      | HepG2 cells                              | Y-MPTS/Si                        | ETV-ICP-MS| 1.12 mg/mL     | [44]       |
|                                      | Milk powder                              | Fe₃O₄@SiO₂@IDA microspheres      | ICP-MS    | 0.26 mg/L      | [45]       |
|                                      | Human hair samples                       | H2Dz-SCMNPs                     | ICP-OES   | 62 mg/L        | [46]       |

5. Conclusion

MSPE based on several of modified magnetic nanoparticles have been widely applied for determination of lead in environmental, food and biological samples, including inorganic materials (nanosized spongelike Mn₃O₄), carbonaceous materials (Fe₃O₄/GO), molecular imprinted materials (MIIPs) and et al. The determination of environmental samples were always coupled with FAAS, while food and biological samples due to its complexity of real sample matrix and effects of interfering species required higher sensitivity and accuracy instrumentals, such as ICP-OES and ICP-MS.

Acknowledgments

This work was financially supported by the Hangzhou Foundation for Development of Science and Technology (NO. 20180533B95, NO. 20181228Y28), the Medical Health Foundation for Key Talents in Zhejiang Province, China (NO. 2016KYB241, NO. 2018KY640, NO. 2019KY543).

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