Different Kinds of Methods and Materials for Determination of Bisphenol A in Urine and In Water

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Abstract. Bisphenol A (BPA; 4,4’-(propane-2,2-diyl) diphenol) is a very important chemical raw material, but which is damaged to human beings and animals. Then, enrichment and detection of BPA in urine and water is particularly important. This paper summarized and compared the difference kinds of methods and materials for determination of Bisphenol A in human urine and water.

1. Introduction

BPA is mainly used in the production of epoxy resin, polycarbonate acid vinegar [1]. More than 27 million tons of plastics containing BPA are produced worldwide every year. BPA also is an endocrine disruptor, which is released into the environment in large quantities and will cause great harm to human body and the environment.

BPA interferes with normal functions of the body through a variety of metabolic pathways, especially the function of the reproductive system. In addition, BPA may also have genetic toxicity and change the normal cell proliferation, which may cause symptoms such as obesity, diabetes, heart disease, liver toxicity and neurotoxicity. Then, the enrichment and detection of BPA in human urine is particularly important.

A series of analytical methods have been developed for determination of BPA in urine, such as, HPLC [2], GC–MS [3], HPLC–MS/MS [4], or UV spectroscopy. The spectrophotometry and fluorescence spectrophotometry instruments have low cost, simple operation and relatively low sensitivity. GC–MS and HPLC–MS are expensive, which greatly improve the qualitative ability of BPA and the detection sensitivity. Solid phase extraction saves the pretreatment time of samples and simplifies the operation procedures. Because of this, researchers have developed lots of materials as adsorbent in solid phase extraction.

This paper summarized various kinds of methods and materials for determination of Bisphenol A in Urine and water, and described the advantages and compared difference between different kinds of methods and materials.

2. Different methods for determination of BPA in human urine

Researchers have developed lots of methods for determination of BPA in urine, such as HPLC–MS, GC–MS, HPLC, or HPLC–FLD spectroscopy. Table 1 showed different methods for determination of
BPA in human and showed that HPLC is the most widely used method in detecting BPA in water and urine.

### Table. 1 Different methods for determination of BPA in human urine

| Analyte  | Method                  | LOD (ng/mL) | References |
|----------|-------------------------|-------------|------------|
| BPA      | HPLC                    | 1.0         | [2]        |
|          | UPLC-MS/MS              | 0.10        | [5]        |
|          | HPLC-MS/MS              | 0.32        | [6]        |
|          | GC-MS                   | 0.13        | [3]        |
|          | MD-GC/MS                | 0.03        | [7]        |
|          | Aptamer/Graphene Oxide FRET Biosensor | 0.05 | [8] |
|          | SPE-GC–MS               | 0.0002–0.0018 | [9] |
|          | HPLC-MS/MS              | 0.00073     | [10]       |
|          | ID-GC–MS                | 0.03        | [11]       |
|          | HPLC-DAD                | 2.60        | [12]       |
|          | HPLC-FLD                | 0.1         | [13]       |

3. Different materials for determination of BPA in urine

According to reports, little materials were invented to apply to extract BPA from urine. Because of this, some researchers have developed some materials which are easy preparation, low-cost, easy operation and easy to store. Table 2 showed that little materials was applied to detect BPA in urine.

### Table. 2 Different materials for determination of Bisphenol A in Urine

| Analyte | Materials             | Method               | LOD or LOQ (ng/mL) | References |
|---------|-----------------------|----------------------|--------------------|------------|
| BPA     | Porous Organogel Materials | HPLC-MS/MS         | <1.0               | [14]       |
|         | MIPs                  | GC-MS               | 50                 | [15]       |

4. Different methods for determination of BPA in water

From then on, researchers have invented lots of methods for removal and determination of BPA in water, such as HPLC–MS, GC–MS, HPLC, or HPLC-FLD spectroscopy. Razieh Sohrabi [16] used HPLC to detect BPA in water. The limits of detection and enrichment factor could be reach 0.02 ng/mL and 333, respectively. Feng Tan [17] invented an electrochemical sensor for detecting BPA in water, and the method is very simple. The limits of detection and enrichment factor could be reach 0.04 ng/mL. The result of table 3 showed that HPLC was the most widely used in detecting BPA in water and the limits of detection can reach from 0.003 ng/mL to 0.34 ng/mL.

### Table. 3 Different methods for determination of BPA in water

| Analyte | Method                      | LOD (ng/mL) | References |
|---------|-----------------------------|-------------|------------|
| BPA     | HPLC                        | 0.02        | [16]       |
|         | SPE-HPLC-UV                 | 0.3         | [18]       |
|         | HPLC-DAD                    | 0.07        | [19]       |
|         | MI-MSPE- HPLC-DAD           | 0.003       | [20]       |
|         | An Electrochemical Sensor   | 0.04        | [17]       |
|         | Fe@MgAl-LDH  -HPLC          | 0.24–0.34   | [21]       |
|         | AuNPs-Colorimetric Aptasensor | 0.11   | [22]       |
|         | MMSPD- DLLME- HPLC–FLU     | 0.003       | [23]       |
|         | SPE-HPLC                    | 0.07        | [24]       |
|         | MEPS-HPLC-UV                | 0.0416      | [25]       |
5. Different materials for determination of BPA in water

Researchers are more interested in AC, graphene and graphene-based composites since they found AC, graphene and graphene-based composites with special properties and multiples of capability of adsorption. In recent years, researchers try their best to invent various kinds of graphene-based composites and AC for detecting BPA in water, such as ILGNPE [26], MWCNT/GONRs [27], MIP-coated CDs nanocomposite [28] and MWCNTs [29] etc. Most of them are with large surface area, unique mechanical and physical properties. Xiaodong Xin [27] invented an electrochemical BPA sensor showed shows low detection limit (0.001 ng/mL), good reproducibility, selectivity, and acceptable stability. AMaria Stella Cosioa [30], Lingling Wang [31] and Leena Omer [29] applied MWCNTs to detect BPA in water. The limits of detection were 0.81 ng/mL, 0.10 ng/mL ~0.30 ng/mL and 0.81 ng/mL. The limits detection of combining MWCNTs with HPLC is lower.

However, separating this kind of adsorbents from aqueous solution is difficult. Therefore, synthesizing new materials with magnetism, such as magG@PDA@Zr-MOF [32], 3DG/ZnFe2O4[33] and Fe@Fe2O3/GO [34], is easy for them to separate adsorbents from aqueous solution. Meanwhile, all studies discussed the pH of solution affected the extraction.

Table. 4 Graphene-based composites and AC for determination of BPA in water

| Analyte | Materials                          | Method                          | LOD (ng/mL) | References |
|---------|------------------------------------|---------------------------------|-------------|------------|
| BPA     | MWCNT/GONRs                        | Electrochemical bisphenol A sensor | 0.001       | [27]       |
|         | ILGNPE                             | Electrochemical bisphenol A sensor | 55.0        | [26]       |
|         | magG@PDA@Zr-MOF                    | HPLC                            | 0.1~1.0     | [32]       |
|         | 3DG/ZnFe2O4                        | HPLC                            | 0.05~0.18   | [33]       |
|         | MIP-coated CDs nanocomposite       | A new fluorescent approach      | 30          | [28]       |
|         | Fe@Fe2O3/GO                        | HPLC                            | 0.08~0.10   | [34]       |
|         | MWCNTs                             | A novel amperometric sensor     | 0.81        | [30]       |
|         | GA                                 | HPLC                            | 0.01~0.11   | [35]       |
|         | MWCNTs                             | HPLC                            | 0.10~0.30   | [36]       |
|         | MWCNTs                             | HPLC                            | 0.30        | [29]       |
|         | 3D-PSGR                            | HPLC                            | 0.39~3.97   | [31]       |
|         | GNP-AuNPs                          | HPLC                            | 0.027       | [37]       |

6. Other materials for determination of BPA in water

Before researchers invented graphene-based and AC composites, many materials had been applied to detect BPA in water due to their easy preparation, low-cost, the ease of operation and easy to store. Compared with graphene-based composites and AC, those materials have fewer mechanical properties and less specific surface area. Because of low-cost and easy preparation, those materials are still widely used. With the technology developing, researchers developed lots of nanometer materials, such as DFMNPs [38], PDA@Fe3O4 [39], Fe3O4/SiO2/TiO2 NPs [1] and so on. New materials also show preferable extraction capacity. Meanwhile, those materials can be used to others fields. Table 5 showed other materials for determination of BPA in water.
### Table 5 Other materials for determination of BPA in water

| Analyte       | Materials      | Method | LOD (ng/mL) | References |
|---------------|----------------|--------|-------------|------------|
| BPA           | DFMNPs         | HPLC   | 20.0        | [38]       |
|               | PDA@Fe3O4      | HPLC   | 0.16–1.2    | [39]       |
|               | Fe3O4/SiO2/TiO2 NPs | HPLC | 0.5         | [1]        |
|               | Fe3O4@SiO2     | HPLC   | 0.09        | [40]       |
|               | Magnetic-MMT   | HPLC   | 0.15        | [41]       |
|               | PANI@SiO2@Fe   | HPLC   | 0.009–0.04  | [42]       |
|               | P-CDP          | HPLC   | 0.3         | [43]       |
|               | MI-MNP         | HPLC   | 0.3         | [44]       |
|               | XOD/GCE        | Biosensor | 1.0        | [45]       |
|               | Octadecylsilane/Nylon-6 | HPLC | 0.05        | [46]       |
|               | ON-MNPs        | HPLC   | 0.1         | [47]       |

### 7. Conclusion

Many methods have been applied to detect BPA in water and urine, such as HPLC–MS, GC–MS, or HPLC-FLD spectroscopy. Moreover, HPLC is the most widely used method in detecting BPA in water and urine. At the same time, many materials have been applied to determination of BPA in water, such as activated carbon, Graphene-based composites and so on. Compared with other materials, activated carbon and Graphene-based composites have large specific surface area, high selectivity, low-cost, and good stability. However, little materials have been applied to determination of BPA in urine. Because of this, researchers can try to apply graphene-based composites and Activated carbon to detecting BPA in urine.

### Acknowledgments

This work was financially supported by the Medical Health Foundation for Key Talents in Zhejiang Province, 322 China (2019KY543), National Natural Science Foundation of China (No. 21775138,32121607135) and Jinhua Science and Technology Bureau (No.3202018-4-006).

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