Detection techniques for monitoring dioxin-like compounds: latest techniques and the comparison

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Abstract. In order to clarify the necessity and urgency of dioxin detection, the characteristics and emission sources were firstly studied in this paper. The current dioxin detection techniques were then summarized, including chemical detection technique represented by HRGC/MS, biological detection technique covering immunology and biotechnology, and laser mass spectrometry technique using fusion ionization technology and time-of-flight mass spectrometry. Then the advantages and disadvantages, representative technologies, development directions and application prospects of various detection methods were analyzed. Eventually, the future development direction of dioxin detection technology was prospected.

1. Introduction
Dioxin-like compounds (DLCs) are a series of compounds with similar structures and common action mechanisms, which can persistently exist in the environment and organisms. DLCs mainly includes polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and other related substances [1]. Specially, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is considered as the most toxic dioxin monomer among currently known compounds. It is designated as a first-class carcinogen by the International Cancer Research Center of the World Health Organization. In term of DLCs’ sources, it has been pointed out that PCDDs and PCDFs mainly come from incineration and organic synthesis procedures, while PCBs from coolants or dielectrics in capacitors, motors and transformers [2]. However, PCDDs and PCDFs are not the targeted products of various industrial processes. Both of them can not only persistently exist in the environment, but also have stable properties and strong lipophilic. They act on aromatic hydrocarbon receptors in the organism [3], causing carcinogenesis, teratogenicity, interfering with the endocrine system, and harming human growth and reproduction. [4] Therefore, timely and accurate detection of DLCs is of great significance to the prevention of environmental pollution and the protection of human health.

1.1. Properties of DLCs
Physically, DLCs is a solid state under standard conditions, with melting point of 303°C~305°C, and decomposition temperature >700°C, while it is chemically stable, extremely difficult to dissolve in
water, but soluble in organic solvents, and extremely soluble in fat. Therefore, when it enters the human body, it is difficult to be excreted, which can be enriched in animal and human fat and milk through the food chain. In addition, it is easily adsorbed by the soil. The half-life of 2, 3, 7, 8-TCDD in deep soils is as long as 10-20a [5]; and it is semi-volatile which can spread over long distances, resulting in "global distillation effect" or "grasshopper jumping effect" [6].

In order to carry out a unified toxicity evaluation for DLCs, the toxic equivalent factor method (TEF) is often used presently to characterize the overall pollution degree of DLCs by calculating the total toxic equivalent quantity (TEQ). Specifically, 2, 3, 7, 8-TCDD is used as an index chemical, and the corresponding toxicity equivalent factor (TEF) value is defined as 1. Each monomer of other DLCs is then compared with 2, 3, 7, 8-TCDD and the TEF can be gained which is less than 1. And then, the concentration of each monomer in dioxin is multiplied by the respective TEF equals the DLCs’ TEQ [7]. It is recommended that the limit of DLCs is 1pico-4pico per kilogram of body weight (1pico=10^-12g) by the International Health Organization [8].

1.2. Emission sources of DLCs

DLCs are not inherent in nature, but man-made. The main source of DLCs is the incomplete combustion process in nature or industrial production. It has been shown that any combustion process can produce more or less DLCs [9]; The other source of DLCs is the production and use process of chlorine-containing chemicals, such as the production of pesticides, PCB production, and papermaking processes, which is shown in table 1 in detail.

| Category   | Production process | Main sources | Description                                                                 |
|------------|--------------------|--------------|-----------------------------------------------------------------------------|
| I          | incomplete         | waste incineration | Chlorine-containing organic compounds in domestic waste [10], medical waste [11], and hazardous waste [12], such as vinyl chloride, chlorinated benzene, etc., can synthesize DLCs with O2, HCl, etc, under the catalytic effect of FeCl3, CuCl2 at a suitable temperature. |
|            | combustion         | metal smelting steel smelting | In the iron and steel smelting industry, dioxin is mainly produced in iron ore sintering and electric furnace steelmaking [13]. The DLCs mainly comes from sintered fly ash during the sintering process [14]. Organic compounds and chlorides commonly exist in scrap steel. When they are used in electric furnace steelmaking, certain amounts of DLCs. Will appear in the flue gas [15]. |
non-ferrous metal smelting

There are currently few studies on the emission of DLCs in the smelting of primary non-ferrous metals. The smelting process of recycled non-ferrous metal are more concentrated such as secondary copper [16, 17], secondary aluminum [16, 18], secondary zinc [19], secondary lead [20, 21], etc. It has been proven that when the feed contains waste engine oil, PVC, etc., dioxins are more likely to be produced during the smelting process [22].

The factors that promote the formation of DLCs are not obvious in coal combustion because of the low chlorine content and relatively steady combustion. Therefore, the generation of dioxin during coal combustion is relatively small [23]. At present, there are relatively few domestic studies on DLCs emissions from coal-fired power plants [24].

coal-fired heating and power supply

The production process of 1,4 dichlorobenzene [25,], tetrachloroquinone [26], chlor-alkali [27] and other chlorinated compounds.

production chemical production

The bleaching process using chlorine-containing bleach is the main source of dioxins [28]. The production pathways mainly include the direct chlorination, conversion from precursors, rechlorination of the analogs, and direct condensation of exogenous chlorophenols [29].

II Production and use of chlorine-containing chemicals

usage papermaking process

According to the toxic hazards and wide range of emission sources, it is imperative to timely monitor DLCs ‘concentration in the surrounding environment of the emission source and essential to develop accurate and easy-to-operate detection technique.

2. Detection techniques for monitoring DLCs

The concentration of DLCs is extremely low in the environment, and the detection operation belongs to ultra-trace, multi-component analysis. Based on a large number of literature reports, the detection techniques of DLCs can be summarized into three aspects: 1) chemical detection technology represented by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS); 2) biological detection technology based on the mechanism of dioxin toxicity; 3) laser mass spectrometry

III Others

cigarettes, automobile exhaust, volcanic eruptions, forest fires, cremation of remains, biochemical effects of microorganisms, etc.
detection technology that relies on resonance multi-photon ionization-time-of-flight mass spectrometry (REMPI/TOFMS) and vacuum ultraviolet time-of-flight mass spectrometry (VUV/TOFMS). The classification diagram is shown in Figure 1.

![Detection techniques for monitoring DLCs](image)

**Figure 1.** Scheme of techniques for monitoring dioxin-like compounds.

In the following, the detection principles, procedures, advantages and disadvantages, and development directions of each detection technique will be analyzed in detail.

### 2.1. HRGC/HRMS

Chromatography-mass spectrometry is a recognized standard method for detection of DLCs, especially High-resolution Gas Chromatography/High-resolution Mass Spectrometry (HRGC/HRMS), which is regarded as the "gold standard" for DLCs super-trace detection. U.S. 'standards of EPA1613, EPA0023A, EPA8290A, Japanese industrial standards of JISK0311, 0312, EU EN1948, and China's HJ77 standard are all formulated according to HRGC/HRMS. The detection process of HRGC/HRMS is more complicated that mainly includes the sampling, extraction, purification and concentration, isotope dilution, data processing, etc.

The advantages of HRGC/HRMS are extremely low detection limit, high sensitivity, strong selectivity, and accurate qualitative and quantitative determination of dioxin monomer, while it has disadvantages that the sample pre-processing steps are cumbersome, the processing cycle is long, the cost is high, and the technical requirements for the analysts are very high.

In order to further improve this technique, many experts and scholars have made new attempts to replace the traditional soxhlet extraction method, such as ultrasonic extraction [30], supercritical fluid extraction [31], accelerated solvent extraction [32, 33], microwave extraction [34]. They not only save the extraction time, but also reduce organic solvents dosage. Among them, accelerated solvent extraction is considered to be a fast, efficient, organic solvent-saving, and better extraction effect method [32, 35, 36].

Purification is an essential step in HRGC/HRMS, which is also a time-consuming procedure. It is mainly divided into manual purification technology and automatic purification technology. Manual purification technology mainly uses multi-stage chromatography columns filled with different adsorbents. The procedures are cumbersome and time-consuming which takes about 2 days for one sample. The automatic purification technology was introduced by Smith et al. in the 1980s [37], which can automate the entire process from extraction to purification. However, due to the switching between different valve bodies, it is easy to cause leakage and blockage [38], which limite the wide application.

In addition, using a triple quadrupole mass spectrometer to replace the high-resolution mass
spectrometer can significantly reduce the cost of analysis and detection on the basis of ensuring the accuracy of detection results.

Therefore, simplifying the processing steps, shortening the processing cycle, and reducing the detection cost are the development trends of improving the HRGC/HRMS in the future. More attempts are needed in precise extraction, automated purification, and cost reduction.

2.2. Biological detection technology

The toxic mechanism of DLCs is not to form adducts with proteins and nucleic acids, nor to directly damage DNA, but to change the enzyme activity through Aryl Hydrocarbon (AhR) and thereby change the proteins' function. [39]

With people’s more understanding of the mechanism of DLCs action and the biological effects they produce after entering the organism, it has been found that the toxicity equivalent of DLCs can be expressed indirectly by the biological toxicity in the body.

Therefore, some biological detection methods can be used in the detection of DLCs, which are summarized as immunological methods and biological methods according to different detection principles. The representative method in each category is shown in Figure 2.

![Figure 2. Scheme of biological techniques for monitoring DLCs.](image)

2.2.1. Immunization. The basic principle of immune response is that when antigen bacteria or other heterogeneous proteins (antigens) invade the body, the body can produce substances and antibodies that recognize the foreign body and excrete it. Thereby, according to this principle, when the dioxin enters the human body, DLCs can be screened out through the specific recognition of the antibody. In 1978, Philip et al. [40, 41] first used the double antibody radioimmunoassay method to detect the concentration of DLCs in environmental samples and biological samples. Secondary antibodies labeled with radioactive iodine are combined competitively with the primary antibody of DLCs. The concentration of DLCs is quantitatively detected by detecting the decrease of radioactivity in the sediment.

Among the immunoassay methods, the time-resolved fluorescence immunoassay method’s Dissociation-enhanced lanthanide fluorescence immunoassay analysis (DELFIA) is relatively advanced. The basic principle is to let the antigen-bonded europium ions selected by biological gene technology compete with the DLCs for monoclonal antibodies. After the reaction is completed, fluorescence enhancer is added.

The europium ions then dissociate from the antigen, and enter the enhancer, form micelles, and emit fluorescence efficiently. Finally, it is analyzed with time-resolved fluorescence method.
fluorescence intensity is inversely proportional to the TEQ value of DLCs, thus obtaining the TEQ value of DLC in samples.

The general immune method does not require the activation process in the cell, which greatly improves the detection efficiency. It has advantages such as simple operation, rapid detection, good selectivity, and high sensitivity. Thereby, it has been widely used in the field of dioxin detection [42, 43]. However, it also has some disadvantages such as difficulty in antibody preparation and narrow detection range.

In recent years, some affinity biosensors have been used to detect trace environmental pollutants. They do not require secondary labeled antibodies, thereby more convenient than general immunoassays. [44] The principle is mainly to use the mass change caused by the binding process of antigen and antibody to detect DLCs ’s equivalent. At present, quartz crystal microbalance biosensor (QCM) [45] and surface plasma resonance biosensor (SPR) [46] have been used to develop rapid detection systems for monitoring DLCs.

2.2.2 Biology. The biological method is mainly based on the toxic mechanism of DLCs. DLCs bind to the aromatic receptors in the cell, and then the conjugates transfer to the nucleus, and finally the toxicity is expressed through proteins.

The earliest biological detection for DLCs was introduced in the 1970s which mainly detect the increase in the activity of PAHs induced by dioxins using fluorescence quantification. Currently, the most widely used in the field of DLCs detection is the luciferase reporter gene method (CALUX) [47-49].

The principle is to recombine the cytochrome P450 gene and luciferase with genetic engineering. When DLCs enters the cell, it firstly combine with AhR to form a conjugate, which then transfers to the nucleus, and then forms a dimer with high binding force to DNA in the nucleus. This dimer binds to the DLCs response element, activates cytochrome P450, and synthesizes fluorescein with the fluorescence synthase gene. Finally the total amount of DLCs can be measured indirectly by the amount of synthesized fluorescein and fluorescence intensity. [48, 49] This is an efficient, fast, easy-to-operate, and inexpensive biological analysis method, but only the total dioxin toxicity equivalent in the sample can be obtained, and the test results are poor in repeatability.

Therefore, some physical technologies, such as nano gold bio-barcode technology has been applied to rapidly detect DLCs recently, which has better sensitivity and repeatability [50].

However, neither immunoassay nor biological method can detect the specific composition of DLCs and determine the toxicity equivalent of a single dioxin isomer. They can only be used for On-site studies that require quick results, and low-cost semi-quantitative detections such as rapid screening of a large number of samples. Therefore, biological detection technique belongs to rapid test method compared to HRGC/HRMS detection method.

2.3. Laser mass spectrometry technology

Laser mass spectrometry technology is a two-dimensional detection technology; generally referring to the combination of resonance enhanced multiple photoelectron ionization (REMPI) and time-of-flight mass spectrometry (TOFMS). The significant advantages of this EMPI/TOFMS include high selectivity, simultaneous measurement of multiple components, high sensitivity, and resolution. Therefore, it is very suitable for real-time dynamic monitoring of trace pollutant gases [51].

The main principle is to combine the resonant multi-photon ionization process with time-of-flight mass spectrometry by two-dimensional analysis technology, Ionize certain molecules with the right laser wavelength, and proceed with mass selection using a time-of-flight mass spectrometer.

After being separated according to different mass-to-charge ratios, the detector will receive the signal and, the mass spectrum and detection results can then be finally obtained. [52] The schematic diagram is shown in Figure 3. [53]. This type of technology is recently the most likely technique to realize DLCs online monitoring [54].
Laser mass spectrometry technology was firstly used by Weickhardt et al. in 1993 to detect dibenzodioxin, dibenzofuran, and 2,3- and 2,8-dichlorodiphenyl dioxins. [55] The results showed each of the four substances has the own unique spectral structure, as shown in Figure 4 and Figure 5.

In 1996, Zimmermann further detected the DLCs in waste incineration flue gas with REMPI/TOFMS. However, it was pointed out that the spectra of some dioxins monomer molecules are less different because of similar structure. Thus, it can only realize accurate detection for some DLCs [56].

In addition to REMPI, vacuum ultraviolet (VUV) ionization is also a common molecular excitation method. It belongs to "soft ionization", which does not produce or rarely produces fragment peaks with advantages of simple spectra, and high sensitivity [57]. The combination with mass spectrometry technology has also been initially used in the online monitoring of volatile organic compounds [57] and DLCs indicators.

In order to realize the real-time online monitoring of DLCs, the focus of future research is to find DLCs indicators and to realize the indirect measurement of DLCs in real time by establishing the correlation model; and the other is to improve and optimize laser mass spectrometry detection systems. For example, the gas chromatography device is added into the REMPI/TOFMS system to achieve more accurate monitoring of all DLCs.

3. Comparative analysis of three types of detection technologies
A comparative analysis of the above-mentioned DLCs detection technologies is concluded in table 2.

![Diagram of laser mass spectrometry.](image)

**Figure 3.** Diagram of laser mass spectrometry.

![MPI-UV spectra of dibenzofuran (upper trace) and dibenzodioxion (lower trace) in a supersonic molecular beam.](image)

**Figure 4.** MPI-UV spectra of dibenzofuran (upper trace) and dibenzodioxion (lower trace) in a supersonic molecular beam.

![MPI-UV spectra of 2,3-dichlorodibenzodioxin (upper trace) and 2,8-dichlorodibenzodioxin (lower trace) in a supersonic molecular beam.](image)

**Figure 5.** MPI-UV spectra of 2,3-dichlorodibenzodioxin (upper trace) and 2,8-dichlorodibenzodioxin (lower trace) in a supersonic molecular beam.
Table 2. Comparison of three types of detection technologies.

| Detection Techniques for Monitoring DLCs | Representative technique | Advantage | Disadvantage | Improvement direction | Application prospect |
|-----------------------------------------|--------------------------|-----------|--------------|----------------------|---------------------|
| Chemical detection                       | HRGC/HRMS                | 1 accurate test results; 2 identify and detect different dioxin monomers | 1 time consuming; 2 high cost; 3 high requirements for operators | 1 simplify detection procedures; 2 reduce detection cost | where precise and quantitative detection is required |
| Biology detection                        | Immunization             | 1 less time-consuming detection; 2 low detection cost; 3 easy to operate | 1 impossible to detect DLC’s composition and the monomer toxicity equivalent; 2 poor reproducibility of detection results | 1 complementary combination with chemical detection method (HRGC/HRMS); 2 improve the reliability of detection results | rapid screening of large numbers of samples |
| Laser mass spectrometry detection        | REMPI/TOFMS              | 1 high selectivity and sensitivity; 2 identify and detect different dioxin monomers; 3 multi-component measurement simultaneously | 1 Need to know the sample spectral structure in advance; 2 only a few dioxin monomers can be identified and detected | 1 improve the detection device; 2 research DLCs indicators | online real-time monitoring of DLCs |

1) Accuracy. The priority of the three types of detection technology is HRGC/HRMS, laser mass spectrometry technology and biological detection technology. Chemical detection technology is the most accurate method among the three types, and it is also the most authoritative detection method for DLCs. It can not only effectively identify all the isomers of DLCs in the sample, but also accurately measure the toxicity of different monomers. The laser mass spectrometry technology is second in accuracy. It can detect multiple components at the same time, but the current detection system can only effectively identify and detect several dioxin monomers. The accuracy of biological detection technology is the worst, which can not only identify those dioxin substances in the sample, but also not determine the total toxicity equivalent of DLCs in the test sample. Moreover, it is easily affected by...
other aromatic hydrocarbon receptors, and the reproducibility of the test results is relatively poor.

2) Difficulty of operation. The order of difficulty in operation is HRGC/HRMS, the biological detection technology and laser mass spectrometry technology. The HRGC/HRMS detection operation is the most cumbersome. The sampling, extraction, and purification steps in the pre-processing program are relatively complex. Because of the low degree of automation, the detection cycle is usually about 2 weeks while the cycle can be shortened to about 1–3 days with biological detection technology. However, the sample pretreatment process still occupies most of the entire detection process, which restricts the high-throughput development of bioassays [3]. The sample pretreatment process of laser mass spectrometry detection technology is relatively simple and can quickly enter the detection stage. In addition, the mixing of impurities will not cause much impact. It is the fastest of the three types of detection methods, and the measurement cycle is only about 1h.

3) Industrial applications. As mentioned in section 1.2, any industrial production and life process involving combustion may produce DLCs. Although DLCs’ the concentration is very low during pollutants, they are extremely toxic, about 1,000 times more than potassium cyanide. Moreover, in the actual discharge process, the concentration continuously changes over time. The current detection methods including HRGC/HRMS and biological detection method are basically offline monitoring technologies which need to be sent to the laboratory for subsequent testing after on-site sampling. The monitoring frequency is 1-2 times/year, which is far from achieving the goal of effectively monitoring DLCs’ emissions.

According to the above analysis, laser mass spectrometry is the most likely method to realize online real-time monitoring of DLCs on site. However, limited by the current technical level, it has not been widely used. Therefore, in order to realize real-time or irregular emission of DLCs in industrial flue gas emission, the important development direction is to find effective DLCs ‘indicators and to improve the detection system to identify more dioxin monomer maps.

4. Conclusion
DLCs have a wide range of emission sources. Any processes involving combustion and chlorine-containing chemicals may produce DLCs. Although the content of DLCs in the environment is relatively low, they have attracted much more and more attention recently because of extremely strong toxicity and obvious teratogenicity and carcinogenic effects. The detection of DLCs belongs to ultra-trace, multi-component detection, so there is no an ideal detection method currently. Chemical detection, biological detection, and laser mass spectrometry detection each have their limitations. The future development direction of DLCs detection technology should focus on the research and development of fast, accurate, and low-cost detection technique; and on the other hand, realizing an online real-time monitoring system for DLCs through optimizing the laser mass spectrometry detection device, which will be helpful for timely reflecting the daily emission of DLCs in the main industrial emission sources and guiding the pollution reduction work.

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