

Current progress on the detection of glyphosate in environmental samples

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Abstract: Glyphosate is widely used in herbicides and is toxic to organism. Therefore accurate detection of glyphosate content is important for public health and food security. In this paper, methods such as gas chromatography (GC), high performance liquid chromatography (HPLC), gas chromatography-mass spectrometry (GC/MS), liquid chromatography-mass spectrometry (LC/MS), ion chromatography (IC), capillary electrophoresis (CE), enzyme-linked immunosorbent assay (ELISA) and other kinds of analytical methods used for determination of glyphosate were reviewed. The characters of these methods were described to provide consultation for further research.

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Introduction

Glyphosate is a non-selective and internal adsorption herbicide. It is widely applied in agriculture industry due to less toxicity to the mammal animals compared with other herbicide. According to the statics reported in 2014, both the sales and production of glyphosate were highest among all commercial herbicides [1]. However, it is crucial to detect the glyphosate residue in biological, natural water resources, and soils due to the following facts. First, it is directly toxic to the amphibian in end uses. Secondly, glyphosate migrates fast in soils due to the good solubility in water [2].

It is a challenge to detect glyphosate residue due to its poor solubility in common organic solvents, difficult evaporation, high polarity, and absences of chromophores and fluorophores [3]. In the most recent years, scholars explored many approaches to detect glyphosate residues including Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC), Gas Chromatography-Mass Spectrometry (GC/MS), Liquid Chromatography-Mass Spectrometry (LC/MS), Ion Chromatography (IC), and Capillary Electrophoresis (CE). Here are the simple introductions of those methods:

1. GC

Glyphosate is of high polarity and high boiling temperature due to hydrogen group and amino group in the molecule structure, which makes it impossible to detect residues by using GC directly. Therefore, the structure of glyphosate needs to be derivatized by disabling polar groups. The evaporation properties have been improved by most researchers through esterification and acylation [4]. As described in Table 1, the recycle ratios of glyphosate in different samples modified by different reagents are close to or higher than 90%.

In GC, the columns and the detectors are selected according to the properties of each sample, as summarized in Table 2. Generally, the column are selected from mid-polar to non-polar range for the GC testing of derivatized glyphosate. Electron Capture Detector (ECD), Nitrogen Phosphorous Detector (NPD), Flame Photometric Detector (FPD) and Flame Ionization Detector (FID) are commonly used for the detection of glyphosate due to the existence of C, H and P. The lowest limit of detection (LLOD) for glyphosate in soil sample and water sample are 12 µg/kg and 0.5 ng/L, respectively. However, GC is not commonly used in practice due to the complicated derivatization procedure of the detection of glyphosate.

Table 1. Determination of glyphosate in different samples and derivatization reagent using GC

No.	Refer.	Sample	Derivatization reagent	Recovery
1	Tsunoda [5]	water	N-methyl-N-tert.-butyldimethylsilyltrifluoroacetamide and dimethylformamide	> 90%
2	Lou [6]	water	trifluoroacetic anhydride and 4,4,4-trifluoro-1-butanol	> 97%
3	Hiroyuki [7]	soil	isopropyl chloroformate and diazomethane	> 91%
4	Zbigniew [8]	water	trifluoroacetic acid- trifluoroacetic anhydride and trimethyl orthoformate	> 95%
5	Pei [9]	water	propionic anhydride and methanol	–
6	Hu [10]	soil	trifluoroacetic anhydride and 4,4,4-trifluoro-1-butanol	> 84%

Table 2 Determination of glyphosate in different samples and chromatographic conditions using GC after derivatization

No.	Reference	Sample	Column	Detector	LOD
1	Tsunoda [5]	soil	DB-1	FID	–
2	Lou [6]	water	PEG-2M	ECD	1 µg/L
3	Hiroyuki [7]	soil	DB-17 and OV-1	FPD	–
4	Zbigniew [8]	water	DB-17	FID	–
5	Pei [9]	water	DB-5	NPD	0.5 ng/L
6	Hu [10]	soil	Supelcoequity-5	NPD	0.02 mg/kg

Note: LOD stands for the limit of detection

2. HPLC

Unlike GC, HPLC is a common method for detecting the glyphosate residue. However, derivatization procedure including pre-column derivatization and post-column derivatization need to be conducted due to the absence of fluorophore and chromophore, as mentioned earlier [2]. The detection methods of glyphosate derivatized before columns in HPLC are summarized in Table 3 according to different samples, columns, mobile phases, and derivatization reagents.

The UV detector and fluorescence detector (FLD) can be used in the HPLC detection of glyphosate. The derivatization reagents for UV detector [14-15, 17-18] include p-toluenesulphonyl chloride, o-nitrobenzenesulfonyl chloride and 2,5-dimethylbenzenesulfonylchloride. However, 9-fluorenylmethylchloroformate (FMOC) and o-phthalaldehyde are used on FLD detections [11-13, 16, 19-21]. As stated in Table 3, the LLOD for glyphosate samples from soil and water are 0.02 mg/kg and 0.02 µg/L, respectively.

Similar to Table 3, the detection methods of glyphosate using post-column derivatization in HPLC are summarized in Table 4.

As described in Table 4, the FLD detector is used in post-column derivatization for the detection of glyphosate. Two types of reagent are often used. One is a common oxidation reagent named sodium hypochlorite, the other is a mixture of o-phthalaldehyde and mercaptoethanol. The LLOD of aqueous sample is 2 µg/L, as listed in Table 4. Compared with pre-column derivatization, the post-column derivatization is more precise due to the difficulty in controlling derivatization reaction in the reflux system of HPLC for post column.

HPLC can provide fast, precise, repeatable data in glyphosate residue detection. However, as we summarized in Table 3 and Table 4, the pre-column derivatization and post-column derivatization are complicated in practical applications for most end users.

3. Chromatography-mass spectrometry

Chromatography-mass spectrometry is a most recent technique with the capabilities of separation and detection. Glyphosate is an ionic compound with high polar, high solubility and hard gasification, which limits the applications of common GC through standard derivatization. Therefore, GC/MS are rarely reported in the detection of glyphosate residue.

Table 3 Determination of glyphosate in different samples and chromatographic conditions using HPLC after pre-column derivatization

No.	Refer.	Sample	Column	Mobile phase	LOD ($\mu\text{g/L}$)	Derivatization reagent
1	Zhou [11]	water	Anion exchange column (SCX, 250 mm \times 4.6 mm)	0.1M KH_2PO_4 buffer (PH10) : acetonitrile = 65 : 35 (v/v)	5	9-fluorenylmethylchloroformate (FMOC)
2	Liu [12]	water	Atlantis C_{18} column (250 mm \times 4.6 mm, 5 μm)	0.2M H_3PO_4 solution : acetonitrile = 80 : 20 (v/v)	0.05	FMOC
3	Ma [13]	water	X Bridge RP_{18} column	methanol : water = 70 : 30 (v/v)	2	FMOC
4	Si [14]	soil	C_{18} Hypersil ODS column (250 mm \times 4.6 mm, 5 μm)	0.05M phosphate buffer (PH5.5) : methanol = 65 : 35 (v/v)	0.02 (mg/kg)	<i>p</i> -toluenesulphonyl chloride
5	Fang [15]	water	Lichrospher C_{18} column (250 mm \times 4.6 mm, 5 μm)	0.05M phosphate buffer (PH5.5) : methanol = 80 : 20 (v/v)	6.25×10^3	<i>o</i> -nitrobenzenesulfonyl chloride
6	Li [16]	water	DIKMA C_{18} column (250 mm \times 4.6 mm, 5 μm)	0.05M KH_2PO_4 buffer (PH6.0): methanol = 55 : 45 (v/v)	7.5	<i>o</i> -phthalaldehyde
7	Fang [17]	water	Kromasil C_{18} column (250 mm \times 4.6 mm, 5 μm)	0.02M phosphate buffer (PH5.5): acetonitrile : methanol = 80 : 5 : 15 (v/v/v)	67	2,5-dimethylbenzenesulfonylchloride
8	Kawai [18]	water	C_{18} -5 column	0.2M phosphate buffer (PH2.3) : acetonitrile = 85 : 15 (v/v)	10	<i>p</i> -toluenesulphonyl chloride
9	Hidalgo [19]	water	RP C_{18} and weak ion-exchange (coupled column)	0.05M phosphate buffer (PH5.5) : acetonitrile = 65 : 35 (v/v)	0.02	FMOC
10	Sancho [20]	water	RP C_{18} and weak ion-exchange (coupled column)	0.05M KH_2PO_4 buffer (PH5.8): acetonitrile = 70 : 30 (v/v)	0.1	FMOC
11	Nedelkoska [21]	water	polymeric amino column	0.05M phosphate buffer : acetonitrile = 55 : 45(v/v)	0.16	FMOC

Table 4 Determination of glyphosate in different samples and chromatographic conditions using HPLC with post-column derivatization

No.	Refer.	Sample	Column	Mobile phase	LOD ($\mu\text{g/L}$)	Derivatization reagent
1	Hou [22]	water	Waters SAX anion-exchange column (250 mm \times 4.6 mm, 5 μm)	0.4% H_3PO_4 - 0.1% KH_2PO_4 solution	5	SH+PM
2	Wang [23]	water	Potassium cation exchange column (150 mm \times 4.0 mm, 8 μm)	0.4% H_3PO_4 - 0.1% KH_2PO_4 solution	15	SH+PM
3	Wang [24]	river	Potassium cation exchange column (50 mm \times 4.0 mm i.d.)	0.4% H_3PO_4 - 0.1% KH_2PO_4 solution	50	SH+PM
4	Wang [25]	drinking water	Waters IC-Pak ion exclusion column (7.8 mm \times 150 mm)	0.05% H_3PO_4 solution	5	SH+PM
5	Su [26]	water	Potassium cation exchange column (150 mm \times 4.0 mm, 8 μm)	0.4% H_3PO_4 - 0.1% KH_2PO_4 solution	14	SH+PM
6	Chen [27]	water	Potassium cation exchange column (250 mm \times 4.0 mm, 5 μm)	phosphoric acid - methanol eluent	2.5	SH+PM
7	Waters [28]	drinking water	Waters IC-Pak ion exclusion column (7.8 mm \times 150 mm)	0.05% H_3PO_4 solution	4.0	SH+PM
8	Abdullah [29]	water	Waters SAX anion-exchange column	citrate buffer (PH5.0)	2	SH+PM

Note: SH+PM stands for sodium hypochlorite + *o*-phthalaldehyde and mercaptoethanol.

The glyphosate residue in water sample was tested using GC-IT-MS by Royer et al [30]. The derivatization reagents are trifluoroacetic anhydride (TFAA) and 2,2,3,3,4,4,4-heptafluoro-1-butanol (HFB). Elisabet et al [31] determined the LOD of GC/MS is 0.1 µg/L in water, and 0.006 µg/L in soil. Philip et al [32] found that the LOD glyphosate in soil is 0.01mg/kg using GC/MS under SIM. The derivatization reagents in their study are also TFAA and HFB. Cheng et al [33] reported the LOD in water sample is 0.3µg/L using same characterization method.

Until now, chromatography-mass spectrometry methods reported in the detection of glyphosate from environmental samples are mostly LC/MS and LC/MS/MS, which not only avoid the derivatization

procedure but also improve the sensitivity of the detection. These methods are listed in Table 5 with a detailed description of columns, mobile phase.

As showed in Table 5, the common ion source is ESI in LC/MS characterization of glyphosate sample, which can also be used to determine new chemistry structures [43-44]. Mass spectrometry mode are mainly MRM or SRM. The LLOD is 0.06 µg/L for glyphosate samples filtered by 0.02 µm filter. Derivatization is not required in the detection of glyphosate using LC/MS, which simplifies the testing procedure. However, it has not been widely used in the detection of glyphosate due to the cost of LC/MS and the interface technology problem.

Table 5 Determination of glyphosate in different samples and instrument conditions using LC/MS

No.	Refer.	Sample	Column	Mobile phase	MS scanning mode	LOD (µg/L)
1	Zheng [34]	drinking water	Hypercarb column (50 mm × 2.1 mm, 5µm)	A ultrapure water (containing 0.1 % formic acid), B methanol (gradient elution)	MRM	40
2	Zheng [35]	drinking water	Atlantis C ₁₈ column (50 mm × 2.1 mm, 5µm)	A ultrapure water (containing 0.1 % formic acid), B acetonitrile (gradient elution)	MRM	40
3	Liu [36]	drinking water	Synchromis HILIC column (100 mm × 2.1 mm, 5µm)	A ammonium acetate aqueous solution (containing 0.4 % formic acid), B acetonitrile (gradient elution)	SRM	10
4	Guo [37]	Fishpond water	XBridge HILIC column (150 mm × 2.1 mm, 5µm)	0.5 % isopropylamine aqueous solution : acetonitrile = 15:85 (v/v)	MRM	2
5	Guo [38]	drinking water	Hypersil gold aQ column (100 mm × 2.1 mm, 3µm)	A ammonium acetate aqueous solution (containing 0.4 % formic acid), B acetonitrile (gradient elution)	MRM	2
6	Zheng [39]	drinking water	CAPCELL PAK ST column (150 mm × 2.1 mm)	10mM ammonium acetate aqueous solution (PH10.1) : acetonitrile = 72:28 (v/v)	MRM	4
7	Li [40]	drinking water	Hypersil gold C ₁₈ column (150 mm × 2.1 mm, 3µm)	A methanol, B1mM ammonium acetate aqueous solution (gradient elution)	SRM	2.5
8	Kang [41]	drinking water	Atlantis C ₁₈ column (150 mm × 2.1 mm, 5µm)	acetonitrile : water (containing 0.1 % ammonia water) = 20:80 (v/v)	MRM	0.06
9	Hao [42]	Ground water	Acclaim® Mix-mode WAX-1 column (RP and weak anion)	A methanol : water = 50:50 (v/v), B 300mM ammonium acetate in A phase (gradient elution)	MRM	1

4. IC

IC is a branch of HPLC, which is a brand new separation and analysis technique based on ion exchange chromatography. Anion-exchange column and alkaline buffer can be used as the column and eluent due to glyphosate is an ionic compound. However, it is easily hydrolyzed in waters containing chloride, which affects the shape, qualitative and quantitative data of the peaks. Therefore, dechlorination is a necessary step in determining the glyphosate in drinking water by adding

ascorbic acid or sodium thiosulfate in order to improve the precision. In IC, the LLOD of detectability of glyphosate in water and in soil are 17.4 µg/L and 3.2 µg/L respectively. The summaries of the reported methods using IC in glyphosate detection are reported in Table 6.

At the same time, instead of using anion suppression conductometric detectors in IC characterization of glyphosate, You et al [65] built an IC-CNLSD detector which can be used to detect the glyphosate in water samples. Derivatization, pre-concentration and mobile

phase conductivity inhibition are not required in this method. The LOD in water sample is 53 $\mu\text{g/L}$. Guo et al [66] built an IC-ICP method in order to determine the glyphosate residue in water sample. Dionex Ion Pac AS16, 250 mm \times 4 mm, ICP and 20mM eluent were applied in this method. The reported LOD is 0.7 $\mu\text{g/L}$.

The greatest advantage of IC testing is the simple treatment for samples. However, it is only applied in water and soil analysis. Compared with GC, HPLC, and LC/MS, IC has lower sensitivity and higher LOD, which make it hard to spread in practices.

5. CE

Until now, CE has not been used commonly in the detection of glyphosate residue. As described in Table 7, the detection of glyphosate requires derivatization procedure in CE characterization in order to improve the sensitivity of detection. However, it is not required in CE/MS. The LLOD of detectability are 3.2 ng/kg and 0.005 $\mu\text{g/L}$ respectively for glyphosate residue in the soil sample and water sample.

Table 6 Determination of glyphosate in different samples and instrument conditions using IC

No.	Refer.	Sample	Anion-exchange column	Eluent	LOD ($\mu\text{g/L}$)
1	Wu[44]	drinking water	Ion PacAS23 column (250 mm \times 4 mm)	20 mM NaOH solution	5.1
2	Song[45]	drinking water	Metrosep A Supp 5-250 column	6.4 mM Na_2CO_3 and 3.2 mM NaHCO_3	14
3	Ye[46]	drinking water	Ion Pac AS19 column (250 mm \times 0.4 mm)	KOH solution (gradient elution)	2.0×10^5
4	Liu[47]	natural water	Dionex AS19 column (250 mm \times 2 mm)	30mM KOH solution	5
5	Liu, Li[48]	drinking water	Ion Pac AS11-HC column (250 mm \times 4 mm)	20mM KOH solution	1.0×10^2
6	Zhong [49]	water	Ion Pac AS19 column (250 mm \times 4 mm)	30mM KOH solution	15
7	Zhang [50]	drinking water	Ion Pac AS19 column (250 mm \times 4 mm)	30mM KOH solution	15
8	Wang [51]	drinking water	Metrosep A Supp 5 column (150 mm \times 4 mm)	8.0 mM Na_2CO_3 solution	13
9	Wang [52]	water	Ion Pac AS19 column (250 mm \times 4 mm)	30mM KOH solution	5.3
10	Li [53]	drinking water	Ion Pac AS19 column (250 mm \times 4 mm)	KOH solution (gradient elution)	15
11	Zhang [54]	soil	ALLTECH ALLSEP 7 μ column	0.9 mM Na_2CO_3 and 0.85 mM NaHCO_3	17.4
12	Su [55]	drinking water	Ion Pac AS23 column	20 mM NaOH solution	5.1
13	Fang [56]	drinking water	Ion Pac AS23 column	28 mM NaOH solution	11.9
14	Wang [57]	soil	Ion Pac AS14 column	10.0 mM Na_2CO_3 and 5.0 mM NaHCO_3	2.0×10^2
15	Li [58]	river	Ion Pac AS9-HC column	25 mM Na_2CO_3 and 2.0 mM NaOH	30
16	Qi [59]	mineral water	Ion Pac AS19 column	30mM KOH solution	3.2
17	Wu [60]	drinking water	Ion Pac AS19 column	KOH solution (gradient elution)	4.4
18	Wang [61]	drinking water	Metrosep A Supp 5-150 column	8.0 mM Na_2CO_3 solution	8.0
19	Qiu [62]	drinking water	Ion Pac AS19 column	35mM KOH solution	4.8
20	Coutinho [63]	natural water	Dionex AS18 column	33mM KOH solution	38
21	Zhu [64]	natural water	Dionex AS4 SC column	9.0 mM Na_2CO_3 and 4.0 mM NaOH	42

6. Other detection methods

Recently, emerging detection methods for glyphosate residue were applied, such as immunoassay, oscillographic polarography and diffuse reflection spectrophotometric, which have simpler procedure, less work load and higher efficiency. Clegg et al [74] used CI-ELISA to determine the glyphosate residue in water with the LOD of 76 $\mu\text{g/L}$. In order to lower the LOD and improve the sensitivity, Rubio et al [75] used ELISA and made the LOD approach 0.6 $\mu\text{g/L}$. Lee et al [76] improved the LOD to 0.1 $\mu\text{g/L}$ by adopting L-ELISA. Based on ELISA, Miguel [77] improved the LOD to 0.021 $\mu\text{g/L}$ by using a self-invented glyphosate sensor.

Sun et al [78] obtained 96 $\mu\text{g/L}$ as the LOD using single scan oscillographic polarography after the nitroso glyphosate derivatization, which is a simple and fast way to determine the glyphosate residue in soil samples. Silva et al [79] invented a small and portable equipment based on diffuse reflection spectrophotometry method, which can be used in common samples.

7. Conclusion and Future Study

Compared all the currently applied methods in glyphosate detection, Chromatography including HPLC, IC and LC-MS are widely used based on the physical and chemical properties of glyphosate. GC and GC-MS are rarely used in practice.

Among all these methods summarized in this paper, derivatization is necessary in GC, HPLC. However, it is not required in LC/MS and CE-MS characterization. At the same time, LC/MS and CE-MS can characterize time retention and MS qualitatively and quantitatively, which leads to a wide and promising market. More importantly, simplifying the sample treatment procedure, speeding up detection time and improving the sensitivity and efficiency are the directions that require continues development based on the smart materials [80-82] and a better working interface.

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