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Short communication

Determination of glyphosate by ion chromatography

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Abstract

An ion chromatography system for the determination of glyphosate was described. Ion chromatograph was carried out by suppressed conductivity detection (DX-100). The eluent contained 9 mmol l⁻¹ Na₂CO₃ and 4 mmol l⁻¹ NaOH. The detection limit was 0.042 μg ml⁻¹ (*S/N*=3). The relative standard deviation was 1.99% and the correlation coefficient of the calibration curve for area was 0.9995. The linear range was 0.042~100 μg ml⁻¹. Common inorganic ion and organic acids did not interfere. The recovery was 96.4~103.2%. The method was simple, rapid, reliable and inexpensive. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Glyphosate is a very broad spectrum, non-selective, post-emergence herbicide. Glyphosate is the active ingredient in herbicides and is widely used in various applications for weed and vegetation control. Its impact on the environment is becoming more permanent. The difficulties of obtaining a simple method for the determination of this compound at residue levels are mainly due to its properties: its relatively high solubility in water, its insolubility in organic solvents and its complexing behaviour [1].

Procedures for the determination of glyphosate have been reviewed. Although gas chromatographic procedures continue to be of interest, in general they suffer from tedious sample preparation to convert the analytes into volatile derivatives. Because of the requirement for a better detection limit, liquid chromatographic procedures have been developed [2].

For liquid chromatography procedures, both pre- and post-column derivatization methods have been developed because of the limit of absorption detection. Precolumn procedures have focused on derivatization with 9-fluorenyl-methyloxycarbonyl chloroformate (FMOC-Cl) with fluorescence detection [3]. However, other derivatization agents such as 1-fluoro-2,4-dinitrobenzene [4] and *p*-toluenesulfonyl chloride [5] have been used to form glyphosate derivatives that can be detected in the UV-Vis region. Postcolumn derivatization have been commonly used with *o*-phthaldehyde-mercaptoethanol (OPA-MERC) [6–8]. Recently developed rapid procedures involving coupled-column LC and precolumn derivatization with FMOC [9]. Few detection methods for glyphosate are reported without derivatization.

Ion chromatography (IC), since its introduction in the mid-1970 [10], has been a useful tool for detecting ionic substance; the hydrophilic substance can be determined quickly and conveniently [11].

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Glyphosate is a kind of amino acid and has a strongly ionized phosphate group, as a result its pK_{a_1} , pK_{a_2} , K_{a_3} , and pK_{a_4} are 0.78, 2.29, 5.96, and 10.98, respectively, and it is a hydrophilic substance. In fact, it is possible to use IC to analyse glyphosate with both post-column derivatization [7] and UV detection [12]; determination of glyphosate by suppressed conductivity ion chromatography has never been reported. The main objective of this work was to develop a simple and sensitive method for the determination of glyphosate in an aquatic environment with emphasis on a simple clean-up procedure. The determination of the component is based on IC with suppressed conductivity detection.

2. Experimental

2.1. Reagents

Solutions containing glyphosate, sodium carbonate, sodium hydroxide were prepared from analytical reagent chemicals. The eluent was Na_2CO_3 –NaOH. All solutions including eluents, stock solution, standard solution were prepared with distilled water.

2.2. Apparatus

The ion chromatograph used in these experiments was a Dionex 100 ion chromatograph equipped with a conductivity detector (the full scale of which is $30 \mu\text{s V}^{-1}$), Dionex Ionpac AG4SC guard column and AS4SC separating column, anion self-regenerating suppressor (ASRS-I) with electrochemical methods. Eluent is $9 \text{ mmol l}^{-1} \text{ Na}_2\text{CO}_3$ – $4 \text{ mmol l}^{-1} \text{ NaOH}$ at flow-rate 1.5 ml min^{-1} . Injection volume is $50 \mu\text{l}$. Data were acquired by using Yinpu chromatographic data station software installed on a Model 586 computer.

2.3. Procedure

Environmental water samples were taken from the West Lake, Hangzhou, China. A 250-ml sample was taken and spiked with glyphosate. The solution was filtered with $0.45 \mu\text{m}$ membrane filter and extracted with 100 ml dichloromethane to remove organic

compounds. The aqueous phase which contained glyphosate was concentrated to a very small volume (5.0 ml) by rotary evaporation.

Solutions of glyphosate for agriculture were filtered with $0.45 \mu\text{m}$ membrane filter and injected directly.

3. Results and discussion

3.1. Chromatograph condition optimization

As glyphosate is the salt of middle acid and strong retention, the high pH and strong eluent are chosen. Sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) eluents were examined and mixed together with anionic eluents, the IC systems were shown in Fig. 1.

Sodium carbonate is stronger than sodium hydroxide as an eluent since the eluting carbonate ion is divalent whereas hydroxide is monovalent, the retention time of glyphosate noticeably decreased with increasing concentration of the Na_2CO_3 because glyphosate is a multi-valent anion. The optimum glyphosate's determination and resolute with other species, a concentration of Na_2CO_3 was chosen at 9 mmol l^{-1} .

Unlike the common anions which retention time decreased with increasing concentration of NaOH, the retention time of glyphosate increased slowly with increasing concentration of NaOH whose similar with retention time of phosphate. This phenomenon may be caused by the fact that as the pH becomes higher, glyphosate's degree of dissociation increase and retention time slightly longer. To prevent the common anions such as chloride, phosphate, nitrate, sulfate from interfering the determination, it is necessary to use NaOH more than 3.0 mmol l^{-1} , so that the common anions will elute in less than 3 min.

3.2. Calibration curve

The injection solution concentration were 2, 5, 10, 25, 50, $100 \mu\text{g ml}^{-1}$ and calibration curves of peak area and peak height were determined. The linear regression equation was:

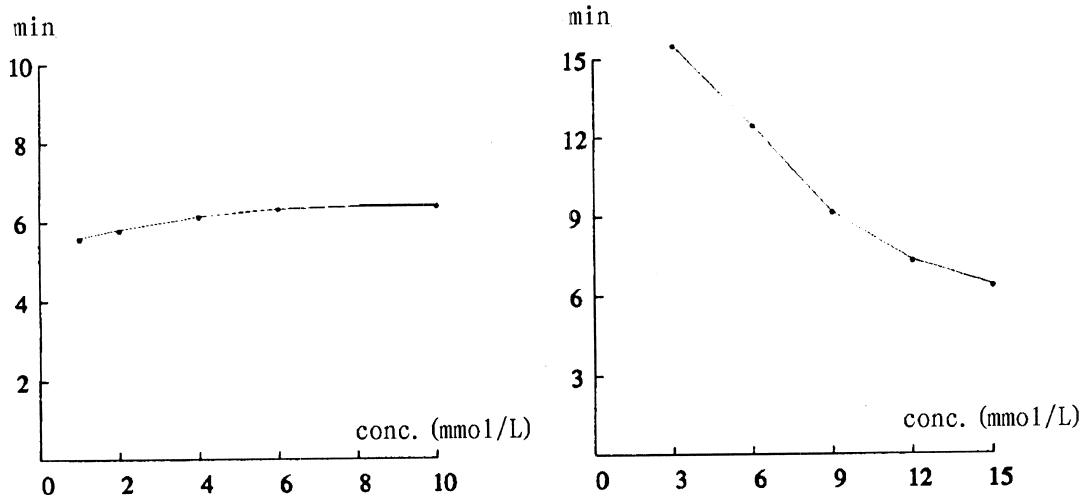


Fig. 1. Relationship between the retention time (min) and Na₂CO₃ (right: NaOH concentration 4 mmol l⁻¹) and NaOH (left: Na₂CO₃ concentration 9 mmol l⁻¹) concentrations.

$$H = 3562x + 10728, r = 0.9979$$

$$A = 112520x - 170378, r = 0.9995$$

where H is integer value of peak height, A is integer value of peak area, x is the concentration (μg ml⁻¹), r is the correlation relationship.

Because of asymmetry of the glyphosate peak, peak area is better than peak height for quantification. Linear range, detection limit and repeatability.

Fig. 2 shows an example of the standard stock solution of glyphosate. Under the above chromatographic conditions, the retention time of standard stock solutions was about 6.5 min. The retention time decreased slightly with increasing concentration of the glyphosate.

The detection limit (LOD, S/N=3) of glyphosate was 0.042 μg ml⁻¹. Fig. 3 shows chromatogram of 2 μg ml⁻¹ glyphosate. The linear range was from the detection limit to 100 μg ml⁻¹. Glyphosate (10.0 μg

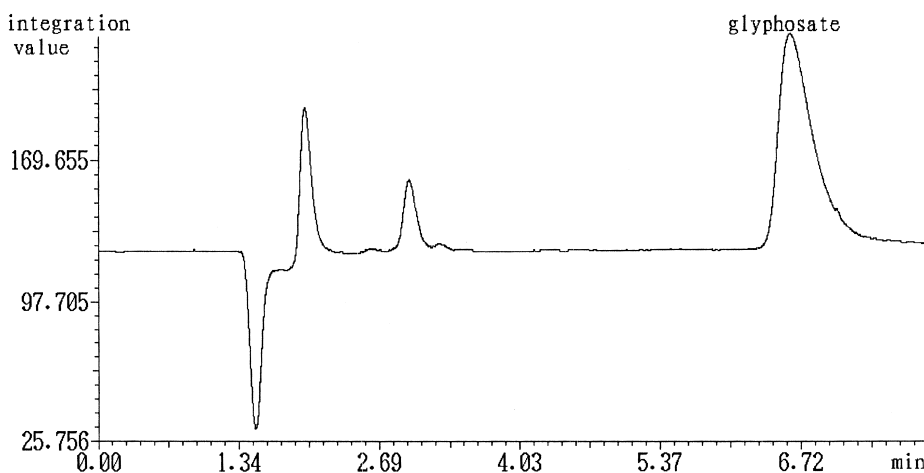


Fig. 2. Typical chromatograms of a standard stock solution (25 μg ml⁻¹).

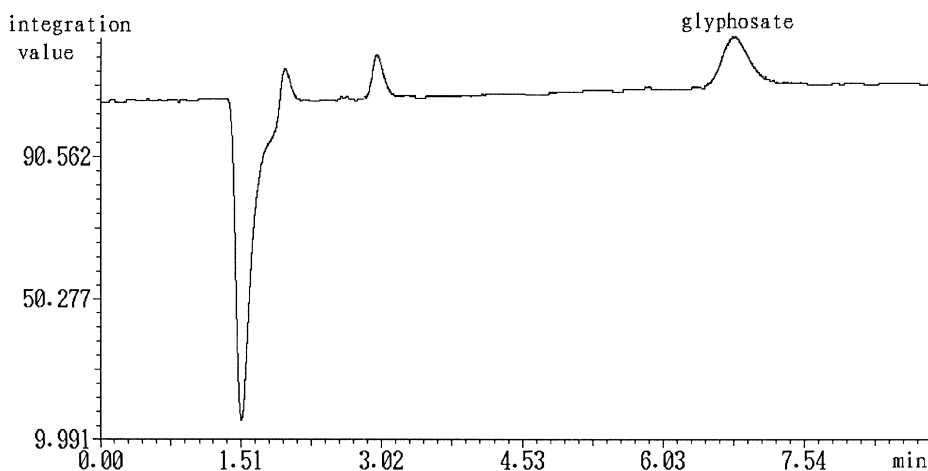


Fig. 3. Typical chromatograms of a standard stock solution ($2 \mu\text{g ml}^{-1}$).

ml^{-1}) was analyzed for repeatability. The RSD of the analytical data for seven injections was 1.87%. It shows good repeatability.

3.3. Interference

Non-ionizing substance and weak ionizing substance whose pK_a is higher than 7.0 did not affect the determination because of almost no conductive value. The results indicate no interference from common inorganic anions such as chloride, phosphate, nitrate, sulfate, because their retention time is very short. Other strong retention time substance such as citrate whose retention time is too long to detect, so it could be separated well from glyphosate. For this reason, this analysis technique has good selectivity and can be used for determination common ions as shown in Table 1.

3.4. Sample determination

Fig. 4 shows the results of determinations. The RSD of the analytical data for nine injections was 0.49% and the concentration of the sample was $66.53 \mu\text{g ml}^{-1}$ glyphosate solution and no glyphosate could be detected in the West Lake, Zhejiang Province, China. The recovery was in the range 96.36~

103.18%, when the standard glyphosate solution of $1\text{--}50 \mu\text{g ml}^{-1}$ was added to the sample for nine injections.

4. Conclusion

Determination of glyphosate by suppressed conductivity ion chromatography is developed. It is a sensitive method for the determination of glyphosate in an aquatic environment with emphasis on a simple clean-up procedure.

Table 1
Interference of common anions

Anion	Retention time (min)	Recovery ^a (%)
F^-	1.92	99.0
Cl^-	2.21	98.6
NO_2^-	2.43	98.8
NO_3^-	2.84	97.6
SO_4^{2-}	3.09	98.2
PO_4^{3-}	3.42	97.9
Citrate	18.7	98.4

^a Recovery of $1 \mu\text{g ml}^{-1}$ glyphosate with 1000-fold (w/w) of anion added.

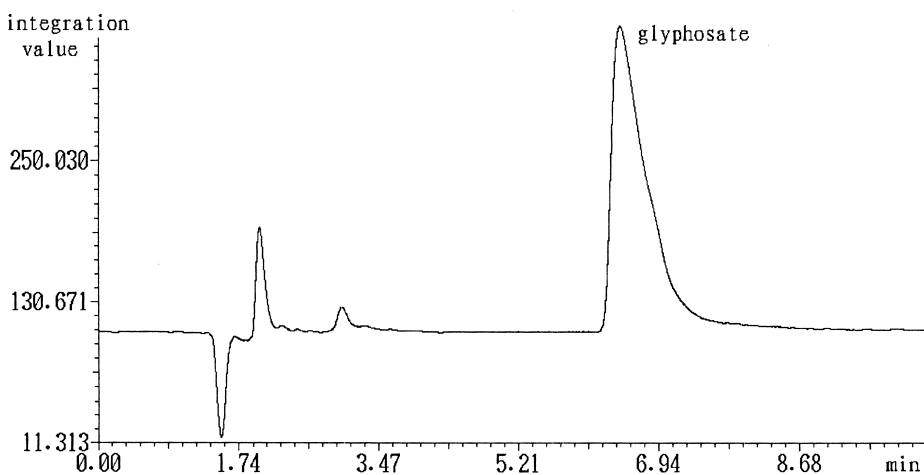


Fig. 4. Determination of glyphosate in solution for agriculture.

Acknowledgements

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