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Article

Rapid determination of nitrite in drinking water using ion-exchange-enhanced infrared spectroscopy

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Abstract: Infrared spectroscopy is an effective method for the determination of compositions and concentrations of liquids, with advantages of fast response, no-sampling, flexible in use and is able for on-line monitoring. However, for trace substances in drinking water, such as nitrates and heavy metals, infrared spectroscopy is not sensitive enough for the quantitative and qualitative measurement. In this study, we improved the sensitivity of infrared spectroscopy for nitrite determination by developing an ion-exchange-enhanced diffuse reflectance spectroscopy, which consist of an accessory based on ion-exchange resin for enrichment and a FTIR spectrometer for measurement. Using this method, the limit of detection for nitrate is 1.7 mg/L, which is enough for drinking water sensing. We also verified the quantitative measurement ability of the method. Furthermore, the limit of detection and quantitative measuring range could be adjusted by changing the mass of resin and adsorption time. This study demonstrated the method can be used to detect trace nitrites in drinking water, can be applied in the field, and is sensitive, rapid, and inexpensive with a wide dynamic range.

Keywords: infrared spectroscopy; diffuse reflectance infrared Fourier transform spectroscopy; ion-exchange resin; drinking water

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1. Introduction

According to the International Fertilizer Association, the global demand for nitrogen in 2014 was 182.3 Tg, and the world average for the nitrogen utilization rate was only 47% [1]. Over fertilization in agriculture and industrial wastewater discharge have led to large amounts of nitrogen entering surface water and groundwater in the form of nitrate and serious pollution [2,3]. High nitrate levels in the drinking water may cause blue baby syndrome and increase the incidence of gastric cancer, colorectal cancer, and other diseases in adults [4,5]. The World Health Organization and many countries have introduced laws to limit the content of nitrate in drinking water. The World Health Organization, the United States, and China all limit nitrate in drinking water to 10 mg/L [6-8]. Therefore, methods for rapid and accurate detection of nitrate in water are required.

The routine method for detection of nitrate in drinking water is laboratory analysis after sampling [9]. However, the methods are time consuming and they use chemical reagents that cause secondary pollution. With the development of analytical instruments and technology, other measurement methods have emerged, including electrochemical methods [10]，ion chromatography [11], ultraviolet spectroscopy [12], and high-performance liquid chromatography [13,14]. However, these methods are complicated and slow, and require sampling and sample pretreatment.

Infrared spectroscopy is a fast, non-contact method, and is widely applied to analysis of liquids, solids, and gases in the field. This method has been widely applied because it is simple, non-destructive, non-contact, and non-polluting [15-17]. For analysis of liquids, infrared spectroscopy is usually coupled with attenuated total reflection (ATR) [17-19]. In the field of sewage analysis, it has been applied to detection of heavy metals [16,20] and organic [21] and inorganic compounds [22,23]. However, infrared spectroscopy suffers from limited sensitivity and is not suitable for the analysis of trace substances. For example, using infrared ATR, the lowest concentration of nitrate that can be detected in water is 200 mg/L, which is much higher than the required level for drinking water monitoring.

Ion-exchange resins are insoluble structured polymers with various functional groups. They can adsorb inorganic salts from solution through exchange of their own ions with the salts. They are very stable adsorbents, and are commonly used for water purification [24-26].

In this study, we try to develop a novel method to determine the trace nitrate in drinking water, by combining FTIR spectroscopy with an ion-exchange resin based DRIFT (Diffuse Reflectance Infrared Fourier Transform) accessory. The nitrate will firstly be enriched by the accessory, and then, its diffuse reflectance spectra will be measured. To the best of our knowledge, this is the first time that infrared spectroscopy has been used to detect trace levels of nitrate in drinking water.

2. Materials and Methods

2.1. Materials

We used a microporous strongly basic anion exchange resin (Tulsion A-62-Mp, Thermax, India), which is a food-grade ion-exchange resin for nitrate removal. The resin is cross-linked polystyrene with quaternary ammonium type-I functional groups and chlorine ions for exchange (Table 1). The nitrate solution used in the experiment was prepared using analytically pure KNO3 in de-ionized water.

Table 1. Characteristics of Tulsion A-62MP

Resin Matrix	Cross linked Polystyrene
Functional group	Quaternary ammonium Type-I
Ionic Form	Chloride
Appearance	Yellow to golden spherical beads
T.E.C. meq/ml in Cl Form	1
Uniformity coefficient	1.56
Particle size(mm)	0.3-1.2
Operational pH range	0-14
Solubility	Insoluble in all common solvents

2.2. Equipment

Spectral data were collected by a V70 Fourier transform infrared (FTIR) spectrometer (Bruker, Karlsruhe, Germany). The experimental system included a MIR/FIR ceramic light source and a MCT unit detector (Bruker, Karlsruhe, Germany), and was cooled by liquid nitrogen. A commercial diffuse reflection accessory- DiffusIR (PIKE, USA) was used in the experiment. An ATR accessory (PIKE, USA) was installed for FTIR-ATR. Spectral data acquisition was performed by OPUS 6.5 (Bruker, Karlsruhe, Germany).

For ion-exchange-enhanced infrared spectra measurement, we combined DiffusIR with ion-exchange resin. A small aluminum box was filled with dry ion-exchange resin. Before measurement, the aluminum box was dipped in the water to enrich the nitrate in drinking water. And then, it was installed in the container of DiffusIR, as shown in Figure 1. In this experiment, different quantities of ion-exchange resin and its adsorption time in water used were tested.

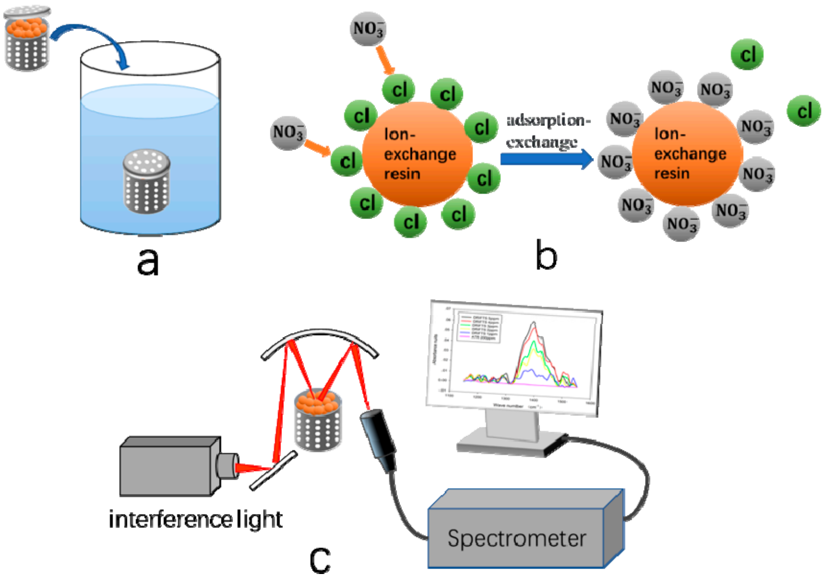

Figure 1. The demonstration of experimental processes. (a) Adding ion-exchange resin into a small aluminum box and dipping it in the water to be measured; (b) The nitrate in water is being adsorbed onto the resin; (c) Inserting the aluminum box onto the DRFIT accessory and measuring its diffusive spectra.

2.3. Spectra measurement

The nitrate concentrations used in this study were 0–8 mg/L (one sample analyzed per 0.5 mg/L), 15–50 mg/L (one sample analyzed per 5 mg/L), and 50–200 mg/L (one sample analyzed per 50 mg/L). In each experiment, 500 mL of a nitrate solution was placed in a container.

For ion-exchange-enhanced infrared spectra measurement, diffuse reflectance spectra were collected using the DRFIT accessory combined with on-exchange resin, as we motioned above. The background was measured using de-ionized water as a sample. While, for FTIR-ATR test, spectra were measured using ATR accessory. Spectra were acquired in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. Each sample was scanned 8 times. The experimental process is shown in Fig. 1. Spectral data acquisition was performed by OPUS 6.5 (Bruker, Karlsruhe, Germany). Baseline calibration and integral processing were performed using the software's built-in functions.

3. Results and Discussion

3.1. Effect of ion-exchange enhancement on infrared spectroscopy

For the determination of compositions of liquid sample using FTIR, ATR is commonly used for accurate measurement of the absorption spectrum. It realizes a steady-state enhancement of the signal using multiple reflections of the optical signal on the surface of the sample to be measured. However, when FTIR-ATR is applied for nitrate measurement in water, the LOD is not suitable for drinking water safety monitoring. It can been studied from Fig. 2, the spectral features is rather tiny even when the nitrate concentration is 200 mg/L. To improve the detection ability, we used the ion-exchange enhancement methods as stated in the experimental part.

Basically, the nitrate in water is enriched onto the ion-exchange resin, which is commonly used water purification in previous studies. Adsorption of nitrate from water on the resin involves reversible exchange of nitrate ions in the solution with chloride ions in the resin. This adsorption is very stable. The general order of adsorption of inorganic acid ions by strongly basic anionic resins is [27]: $SO_4^{2-} > NO_3^- > Cl^- > HCO_3^- > OH^-$.

As described in the experimental part, we firstly added 0.1 g resin into the aluminum box. The adsorption time, which indicates the time of the resin in water, is set as 60 minutes. As shown in Fig. 2, with a nitrate concentration of 2 mg/L or even lower, the spectrum of the resin had an obvious peak at 1385 cm^{-1} [28](Figure 2), which is the absorption spectral features of nitrate. This concentration is low enough for drinking water testing requirements. As the nitrate concentration increased, the intensity of this peak increased. With ATR, this peak was difficult to observe even when the concentration was as high as 200 mg/L (Fig. 2). Therefore, the accessory greatly enhances the ability of infrared spectroscopy to detect nitrate in drinking water compared with the traditional detection method using ATR.

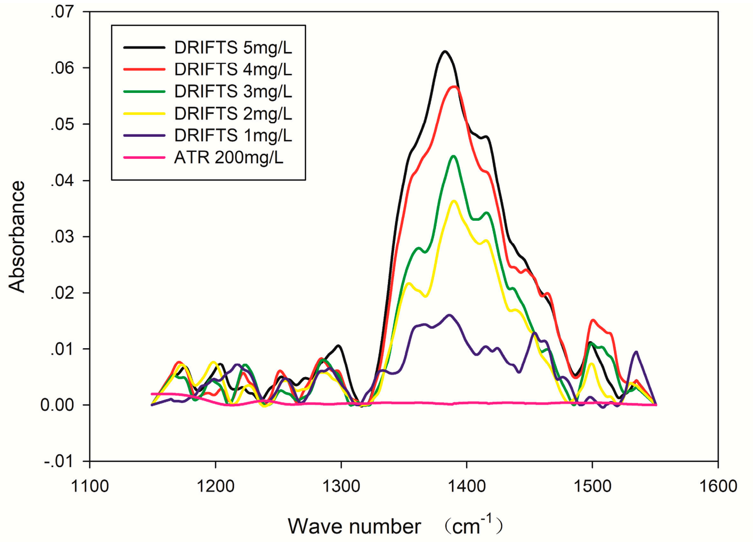

Figure 2. Comparison of FTIR-ATR and ion-exchange enhancement DRIFTS at different concentrations of nitrate in water.

3.2. Effect of the resin dosage and adsorption time on measurement

Because adsorption on the resin occurs via ion exchange, if less resin is used, more nitrates will be likely to be adsorbed per unit of resin, which should increase the spectral intensity. We investigated the performance of measurement using 0.1 g, 0.3 g, and 0.5 g of resin. The concentration of nitrate in the water was 5 mg/L. As the mass of the resin increased, the spectral intensity greatly increased (Figure 3(a)). However, because of the limited sample size used in DRIFTS accessory, the mass of resin must be greater than 0.1 g. Therefore, in this study, we used 0.1 g of resin in the aluminum box and inserted it in to the DRIFTS accessory, if there is no special explanation.

It is obviously that the adsorption time also has effect on the measurement, for some amounts of nitrate will likely to be adsorbed in a longer time. However, it should be noted that the reversible exchange between the resin and nitrate ions will reach equilibrium after a certain time. In a study on the use of resin for water purification, the amount of nitrate adsorbed on the resin increased with time, and the adsorption reached equilibrium near 50 min [24]. We used a nitrate concentration of 5 mg/L and 0.1 g of resin for DRIFTS measurement with different adsorption times. As the adsorption time increased, the spectral intensity increased, and over time, the rate at which it increased gradually gently (Figure 3(b)). After 60 min, the adsorption reached equilibrium, and the spectral intensity no longer increased. Therefore, for 0.1 g of resin, 60 min is the optimum adsorption time. If a shorter adsorption time is used, the sensitivity will decrease. With an adsorption time of 20 min, the spectral intensity was only about half of that with an adsorption time of 60 min (Figure 3(b)).

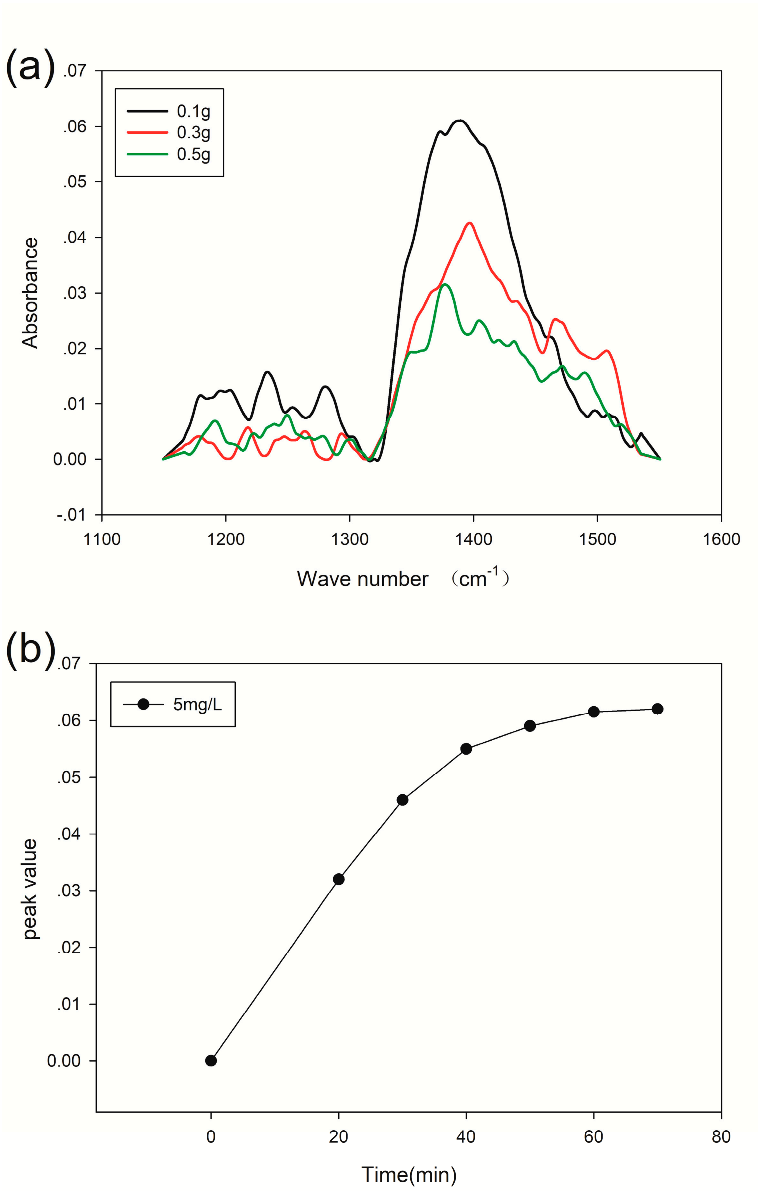

Figure 3. The effect of the resin dosage and adsorption time on measurement. (a) shows the spectral intensities of using different mass of the resin, when the nitrate concentration is 5 mg/L; (b) shows the spectral intensities of using different adsorption time, when the nitrate concentration is 5 mg/L and resin dosage is 0.1 g.

3.3. Quantitative Measurement of Nitrate in Drinking Water

We further studied the ability of our method for the quantitative determination of nitrate in drinking water. Figure 4 (a) demonstrates the relationship between the spectral features of nitrate and its concentrations in water in a range of 0-160 mg/L. The spectral features are calculated by the integration of the absorption spectra of 1350–1475 cm^{-1}, after a baseline correction. It can be studied from the figure that when the concentration was less than 50 mg/L, the spectral intensity increased with nitrate concentration. There was a linear relationship (R^2 = 0.98) between the nitrate concentration and peak intensity, as shown in Fig. 4 (c). However, when the concentration was greater than 50 mg/L, the resin was saturated and the spectral intensity no longer increased, which can also be seen in Fig. 4 (b). Therefore, a nitrate concentration of 50 mg/L can be considered as the upper limit under the current conditions. This upper limit could be increased by increasing the mass of resin or decreasing the adsorption time, as discussed in the previous section.

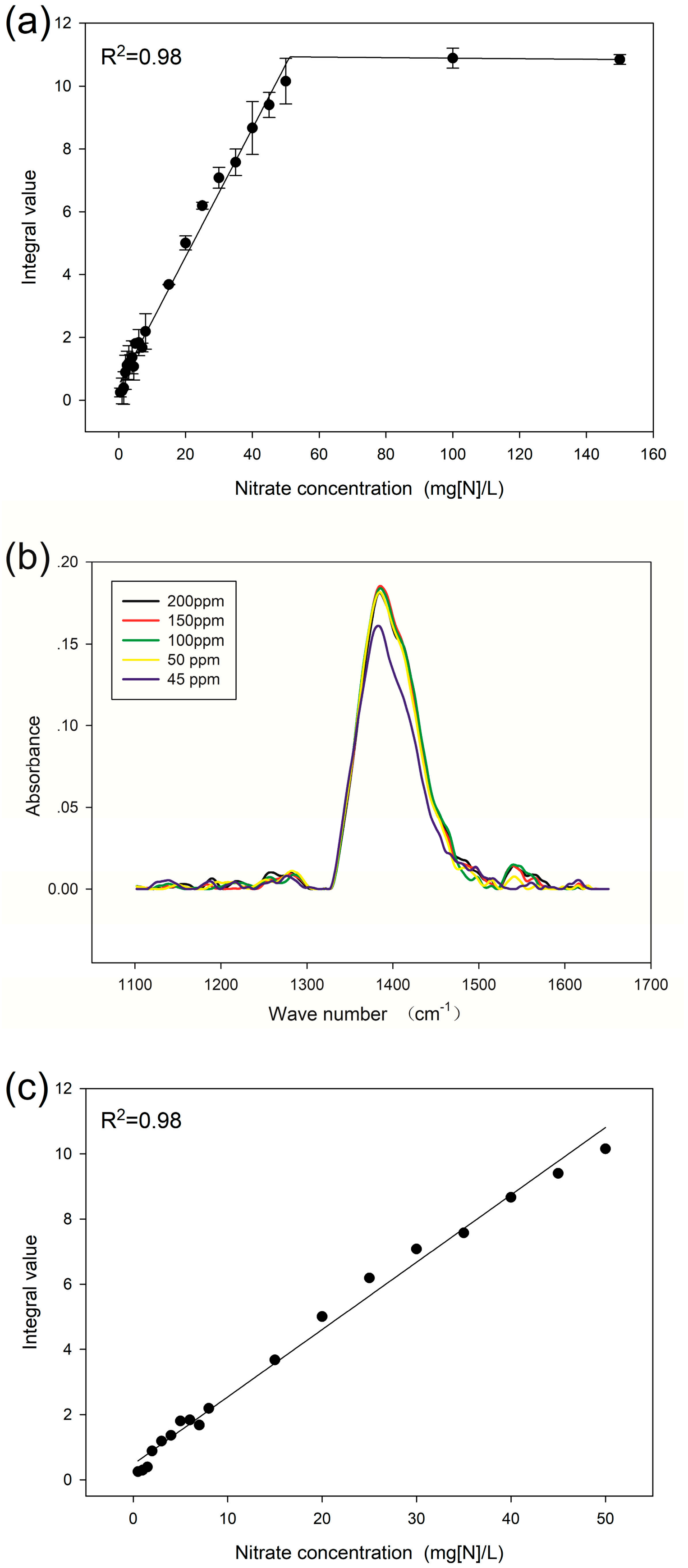

Figure 4. The relationship between the spectral features of nitrate and its concentrations in water. (a) Relationships of absorbance spectra and nitrate concentrations in a range of 0-160 mg/L; (b) The saturation of

the ion-exchange effect of the resin; (c) Calibration curve of the spectral features and nitrate concentrations at 0-50mg/L.

The limit of detection (LOD) can be calculated from the calibration curve. The LOD of the sensor was calculated using the (LOD = 3 σ/S) criteria, where σ and S are the standard deviation and slope of the calibration curve [29]. The nitrate LOD was 1.7 mg/L, which meets the needs of drinking water quality testing. The LOD could be improved by reducing the mass of resin used, as discussed in the previous section. However, it also reduces the upper limit of the range at the same time.

With 0.1 g of resin and a 60 min adsorption time, the LOD was 1.7 mg/L and the linear range was 1.7–50 mg/L. In many field measurements, it may be necessary to shorten the adsorption time. Therefore, using the same mass of resin, we tested an adsorption time of 10 min, and found that the minimum detection concentration was 10 mg/L, which was enough to satisfy the drinking water quality standards. Fig. 5 shows the absorbance spectra of 10 mg/L and 20 mg/L nitrate in water in this situation.

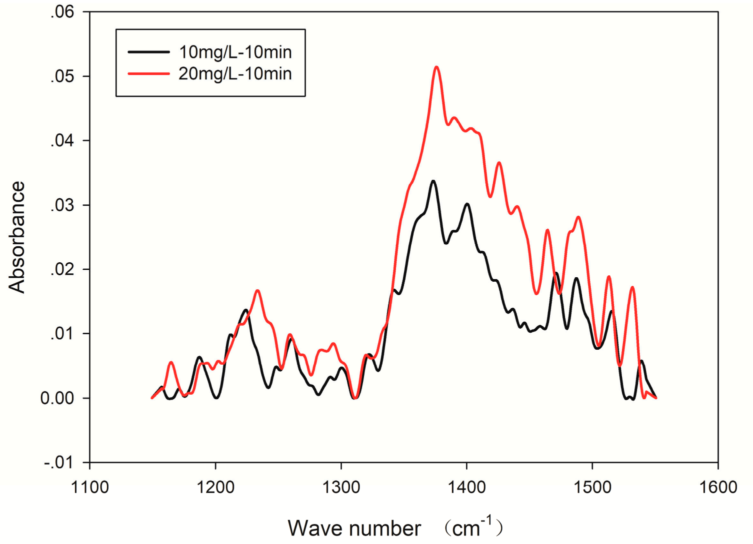

Figure 5. The absorbance spectra of 10 mg/L and 20 mg/L nitrate in water when using 10 min as the adsorption time.

3.4. Resin recycling

We confirmed that the ion-exchange resin improves the detection ability of DRIFTS trace nitrate in water. Because of its short processing time, high sensitivity and good quantification capability, this method could be used to develop a novel kind of DRIFTS accessory. After placing this accessory in water, DRIFTS could be used to quickly enrich the nitrate content. Since the ion exchange process of the resin is reversible, the accessory could be reused. After each adsorption test, the accessory could be washed with NaCl solution for reuse. To confirm this, we used the accessory three times for analysis of a 30 mg/L nitrate solution for a repeatability test. Before each time of measurement, the aluminum box that contain reins was washed using NaCl solution. The absorbance intensity was measured before and after each test (Figure 6). The results showed that the accessory could be repeatedly used.

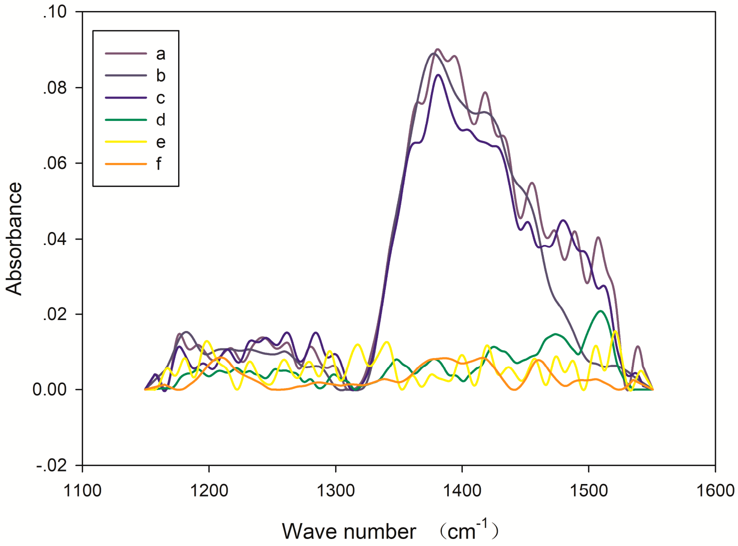

Figure 6. The repeatability test of the ion-exchanged enhanced DRIFTS accessory. (a) Enrichment after two backwashes; (b) Enrichment after a backwash; (c)First enrichment; (d)After two backwashes; (e)After a backwash; (f)The original resin.

4. Conclusions

In this study, we developed a novel kind of DRIFTS accessory, which improves the sensitivity of common FTIR by using ion-exchanged enhancement. Using the method, the detection ability for nitrate in drinking water is greatly improved to meet the requirements of food quality control. The effects of the amount of ion-exchange resin used and the adsorption time on the detection were evaluated. We also performed a quantitative measurement of water nitrate in the range of 1.7–50 mg/L, with a LOD of 1.7 mg/L. Both the LOD and the measuring range can be adjusted by changing the resin dosage and adsorption time. Furthermore, we verified the repeatability of the resin it is reused. Compared with other methods, the ion-exchanged enhanced DRIFTS is pollution-free, reusable and high sensitive, which leads it promising for future investigation of the rapid determination of drinking water quality.

Author Contributions: Daming Dong proposed the method and designed the experiment; Song Ye and Xiuke Du carried out the experiment; Xiuke Du wrote the paper.

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Conflicts of Interest: Daming Dong declares that he has no conflict of interest. Xiuke Du declares that he has no conflict of interest. Song Ye declares that he has no conflict of interest.

Ethical Approval: This article does not contain any studies with human or animal subjects.

Informed Consent: Not applicable.

References

1. Heffer, P.; homme, M.P. Global nitrogen fertiliser demand and supply: trend, current level and outlook. *2016 International Nitrogen Initiative Conference, "Solutions to improve nitrogen use efficiency for the world"* **2016**, www.ini2016.com, doi:www.ini2016.com.

2. Wakida, F.T.; Lerner, D.N. Non-agricultural sources of groundwater nitrate: a review and case study. *Water Res* **2005**, *39*, 3-16, doi:10.1016/j.watres.2004.07.026.
3. Chen, S.; Wu, W.; Hu, K.; Li, W. The effects of land use change and irrigation water resource on nitrate contamination in shallow groundwater at county scale. *Ecological Complexity* **2010**, *7*, 131-138, doi:10.1016/j.ecocom.2010.03.003.
4. Fewtrell, L. Drinking-water nitrate, methemoglobinemia, and global burden of disease: A discussion. *Environ Health Persp* **2004**, *112*, 1371-1374.
5. Esmaeili, A.; Moore, F.; Keshavarzi, B. Nitrate contamination in irrigation groundwater, Isfahan, Iran. *Environ Earth Sci* **2014**, *72*, 2511-2522.
6. Fan, X.M.; Guan, X.H.; Ma, J.; Ai, H.Y. Kinetics and corrosion products of aqueous nitrate reduction by iron powder without reaction conditions control. *J Environ Sci-China* **2009**, *21*, 1028-1035.
7. USEPA. Part 141 — National Primary Drinking Water Regulations. **2010**.
8. WHO. Guidelines for drinking-water quality, fourth edition. **2011**.
9. Doane, T.A.; Horwath, W.R. Spectrophotometric determination of nitrate with a single reagent. *Anal Lett* **2003**, *36*, 2713-2722.
10. Luo, X.; Wu, J.; Ying, Y. Voltammetric detection of nitrate in water sample based on in situ copper-modified electrode. *Ionics* **2013**, *19*, 1171-1177, doi:10.1007/s11581-012-0839-0.
11. Tirumalesh, K. Simultaneous determination of bromide and nitrate in contaminated waters by ion chromatography using amperometry and absorbance detectors. *Talanta* **2008**, *74*, 1428-1434.
12. Mikael Karlsson, B., Ralf J. O. Olsson. Determination of nitrate in municipal waste water by UV spectroscopy. *Analytica Chimica Acta* **1995**, *312*, 107-113, doi:https://doi.org/10.1016/0003-2670(95)00179-4.
13. Akyuz, M.; Ata, S. Determination of low level nitrite and nitrate in biological, food and environmental samples by gas chromatography-mass spectrometry and liquid chromatography with fluorescence detection. *Talanta* **2009**, *79*, 900-904.
14. Khan, M.R.; Wabaidur, S.M.; Alothman, Z.A.; Busquets, R.; Naushad, M. Method for the fast determination of bromate, nitrate and nitrite by ultra performance liquid chromatography-mass spectrometry and their monitoring in Saudi Arabian drinking water with chemometric data treatment. *Talanta* **2016**, *152*, 513-520, doi:10.1016/j.talanta.2016.02.036.
15. Linker, R.; Kenny, A.; Shaviv, A.; Singher, L.; Shmulevich, I. Fourier Transform Infrared-attenuated total reflection nitrate determination of soil pastes using principal component regression, partial least squares, and cross-correlation. *Appl Spectrosc* **2004**, *58*, 516-520.
16. Xia, X.Q.; Mao, Y.Q.; J, J.F. Reflectance Spectroscopy Study of Cd Contamination in the Sediments of the Changjiang River, China. *Environmental Science & Technology* **2007**, *41*, 3449-3459.
17. Jaiswal, P.; Jha, S.N.; Borah, A.; Gautam, A.; Grewal, M.K.; Jindal, G. Detection and quantification of soymilk in cow-buffalo milk using Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR). *Food Chem* **2015**, *168*, 41-47.
18. Blanco, M.; Villarroya, I. NIR spectroscopy: a rapid-response analytical tool. *Trac-Trend Anal Chem* **2002**, *21*, 240-250.
19. Jha, S.N.; Gunasekaran, S. Authentication of sweetness of mango juice using Fourier transform infrared-attenuated total reflection spectroscopy. *J Food Eng* **2010**, *101*, 337-342.

20. Liu, F.; Cai, W.; Shao, X. Selective determination of mercury (II) ion in water by near-infrared diffuse reflection spectroscopy with the aid of preconcentration and multivariate calibration. *Vibrational Spectroscopy* **2013**, *68*, 104-108, doi:10.1016/j.vibspec.2013.05.014.
21. Macedo, M.G.; Laporte, M.F.; Lacroix, C. Quantification of exopolysaccharide, lactic acid, and lactose concentrations in culture broth by near-infrared spectroscopy. *J Agr Food Chem* **2002**, *50*, 1774-1779.
22. Michel, K.; Bureau, B.; Boussard-Plédel, C.; Jouan, T.; Adam, J.L.; Staubmann, K.; Baumann, T. Monitoring of pollutant in waste water by infrared spectroscopy using chalcogenide glass optical fibers. *Sensors and Actuators B: Chemical* **2004**, *101*, 252-259, doi:10.1016/j.snb.2004.03.014.
23. Zhang, Y.; Hao, Y.; Cai, W.; Shao, X. Simultaneous determination of phenol and p-nitrophenol in wastewater using near-infrared diffuse reflectance spectroscopy with adsorption preconcentration. *Analytical Methods* **2011**, *3*, 703, doi:10.1039/c0ay00775g.
24. Nur, T.; Johir, M.A.H.; Loganathan, P.; Vigneswaran, S.; Kandasamy, J. Effectiveness of purolite A500PS and A520E ion exchange resins on the removal of nitrate and phosphate from synthetic water. *Desalination and Water Treatment* **2012**, *47*, 50-58, doi:10.1080/19443994.2012.696424.
25. AkshayShende; Main, J.S. Effect of contact on adsorption of nitrates and phosphates *International Journal of Advanced Technology in Engineering and Science* **2014**, *02*, 117-122.
26. Ye, Y.; Ren, Y.; Zhu, J.; Wang, J.; Li, B. Removal of nitrate and Cr(VI) from drinking water by a macroporous anion exchange resin. *Desalination and Water Treatment* **2016**, *57*, 26427-26439, doi:10.1080/19443994.2016.1164081.
27. Helferich, F. Ion Exchange. *Dover Publication Inc., USA* **1995**.
28. Verma, S.K.; Deb, M.K. Nondestructive and rapid determination of nitrate in soil, dry deposits and aerosol samples using KBr-matrix with diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS). *Anal Chim Acta* **2007**, *582*, 382-389, doi:10.1016/j.aca.2006.09.020.
29. Srivastava, S.; Abraham, S.; Singh, C.; Ali, M.A.; Srivastava, A.; Sumana, G.; Malhotra, B.D. Protein conjugated carboxylated gold@reduced graphene oxide for aflatoxin B-1 detection. *Rsc Adv* **2015**, *5*, 5406-5414.