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RESEARCH ARTICLE

Detecting NO_3^- concentration in nitrate solutions using terahertz time-domain spectroscopy

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Abstract In this paper, we employed terahertz time domain spectroscopy (THz-TDS) to investigate the nitrate () concentration in four types of nitrate solution (sodium nitrate, aluminum nitrate, calcium nitrate and magnesium nitrate). Their absorption coefficient and refractive index were calculated in 0.2–2.5 THz, and a logarithmic relationship was observed between NO_3^- concentrations and selected optical parameters regardless of the kinds of nitrate solution. Partial least square (PLS) model was built between THz-TDS and NO_3^- concentration. The correlation coefficient of PLS model was calculated. The results make the quantitative analysis of NO_3^- concentration possible by THz-TDS and indicate the bright future in practical application.

Keywords terahertz time-domain spectroscopy (THz-TDS), nitrate, solution

1 Introduction

Some anthropogenic activities may lead to water pollution and nitrate is possibly the most widespread groundwater contaminant in the world, which causes a serious threat to drinking water supplies and promotes eutrophication [1–4]. In drinking water, high nitrate concentrations are believed to be a health risk because it increases the toxic nitrite ion by microbiological processes in our stomachs [5–8]. Nitrite ions reduce the oxygen-carrying capacity of blood and may cause methemoglobinemia in infants. They can also react with amino compounds, in many media, to form nitrosamines which are strongly carcinogenic [9–11]. Therefore, it is essential to monitor nitrate concentration in potable water supplies.

Up to now, a lot of detection technologies for the determination of the nitrate (NO_3^-) concentration have been reported, e.g., ion chromatography, UV-visible spectrophotometry, polarography and liquid chromatography/electrospray ionization/mass spectrometry [12–16]. Terahertz time-domain spectroscopy (THz-TDS) is a technique that relays frequency to obtain some optical constants, such as refractive index and absorption coefficient. THz wave relies on the synchronous and coherent detection and has some excellent properties, such as non-destructive testing and a higher signal-to-noise ratio (up to 10000:1). In a THz range (0.1 – 10 THz or λ= 3 – 0.03 mm), many polar molecules have unique spectral fingerprints, which are from the rotational transitions of the molecules. Therefore, many materials may be detected more efficiently or accurately by their relatively simple rotational spectra, rather than their more complex vibrational or rovibrational signatures. In recent years, with the development of THz-TDS technique, researchers begin to focus on the ion detection and the chloride ion concentration has been measured in concrete structures [17]. In this study, we proposed THz-TDS technique to monitor and inspect the NO_3^- concentration c_N of nitrate solutions. The experimental results showed a logarithmic relationship between the concentration of nitrate ion and optical parameters, indicating that it was feasible for the THz-TDS to quantitatively inspect the ions concentration in water.

2 Experiments

A transmission type of the THz-TDS detection method is adopted [18,19]. Four types of nitrate solutions (sodium

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nitrate, aluminum nitrate, calcium nitrate and magnesium nitrate) were selected with nitrate concentrations C_N varying from 10 to 5 × 10^5 ppm[1)]. The nitrate solution was obtained by dissolving nitrate solid in deionized water at a fixed ratio and sealed in a plastic cell with a thickness of 0.12 mm. All of the measurements were performed at room temperature. The system was purged with dry nitrogen gas to eliminate the absorption of water vapor. Fifteen concentration samples of each nitrate were prepared in order to ensure measurement reproducibility. For each kind of sample, we scanned three times to get average value and to decrease the error as well.

3 Results and discussion

Figure 1 showed the time domain signals of reference (empty cell) and samples with different concentrations. The THz wave form in the beam path exhibited a distinctly different shape and magnitude from that in the absence of the sample, which indicated absorption in the nitrate solutions. The THz amplitude of $NaNO_3$, $Ca(NO_3)_2$, $Al(NO_3)_3$ and $Mg(NO_3)_2$ solutions gradually decreased from 0.104, 0.093, 0.139 and 0.132 V to 0.066, 0.065, 0.069 and 0.067 V, while the time delay increased from 10.45, 10.49, 10.49 and 10.19 ps to 10.87, 10.87, 10.83 and 10.64 ps, with the increase of nitrate concentrations C_N with 50, 50, 10 and 25 ppm by 30%, 40%, 40% and 30%, respectively.

A fast Fourier transform was applied to the time-domain data to yield the frequency-dependent spectral amplitude of reference and samples. The absorption coefficient (α) and refractive index (n) were calculated at each frequency based on the ratio and the relative phase difference of the sample and reference power spectra [20]. Figures 2 and 3 gave the $\alpha(\nu)$ and $n(\nu)$ of the selected nitrate solutions in the frequency range from 0.2 to 2.5 THz where ν was the THz frequency. Regarding the frequency dependence of absorption from 0.2 to 1.5 THz in Fig. 2, it was self-evident to approximate $\alpha(\nu)$ with a linear function $\alpha(\nu)$ =

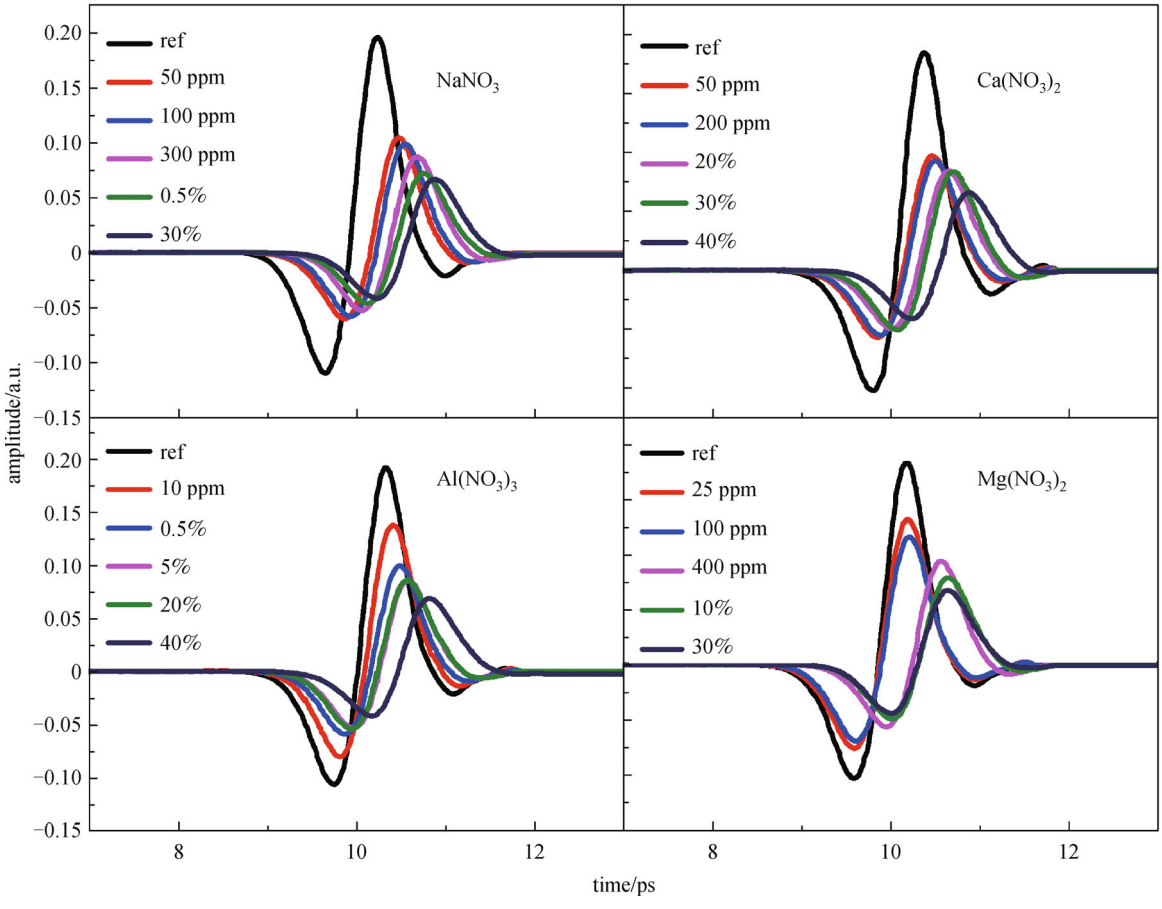

Fig. 1 Terahertz time domain spectroscopy (THz-TDS) of reference (empty cell) and nitrate solution samples with different nitrate concentrations C_N

1) 1 ppm = 1×10^{-6}

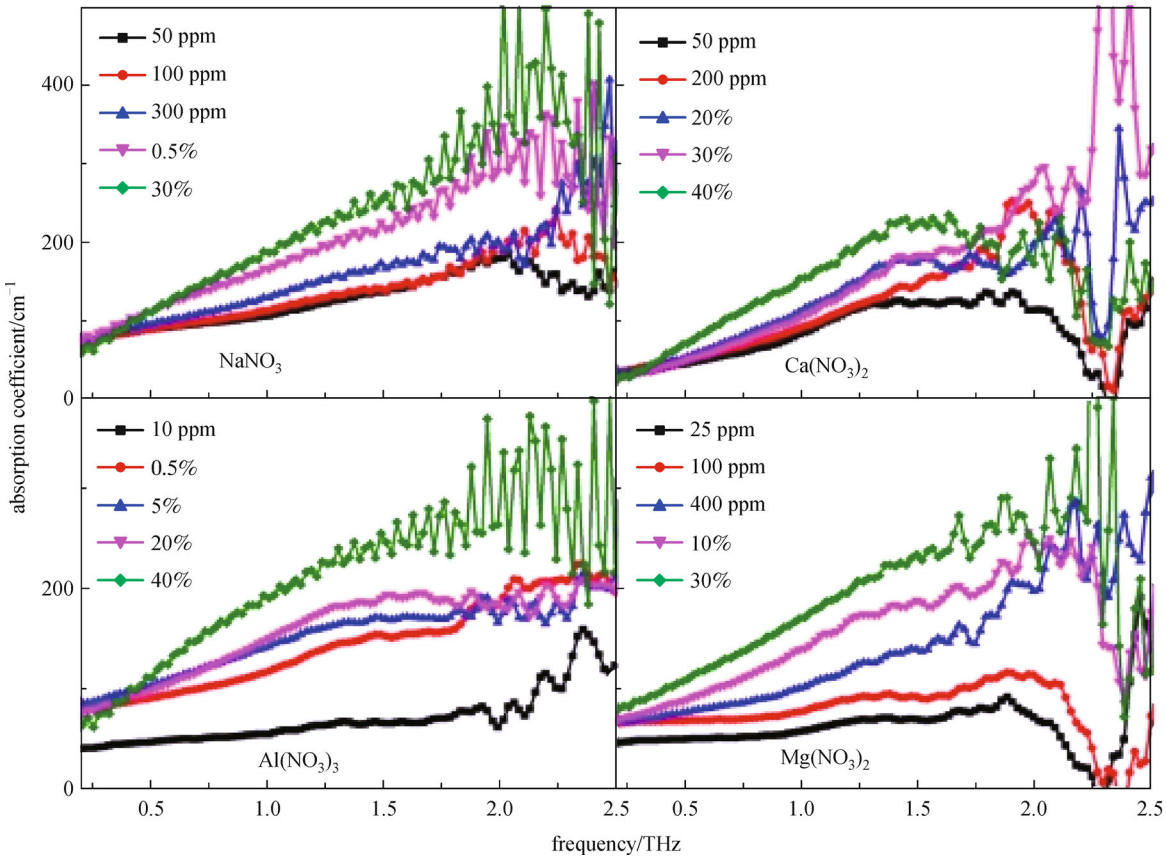

Fig. 2 Absorption coefficient of samples with different nitrate concentration C_N in 0.2–2.5 THz

$k_1v + b_1$, where k_1 and b_1 depended on nitrate solution and its concentration C_N. The slope k_1 of the absorption curve increases with a higher concentration. For the refractive index $n(v)$ of each sample, they all had a gradual and monotonic decrease with increasing C_N in the whole THz region. As shown in Fig. 3, the frequency dependent $n(v)$ can be depicted with $n(v) = -k_2v + b_2$, where the slope k_2 of the refractive index curve lightly depended on nitrate solution and its concentration C_N, while b_2 strongly depended on nitrate concentration.

Figure 4 showed the NO_3^- concentration c_N dependences of $\alpha(v)$ and $n(v)$, respectively, at a selected frequency of 1.24 THz. A logarithmic relationship, α and $n \propto \ln(c_N)$ at 1.24 THz, was obtained and almost independent of the type of nitrate solutions, which was different from Beer-Lambert law where the absorption coefficient was proportional to the concentration. Partial least square (PLS) was adopted to establish the models and predicted the NO_3^- concentration c_N in nitrate solutions. All of the samples were divided into two parts, where one part was used for calibration and the other one for validation. The result in Fig. 5 demonstrated the agreement between actual and predicted values, which indicated that the PLS methods can precisely determine the C_N in nitrate solutions.

To evaluate the performance of the calibration and validation models, correlation coefficient R was calculated. Here R is an index correlation determined by the degree of linear relationship between actual and predicted concentrations. The closer R is to 1, the higher the model prediction precision is. In the present, R of calibration and validation were equal to 0.9898 and 0.9975, respectively, proving that the THz-TDS was a reliable way to quantitatively detect the NO_3^- content in nitrate solutions.

4 Conclusions

In summary, THz-TDS is used to inspect the NO_3^- concentration in nitrate solutions. The results showed a logarithmic relationship between the optical parameters and NO_3^- concentration for all the nitrate solutions. PLS model was built between THz-TDS and NO_3^- concentration. The correlation coefficient of PLS model was close to 1. The overall results indicate that THz-TDS may be a promising method for the rapid determination of ion concentration in domestic and industrial water.

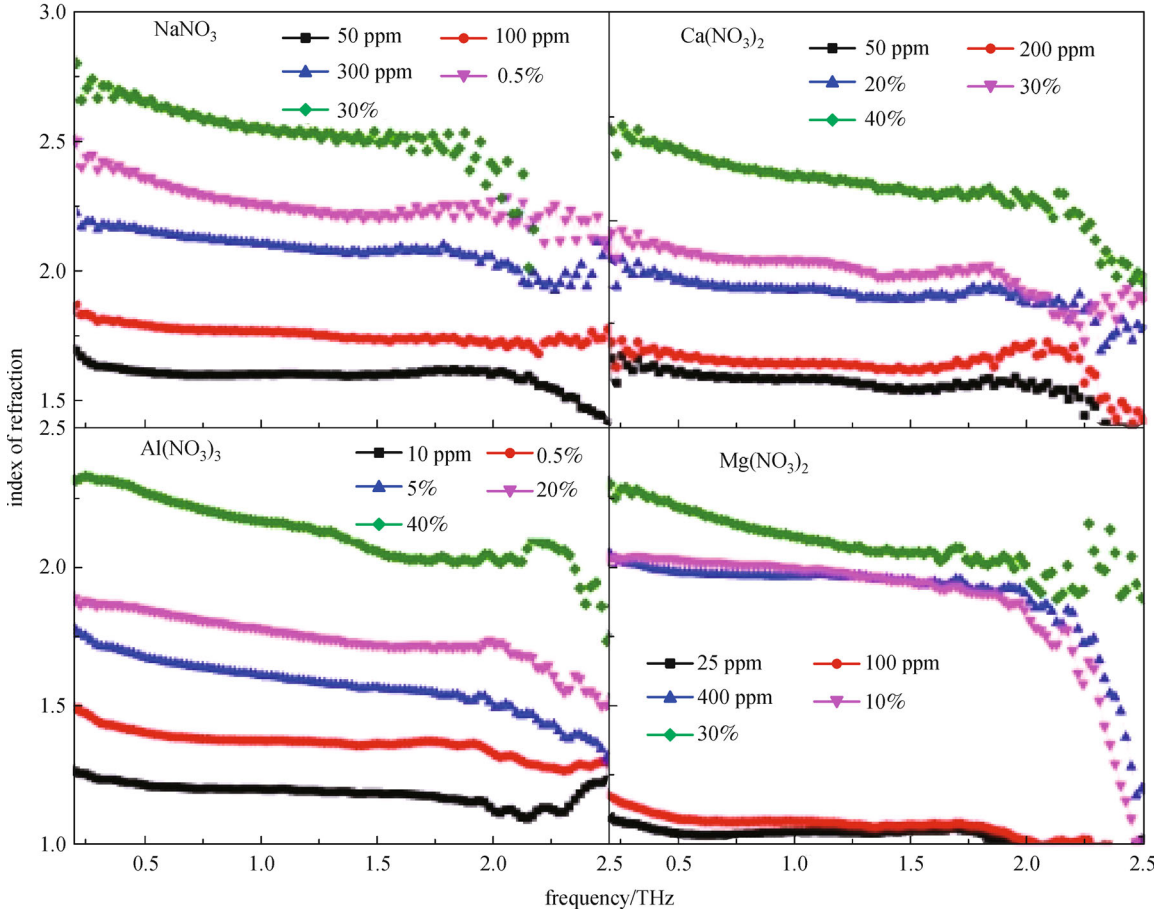

Fig. 3 Refractive index of samples with different nitrate concentration C_N in 0.2–2.5 THz

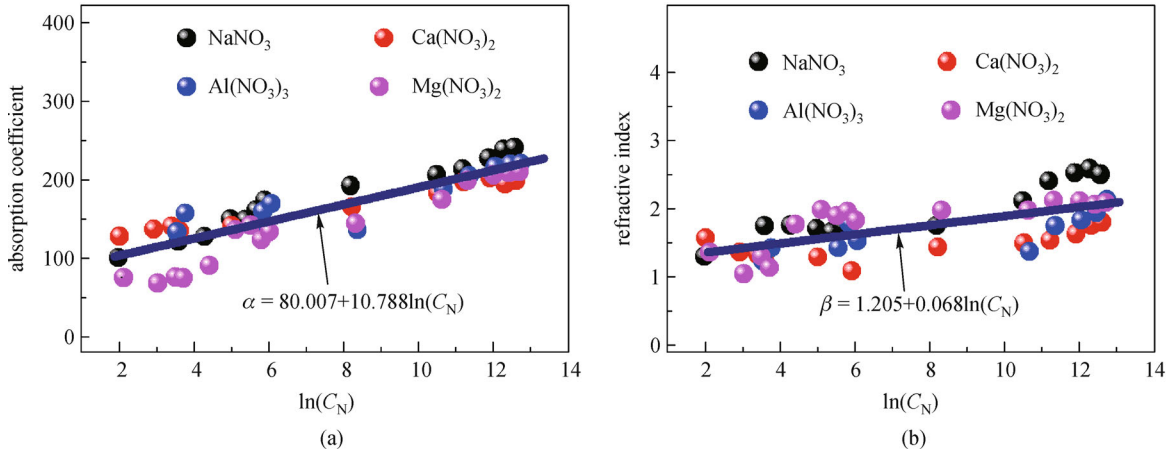

Fig. 4 (a) Absorption coefficient and (b) refractive index as a function of the NO_3^- concentration c_N of $NaNO_3$, $Ca(NO_3)_2$, $Al(NO_3)_3$ and $Mg(NO_3)_2$ solutions at 1.24 THz

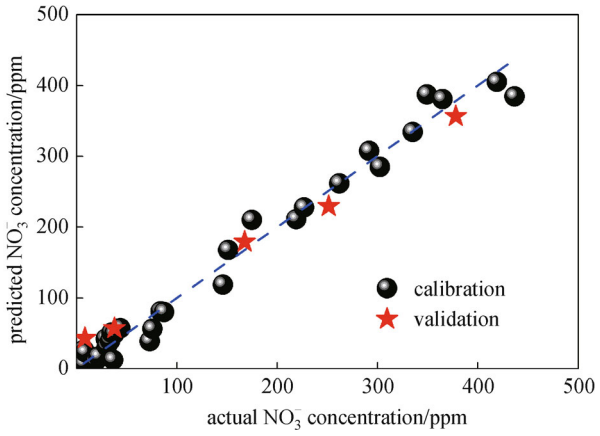

Fig. 5 Predicted NO_3^- concentration against actual concentration from partial least square (PLS) model

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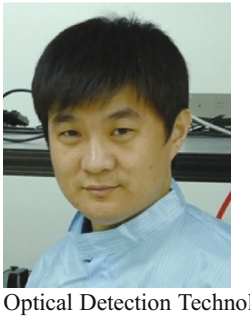

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