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## Technical Notes

# UV Resonance Raman Spectroscopic Detection of Nitrate and Nitrite in Wastewater Treatment Processes

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**The 204- and 229-nm excited UV resonance Raman spectra of wastewater solutions containing sodium nitrite and nitrate were measured in the concentration range 7  $\mu\text{M}$  to 3.5 mM (0.1–50 ppm nitrogen). The other chemical species present in wastewater do not interfere with Raman measurements of  $\text{NO}_2^-/\text{NO}_3^-$  bands. We observe detection limits of  $<14 \mu\text{M}$  ( $<200 \text{ ppb}$ ) for both  $\text{NO}_2^-$  and  $\text{NO}_3^-$ . UV resonance Raman spectroscopy appears to be an excellent tool for on-line monitoring of  $\text{NO}_2^-/\text{NO}_3^-$  in wastewater for the real-time control of water treatment plants.**

The reliability and performance of biological nutrient removal (BNR) wastewater treatment plants (WWTPs) can be enhanced by the ability to monitor nitrate and nitrite in BNR activated sludge reactors without the need for reagent additions or complex calibration procedures. Real-time on-line monitoring of these parameters provides input to the process control systems to optimize performance of treatment systems designed for low nitrogen and phosphorus effluent concentrations.<sup>1</sup> According to the Water Environment Research Foundation (WERF), poor sensor performance and high maintenance costs are the major stumbling blocks to improved automation.<sup>2</sup>

In the work here, we demonstrate the utility of UV resonance Raman<sup>3–8</sup> spectroscopy to monitor nitrate and nitrite in wastewater treatment process reactors in real time. Excitation within the strong UV absorption bands of nitrate and nitrite results in the

selective enhancement of the vibrations of these species. We observe little interference from other species in the wastewater. Further, UV excitation avoids fluorescence interference<sup>5</sup> from other species present in the wastewater, thus yielding high signal-to-noise spectra for determining the nitrate and nitrite concentrations.

## MATERIALS AND EXPERIMENTAL EQUIPMENT

**Chemical Reagents.** Nitrate and nitrite solutions were prepared from 0.07 and 0.1 M reagent grade stock solutions in reagent grade type II water, respectively. Both standard stock solutions were traceable to NIST primary standard sources.

**Wastewater Solutions.** Samples representative of the soluble components of an activated sludge process reactor were obtained from the Grand Coulee, WA municipal wastewater treatment plant (design capacity 0.30 MGD), which uses a cyclic aerobic/anoxic process operating mode. A sample of mixed liquor was drawn from the aeration basin just at the end of an anoxic period when all of the nitrate and nitrite had been depleted. The sample was immediately filtered through a  $0.45\text{-}\mu\text{m}$  membrane filter to obtain a solution containing only the soluble components of the mixed liquor. Sodium nitrite and nitrate were added to this wastewater sample.

Additional wastewater sample solutions were obtained in a similar manner from the Grand Coulee, WA, WWTP, and from the Bingen, WA, WWTP (design capacity 0.80 MGD) which utilizes a cyclic aerobic/anoxic process operating mode very similar to Grand Coulee. Both of these samples were fully depleted of nitrate and nitrite at the time they were collected and filtered.

The third sample was obtained from the Zillah, WA, WWTP (design capacity 0.31 MGD).

When the sample was collected, the Zillah plant was experiencing a mild process upset with a more turbid effluent than normal. The upset conditions began two weeks previously. Because of the timing of the sample collection, it was not possible to collect a sample that was fully depleted of nitrate and nitrite. In lieu of reaching the depletion end point, the filtered sample was analyzed for nitrate plus nitrite (often referred to as  $\text{NO}_x^-$ ) using the Hach

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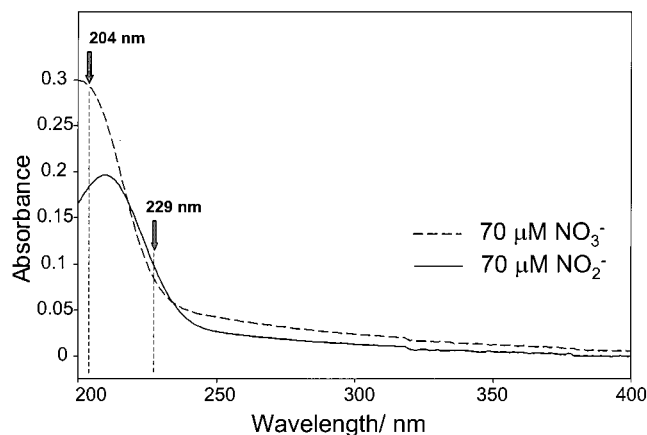


Figure 1. UV absorption spectra of sodium nitrite and nitrate in pure water. Path length, 0.5 cm.

cadmium reduction method.<sup>9</sup> This method usually provides an acceptable approximation for nitrate since nitrite concentrations are typically much lower than nitrate concentrations. The result of this analysis was 0.3 mM  $\text{NO}_x$ .

**UV Resonance Raman Spectroscopy.** The UV resonance Raman spectral measurements used either 204-nm excitation obtained by anti-Stokes Raman shifting the third harmonic of a Coherent Inc. Infinity Nd:YAG laser<sup>10</sup> in  $\text{H}_2$  or 229-nm excitation from a Coherent Inc. CW intracavity frequency-doubled argon ion laser.<sup>11</sup> The Raman scattered light was collected in a  $\sim 135^\circ$  backscattering geometry and dispersed by a Spex double or single monochromator. An intensified CCD detector (Princeton Instrument Co.) was used for detection. Winspec software was used to accumulate the spectra, and Grams software was used for the spectra treatment and analysis.

Typically, an accumulation time of 10 min was used to collect the spectra. The samples were measured in a free-surface flowing stream.<sup>10</sup> The  $1379\text{-cm}^{-1}$  Teflon band was used as an external Raman intensity standard.<sup>12</sup> The Raman spectrum of Teflon was recorded before or immediately after acquisition of the sample spectrum. The  $1640\text{-cm}^{-1}$  water band was used as the internal Raman intensity standard.

Absorption spectra were obtained with a Perkin-Elmer Lambda 9 spectrophotometer in a 0.5-cm cuvette.

## RESULTS AND DISCUSSION

**Absorption Spectra.** Figure 1 shows the absorption spectra of nitrate and nitrite. The absorption maximum of  $\text{NO}_3^-$  is slightly blue-shifted (maximum near 200 nm) compared to that of  $\text{NO}_2^-$  (maximum near 210 nm). In addition, the maximum  $\text{NO}_3^-$  molar absorptivity was  $8.4 \times 10^3 \text{ L}/(\text{M}\cdot\text{cm})$ , which is  $\sim 50\%$  higher than that of  $\text{NO}_2^-$  ( $5.6 \times 10^3 \text{ L}/(\text{M}\cdot\text{cm})$ ).

**UV Resonance Raman Spectra.** Figure 2 shows the UV resonance Raman spectra of nitrate and nitrite in pure water.

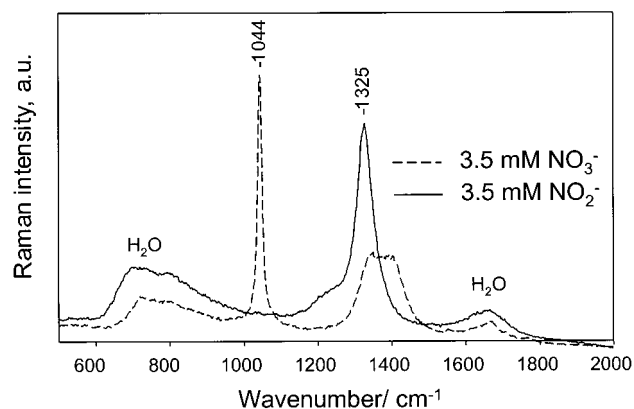


Figure 2. UV resonance Raman spectra of 3.5 mM solutions of  $\text{NaNO}_2$  and  $\text{NaNO}_3$ . Excitation wavelength, 204 nm; power, 10 mW; accumulation time, 10 min. The spectra were measured in a free-surface stream.

Symmetric N–O stretching vibrations give rise to the strong bands at  $1044\text{-cm}^{-1}$  for  $\text{NO}_3^-$  and at  $1325\text{-cm}^{-1}$  for  $\text{NO}_2^-$ . Some medium-intensity bands in the spectrum of  $\text{NO}_3^-$  are also observed between  $1300$  and  $1500\text{-cm}^{-1}$ .

Obviously, nitrate and nitrite are spectrally distinct and can be easily distinguished. There is a partial overlap of the  $1325\text{-cm}^{-1}$   $\text{NO}_2^-$  band with the weaker  $\text{NO}_3^-$  band at  $\sim 1400\text{-cm}^{-1}$ . However, we can easily numerically remove the contributions from nitrate in that spectral interval to obtain the pure nitrite Raman band.

**Nitrate and Nitrite Detection Limits.** To determine the UV resonance Raman spectral detection limits, we examined the dependence of the UV resonance Raman spectra as a function of nitrate/nitrite concentration in pure water (Figure 3). We observe a linear intensity dependence of the absolute Raman intensities over the analyte concentration range of  $7\text{ }\mu\text{M}$  to 3.5 mM. This indicates that, for 229-nm excitation, self-absorption has little impact on the measured intensities since excitation is on the red edge of the absorption band.

To determine the detection limit for measurements of the nitrate/nitrite concentrations using UV resonance Raman spectroscopy, we carefully analyzed spectra at the lowest concentrations measured: 7, 14, and  $35\text{ }\mu\text{M}$  (Figure 3, insets). Raman bands from nitrate and nitrite were clearly observed for analyte concentrations as low as  $14\text{ }\mu\text{M}$ . At  $7\text{ }\mu\text{M}$ , the Raman signal is almost undetectable because of the noise. Therefore, the detection limits for nitrate and nitrite under these conditions is  $<14\text{ }\mu\text{M}$  ( $<200\text{ ppb}$ ).

**Filtered Activated Sludge Wastewater Samples.** Figure 4 shows the  $\text{NO}_2^-$  and  $\text{NO}_3^-$  concentration dependence of the UV resonance Raman spectra in filtered activated sludge wastewater samples. The spectra of the filtered activated sludge wastewater are essentially identical to those of pure water. As in pure water, the Raman intensity decreases as the concentration of analyte decreases. We observe identical Raman detection limits of  $<14\text{ }\mu\text{M}$  ( $<200\text{ ppb}$ ).

**Choice of Excitation Wavelength.** The 204-nm excited UV Raman spectra of  $\text{NaNO}_2$  and  $\text{NaNO}_3$  are essentially identical to those excited at 229 nm (data not shown). The absolute intensities of the  $1325\text{-}$  and  $1044\text{-cm}^{-1}$  bands increase with concentration in the range  $7\text{ }\mu\text{M}$  to 0.35 mM. However, the absolute intensities do

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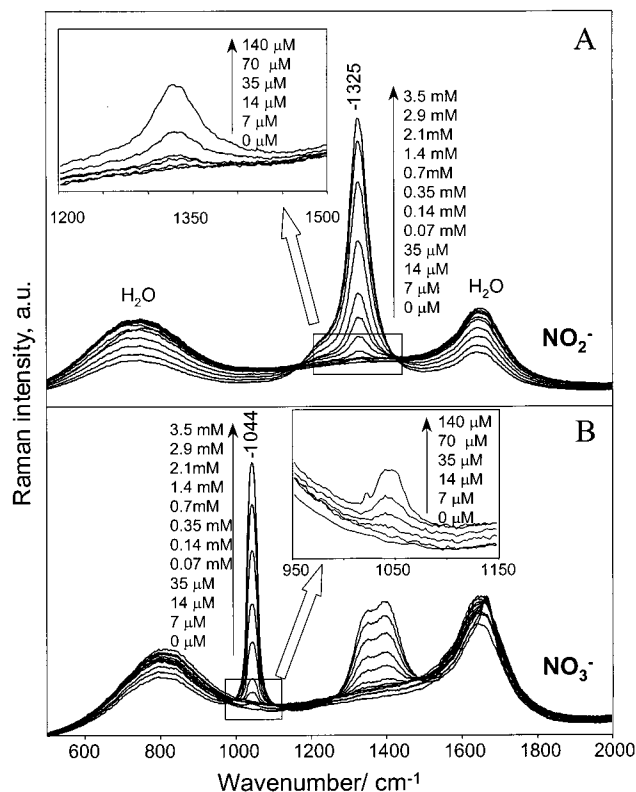


Figure 3. UV resonance Raman spectra of  $\text{NaNO}_2$  (A) and  $\text{NaNO}_3$  (B) in pure water as a function of concentration. Excitation wavelength, 229 nm; power, 10 mW; accumulation time, 10 min. The spectra were measured in a free-surface stream.

not linearly increase at higher concentrations due to self-absorption (Figure 5). The relative intensity ratios of the analyte to the  $1640\text{-cm}^{-1}$  internal standard water band, however, do increase linearly with concentration (Figure 5).

The data indicate that the  $\text{NO}_2^-$  relative to the  $1640\text{-cm}^{-1}$  water band<sup>13</sup> Raman intensity does not significantly change for 204-nm ( $I(1325)/I(1640) = 0.6$ ) excitation compared to 229-nm excitation ( $I(1325)/I(1640) = 0.7$ ). In contrast, we observe an  $\sim 2.5$ -fold increase in the 204-nm  $\text{NO}_3^-$  relative Raman intensity ( $I(1044)/I(1640) = 1.44$ ) compared to 229-nm ( $I(1044)/I(1640) = 0.72$ ) intensity. Thus, 204-nm excitation is preferable for nitrate detection.

**Detection of Nitrate and Nitrite in Filtered Activated Sludge Wastewater Samples.** Filtered mixed liquor samples from the extended aeration activated sludge treatment plants were measured using 229-nm excitation. A mixed liquor filtrate from the Bingen, WA, activated sludge treatment plant showed Raman spectra similar to those from Grand Coulee (Figure 4), which showed no detectable nitrate or nitrite bands, as well as no bands other than those of water.

The sample from the Zillah, WA, WWTP, which was experiencing a mild process upset, was somewhat turbid and showed the Figure 6A absorption spectrum. The absorption below 240 nm is much higher for the Zillah sample than for the other filtered wastewater samples and the pure water 0.07 mM sodium nitrate and nitrite solutions. This results from the fact that the Zillah sample contains 0.3 mM  $\text{NO}_x$ .

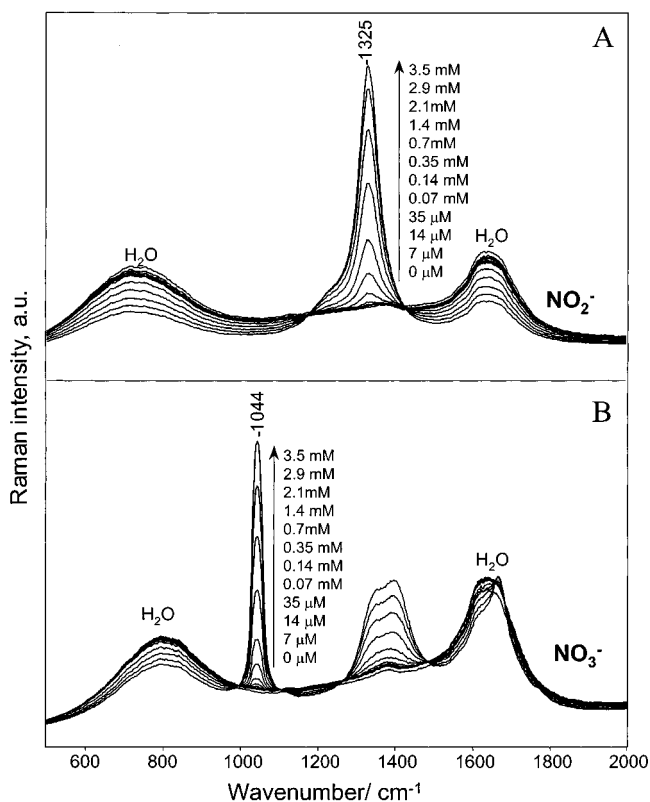


Figure 4. UV resonance Raman spectra of  $\text{NaNO}_2$  (A) and  $\text{NaNO}_3$  (B) in filtered activated sludge wastewater as a function of concentration. Excitation wavelength, 229 nm; power, 10 mW; accumulation time, 10 min. The spectra were measured in a free-surface stream.

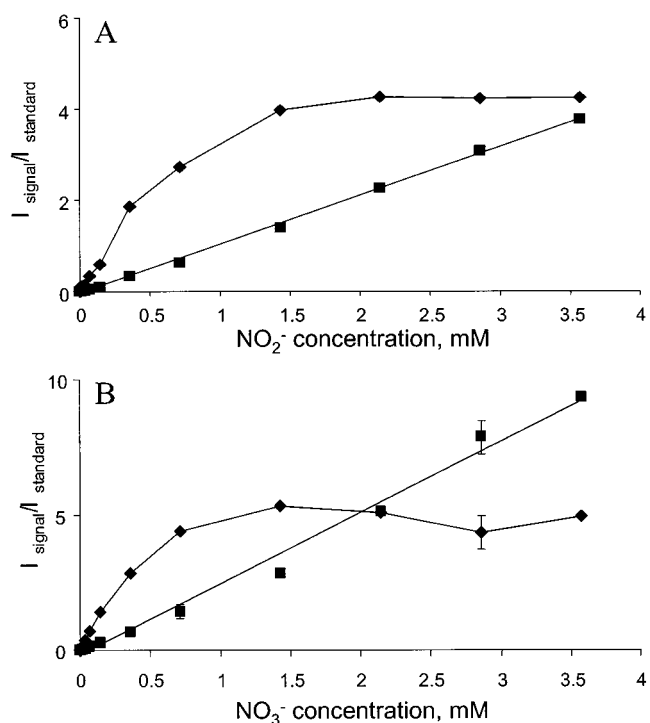


Figure 5. Relative intensities of the 204-nm excited  $\text{NaNO}_2$   $1325\text{-cm}^{-1}$  (A) and  $\text{NaNO}_3$   $1044\text{-cm}^{-1}$  (B) Raman bands as a function of concentration. Diamonds,  $1379\text{-cm}^{-1}$  Teflon band is used as external standard; squares,  $1640\text{-cm}^{-1}$  water band is used as internal standard.

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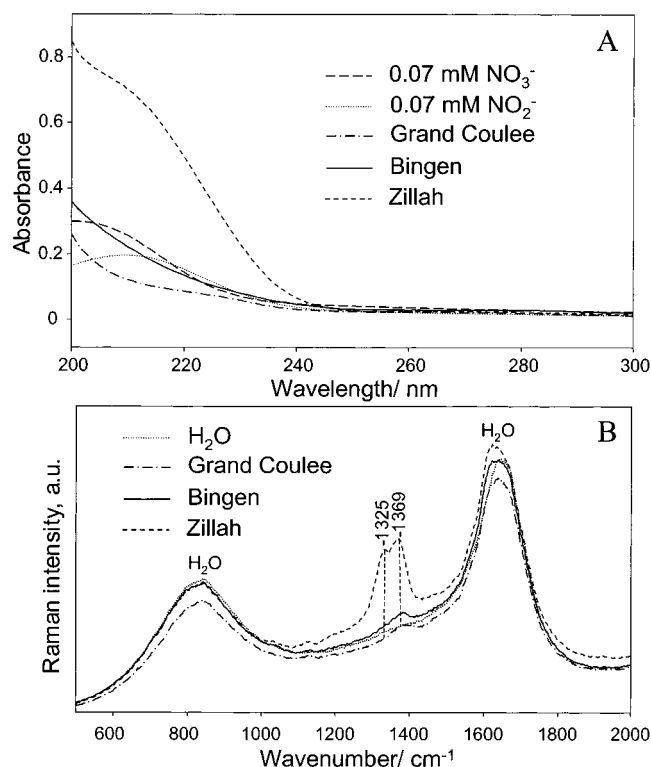


Figure 6. (A) UV absorption spectra of nitrite and nitrate in pure water and of filtered activated sludge wastewater samples. Path length, 0.5 cm. (B) UV resonance Raman spectra of pure water and three filtered activated sludge wastewater samples. Zillah WWTP sample was measured as containing 0.3 mM  $\text{NO}_x$ . Excitation wavelength, 229 nm; power, 10 mW; accumulation time, 10 min. The spectra were measured in a free-surface stream.

Figure 6B shows the Raman spectra at 229-nm excitation for the three filtered activated sludge wastewater samples and pure water. The Raman spectra of the Grand Coulee and Bingen samples are very close to that of pure water. The only additional spectral feature is a weak band at 1369  $\text{cm}^{-1}$ . Thus, it is easy to analyze for species such as  $\text{NO}_3^-$  and  $\text{NO}_2^-$  in wastewater.

The Zillah plant sample, however, shows a 1325- $\text{cm}^{-1}$   $\text{NO}_2^-$  band in addition to another band at 1369  $\text{cm}^{-1}$ . There is no

evidence for the  $\text{NO}_3^-$  at 1044  $\text{cm}^{-1}$ . Thus, all of the  $\text{NO}_x$  measured by the cadmium reduction method was in the form of nitrite. In retrospect, this result can be explained by the upset conditions at the treatment plant in which the *Nitrobacter* bacteria had been lost from the system. This result directly demonstrates the analytical power of UV Raman spectroscopy, which was able to simultaneously measure nitrate and nitrite down to very low detection levels. These data could be used to provide both process control variable input and diagnostic capabilities for wastewater plant upset conditions.

We are as yet unsure of the origin of the  $\sim 1369\text{-cm}^{-1}$  band, which is weak but evident in every wastewater sample. From its frequency and band shape, we tentatively assign it to the symmetric C–O stretch vibration of  $\text{HCO}_3^-$  from dissolved carbon dioxide.<sup>14</sup> Whatever the ultimate assignment, this band is far enough from the 1325- $\text{cm}^{-1}$   $\text{NO}_2^-$  band that it does not interfere with  $\text{NO}_2^-$  determination.

## SUMMARY AND CONCLUSIONS

We have successfully demonstrated the potential of UV resonance Raman spectroscopy for on-line monitoring and process control to improve the reliability and performance of biological nutrient removal wastewater treatment plants. Typical wastewater samples do not show interfering spectral bands or significant interfering absorption features. Routine 10-min spectral measurement gives rise to  $<14\text{ }\mu\text{M}$  (200 ppb) UV resonance Raman detection limits for nitrate and nitrite in water. Excitation wavelengths between 230 and 204 nm are suitable for nitrate and nitrite determination.

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