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Development of a Real-Time, *in situ* Nitrate Sensor

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Development of a Real-Time, In-situ Nitrate sensor

Abstract

Although nitrate fertilizers are critical for enhancing crop production, excess application of nitrate fertilizer can result in ground water contamination leading to the so called "nitrate problem". Health and environmental problems related to this "nitrate problem" have led to serious concerns in many parts of the world including the United States and Israel. These concerns have resulted in legislation limiting the amount of nitrate N in drinking water to 10 µg/g. Development of a fast, reliable, nitrate sensor for in-situ application can be extremely useful in dynamic monitoring of environmentally sensitive locations and applying site-specific amounts of nitrate fertilizer in a precision farming system. The long range objective of this study is to develop a fast, reliable, real-time nitrate sensor. The specific objective of this one year feasibility study was to explore the possible use of nitrate sensor based on mid-IR spectroscopy developed at UCD along with the silver halide fiber ATR (i.e. attenuated total internal reflection) sensor developed at TAU to detect nitrate content in solution and soil paste in the presence of interfering compounds.

Experiments conducted at Technion and UCD clearly demonstrate the feasibility of detecting nitrate content in solutions as well as soil pastes using mid-IR spectroscopy and an ATR technique. When interfering compounds such as carbonates, bicarbonates, organic matter etc. are present special data analysis technique such as singular value decomposition (SVD) or cross correlation was necessary to detect nitrate concentrations successfully. Experiments conducted in Israel show that silver halide ATR fiber based FEWS, particularly flat FEWS, resulted in low standard error and high coefficient of determination (i.e. R^2 values) indicating the potential of the flat Fiberoptic Evanescent Wave Spectroscopy (FEWS) for direct determinations of nitrate. Moreover, they found that it was possible to detect nitrate and other anion concentrations using anion exchange membranes and MIR spectroscopy. The combination of the ion-exchange membranes with fiberoptics offers one more option to direct determination of nitrate in environmental systems.

Achievements:

Direct and real time monitoring of nitrate and other agro-chemicals (e.g. phosphate, ammonium, organic compounds) in soils or agricultural drainage is extremely important for managing nutrients and/or agrochemical application and maintaining a safer and healthier environment. Eshani et al. (2001) used a mid-IR (MIR) diffuse reflectance technique along with a DTGS detector to determine the nitrate content of soil. They found that nitrate ion has a strong absorption peak at 1395 cm^{-1} (asymmetric in-plane stretch mode). Using wavelet analysis technique they were able to determine high concentrations of nitrate ions in soils. They speculated that if an attenuated total internal reflection (ATR) technique is used along with MCT detector which has maximum sensitivity in the range where the dominant nitrate peak exits (1395 cm^{-1}), a real-time nitrate sensor can be developed.

ATR technique has been used in the last few decades for the study of liquids, pastes and powders, in which intense scattering or absorption precluded transmission of a probe beam (e.g., Johnston and Aochi, 1996). When light is totally internally reflected in waveguides (or prisms) placed in vacuum, there is an evanescent wave that decays exponentially outside the waveguide over a distance of half a wavelength. When the waveguide is immersed in a liquid or other medium, the evanescent wave may be partially or totally absorbed and the transmission may be reduced. With the development of ATR fibers that can transmit well into the mid-IR, it is now possible to successfully use these elements in ATR systems. Short segments of ATR fibers, such as mixed silver halide ($\text{AgCl}_x\text{Br}_{1-x}$) IR fibers, can be used as sensing ATR elements in FTIR systems. These fibers offer several important advantages over common ATR elements being easy to prepare, inexpensive and handy for *in-situ* or direct application. These features have played a crucial role in the introduction of Fiberoptic Evanescent Wave Spectroscopy - FEWS (Messica, et al., 1996). This novel system consists of four parts: IR source, two long IR cables, a short ATR/FEWS sensor element, and an IR detector, shown in Fig. A1. The FEWS system can be used for spectroscopic measurements in real-time and in remote locations.

In both common ATR and FEWS systems noise and soil solution/paste constituents can interfere with the signals of nitrate and other polyatomic ions of interest. Therefore, efforts were devoted in this work to the identification of the possible sources of interference and to the improvement of methods for treating and processing the signals obtained from the FTIR spectrometer. The details of the experimental techniques, data analysis procedure, and

results are included in Appendix A (contributions from Israel) and Appendix B (contributions from US). Significant achievements are listed below:

- ◆ Use of ATR technique and MCT detector along with MIR spectroscopy reconfirmed the existence of asymmetric in-plane stretch peak for nitrate ion at 1395 cm^{-1} . However, the base width of the peak was 200 wavenumber within which peaks corresponding to organic matter, carbonates, and bicarbonates significantly overlapped;
- ◆ Use of single value decomposition (SVD) or cross correlation (CC) could overcome the interfering chemicals such as organic matter and carbonates, and predict nitrate ion concentration with very high coefficient of determination;
- ◆ In general, use of Flat FEWS was superior to cylindrical FEWS or regular ATR techniques. These fibers are two to three orders of magnitude cheaper than ATR crystals and can be employed for sensing nitrate concentrations in remote locations;
- ◆ The technique worked better with 2:1 water to soil extract and soil paste than with 10:1 water to soil extract;
- ◆ Although the UC Davis experiments were limited to nitrate solutions and Yolo loam soils, the tests conducted in Technion included eight different soils from sandy loam to clay including peat which indicates that the potential exists for a nitrate sensor based on MIR spectroscopy using flat FEWS.
- ◆ Anion exchange membranes and MIR spectroscopy can also be used to detect nitrate and other anion concentrations in soil.

Thus we have established the feasibility of determining nitrate ion concentration in soil solutions or soils pastes using MIR spectroscopy and ATR techniques. Key to successfully determining nitrate ion concentration is the use of SVD or CC data analysis techniques that are capable of removing interfering effects of other chemicals such as organic matter, carbonates, and bicarbonates.

Impact: Nitrate contamination of ground water has become a serious concern worldwide due to the health and environmental problems related to this “nitrate problem”. These concerns have resulted in legislation limiting the amount of nitrate N in drinking water to $10\text{ }\mu\text{g/g}$. Development of a fast, reliable, nitrate sensor for in-situ application can be extremely useful in dynamic monitoring of environmentally sensitive locations and applying site-specific amounts of nitrate fertilizer in a precision farming system.

Details of cooperation: Telephone and e-mail communications have been the primary means of communications during this one year period. Dr. Katzir visited UC Davis and discussed ATR technique and the use of FEWS with Dr. Upadhyaya and his associates. Drs. Upadhyaya and Shmulevich had further discussions on the project during the American Society of Agricultural Engineers meeting in US.

Publications:

Poster presentation: Kenny, A. Y. Shmulevich, Y. Reichlin, A. Katzir, and A. Shaviv. 2001. IR fiberoptic systems for *in situ* and real-time monitoring of mineral N in water and environmental systems. 11th N. Workgroup, September 2001. France.

Proposed Paper Presentation: Shaviv, A, A. Kenny, I. Shmulevitch, Y. Reichlin, and A. Katzir. 2002. Real-time and remote monitoring of soil and water pollutants by mid-IR fiberoptics. To be presented at the 17th World Congress of Soil science, August 2002, Bangkok, Thailand.

Brroksby, A. P., S. K. Upadhyaya, and D. S. Slaughter plan to present their results at the 2003 American Society of Agricultural Engineers Annual meeting in Las Vegas, US.

Paper In Preparation: Avi SHAVIV, A. KENNY, I. SHMULEVITCH, L. Singer, Y. REICHLIN & A. KATZIR, Direct and real time determination of nitrate in solutions and soil samples by mid-IR Fibreoptics, to be submitted to ES&T.

Appendix A: Details of Investigations conducted in Israel

Investigators: Avi Shaviv, A. Kenny, and I. Shmulevitch

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Materials and Methods

Experiments were performed in a system similar to the one shown in Figure A1 using a BRÜKER VECTOR 22 FTIR spectrometer. Spectra of the different samples were determined in the range of 800 to 2000 cm^{-1} using the FEWS with cylindrical or flattened fibers and compared with the spectra obtained with ZnSe-ATR crystals and DTGS detector. Experiments were conducted with pure solutions and with soil water extracts, suspensions and pastes. Some basic characteristics of the soils used for this study are given in Table A1. The work consisted of several stages, which are detailed below:

1. MIR spectra of common anions in solutions of de-ionized water –

Spectra of NO_3^- , NH_4^+ , $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$, HCO_3^- , and SO_4^{2-} in water were obtained with a conventional ZnSe ATR crystal placed in the FTIR spectrometer with a DTGS detector. The concentrations of the ions were in the range of 500 to 1000 meq l^{-1} . The spectra assisted in defining the wave numbers of the main peaks associated with these ions, the identification of possible interference with nitrate and they served for the more complex signal processing. This set of spectra is denoted as the reference set.

Figure A1- Schematic of the experimental system consisting of an IR source (tunable IR source or FTIR source), silver halide fibers as wave-guides, FEWS or ATR sensing element and detector.

Table A1 – Basic features of the eight soils used for nitrate determinations.

Soil Name	Soil Type	Saturated paste – moisture, w/w %
Hamra A1 (non-agricultural)	Sandy Loam	35%
Hamra 1 (agricultural soil)	Sandy Loam	38.5%
Grumusol	Clay	76.5%
Loess – Besor	Loam	40.3%
Volcanic-	Clay	59.9%
Loess-Germany	Loam	44.4%
Bet-Shèan	Clay, Calcareous	49.2%
Tourba	Peat	356.0%

2. Nitrate in de-ionized water with silver halide fibers –

Two types of fibers were used in this study. These two types were: cylindrical one - about 0.9 mm diameter, 80 mm long, and flattened ones 0.17 mm thick, 4 mm wide and 40 mm long (Hahn et al., 2001). Samples were poured in a special cell in which fibers were mounted. This enabled addition of solutions, suspensions or pastes to the cell in which the fiber serves as a FEWS device (Walsh et al., 1996, Regan et al., 1996). Special lenses were used to connect the cell to the IR source of FTIR spectrometer and an integral MCT detector. Nitrate concentration range tested with the cylindrical fiber was 0 to 300 and with the flattened fiber it was 0 to 100 and 0 to 300 mg N l⁻¹. The results obtained with the FEWS were compared to two experimental sets run with the ZnSE ATR crystal with nitrate concentrations in the range of 0 to 300 mg N l⁻¹. Calibration curves were developed on the basis of absorbance difference between the nitrate peak at 1350 cm⁻¹ and the baseline at about 1250 cm⁻¹ (This similar to colorimetry, where one wave length is used for measurement. The base line at 1250 cm⁻¹ is used as an internal standard). These were compared to calibration curves obtained applying the Cross-Correlation method (Smith 1997) for the same data. In this case the correlation was done over the range of 1229 to 1471cm⁻¹.

3. Nitrate in different soil water extracts or suspensions with improved flattened silver halide fibers and with ZnSe ATR devices-

These tests were conducted with improved flattened fibers. It consisted of experiments with different soil to water extracts or suspensions as described below:

i. In the first series of tests, nitrate was added to 1:10 soil : de-ionized water (weight basis) suspensions to achieve solution concentrations in the range of 0 to 500 mg-N l⁻¹. The soils (Table A1) used for this purpose was a sandy loam (Hamra 1) and a calcareous clay (Grumusol). This was compared to spectra obtained with nitrate that was added to a 1% Na-Montmorillonite suspension.

ii. The second set of tests was conducted with 2:1 water to soil extracts to which nitrate was added (0 to 500 mg-N l⁻¹). The spectra were obtained for the clay (Grumusol) and sandy loam (Hamra) soils (Table A1). The extracts were done in two ways - a. extraction with 0.05N CaCl₂ and b. *acidic* extraction by addition of HCl to create a pH of 2.5 in the sandy loam and 4.5 in the Grumusol.

iii. The third set of tests was performed with 7 different soils and water to which de-ionized water was added to form a "saturated paste". The sensor in this case was a ZnSe ATR crystal since it was more robust compared to the flat FEWS. Note that in this case a sandy loam soil Hamra 1 was used (agricultural source). Nitrate was added to the "pastes" to obtain solution concentrations in the range of a few to about 1000 mg-N l⁻¹ ("real" concentrations were determined individually for each soil by an auto-analyzer before "spiking" with nitrate solutions of known concentrations). For the special treatment and optimization procedures this set of the seven different soils was denoted as the basic set. In addition to the basic set of soils one more soil, a sandy loam, Hamra A1, (non-agricultural) was created similarly to serve as a validation set.

4. Spectrum of soil before and after burning at 550°C –

Spectra were obtained for saturated pastes of the Hamra soils before and after burning at 550°C. These were also compared to spectra obtained for treated effluents, which are known to contain soluble organic compounds.

5. Direct determination of anion concentration on ion-exchange membranes by MIR transmission

Anion exchange membranes with OH⁻ as the counter ion (BDH, type B551642S, ion exchange capacity ~ 100 micro-equivalent cm⁻²) were used as anion sinks from water solutions. One cm² pieces of the anion exchange membrane were placed in small vials containing potassium salt solutions (nitrate, or bicarbonate) at levels, which allowed partial loading (0 to about 70%) of the membrane with anions. The sorption was fast and occurred in less than 5 min. The membrane was transferred to the FTIR spectrometer after gentle wiping. The pieces were mounted on a special holder and MIR light was transmitted through them. An optical band-pass filter combined with an MCT detector was used in this case. The absorbance of peaks (subtracting the baseline) at 1350 and 1365 cm⁻¹ were correlated with the added equivalent fraction of nitrate and bicarbonate concentrations, respectively.

6. Data processing of Spectra and Calibration Curves

The spectra were first treated by using a moving average filter, and/or a custom filter. The custom filter was built on the basis of the variance of 30 repeated measurements of water. Calibration curves were obtained assuming linear correlation between the absorbance and concentration and for each curve the standard error of estimate, SEE, the coefficient of determination, R², and normalized standard error index, SEEI (SEE divided the mean value of measurements) were calculated.

The standard error of estimate (SEE) is given by:

$$SEE = \sqrt{\frac{\sum (y - \hat{y})^2}{n - d}}$$

Where, y is the actual value, $\hat{y}$ is an predicted value of y , n is the number of measurements, d denotes the number of degrees of freedom – for linear correlation between y and $\hat{y}$, $d=2$.

The second calibration technique was based on the cross correlation (CC) method (Smith 1997), in which the spectrum of a given sample (with known concentration), in the range of 1229 to 1471cm⁻¹, was correlated with that of nitrate spectrum obtained in experiments described in section 1.

Results and Discussion

Spectra of common anions in soil solution

Typical spectra of nitrate, phosphate, bicarbonate and sulphate solutions are shown in Figure A2. The peak with the highest chance to interfere with nitrate (1350 cm^{-1}) is that of bicarbonate (1365 cm^{-1}). Fortunately, the peaks of nitrate and carbonate are not symmetric, nitrate having a shoulder towards the higher wavenumber and bicarbonate to the other direction. Some minor overlapping occurs with ammonium, sulphate and phosphate (H_2PO_4^-) also. The spectra of this reference set were used for advanced signal processing using Cross Correlation and an optimization procedure.

Nitrate in de-ionized water –cylindrical and flattened fibers

To compare the accuracy that can be achieved with a given system, values of the SEE, SEEI and R^2 obtained for single point calibration curves and for the simple application mode of the Cross Correlation method were used as primary estimators of the performance of the different sensors in different water and soil systems (Tables A2 and A3) Considering the single point calibration results (Table A2) the cylindrical fiber ($R^2 = 0.837$, SEEI=23.8%) appears to be inferior to the flat FEWS and the common ZnSe ATR crystal for nitrate in de-ionized water. The flat FEWS (Table A2) performs better than the ATR in this case but at this stage the fiber can be used only for a limited number of determinations (between 6 to 15 in soils).

The improved performance of the flat FEWS indicates the importance of the flattening the fibers. The improvement was obtained despite the shorter length of the flat fiber (40 mm) as compared to the cylindrical one (80 mm). The use of improved flattened fibers in the subsequent experiments resulted in even better results. It is assumed that the detection limit can be improved by further flattening the fibers and/or by using a stronger IR source.

Application of the simple mode of the Cross Correlation method to the results obtained for the flat fiber and the ZnSe crystal further improved the results particularly for the ZnSe (compare Table A3 to Table A2).

Table A2 – Values of SEE, SEEI, R^2 , for linear regression, obtained for “one point calibration curves” of nitrate in water, water extracts, suspensions and soils paste, by different ATR/FEWS devices and under different conditions

Experiment Number	Sample Media / Measurement Sensor	Concentration Range [ppm-N]	Number of Samples	single point calibration ¹		
				R^2	SEE [mg/l]	SEEI
2	Water (Flat FEWS)	10-100	10	0.994	2.76	4.77%
2	Water (Cylindrical FEWS)	10-300	29	0.837	36.8	23.8%
2	Water (ATR)	0-300	31	0.898	29.5	19.66%
2	Water (ATR)	0-300	31	0.833	37.8	25.22%
3 i	Montmorillonite suspen. (Flat FEWS)	50-500	6	0.994	17.2	6.66%
3 i	Sandy Loam 10:1 extr. (Flat FEWS)	0-1000	7	0.616	246.1	68.91%
3 i	Grumosol 10:1 extr. (Flat FEWS)	0-400	5	0.670	110.7	63.26%
3 ii	Sandy Loam 2:1 extr. (Flat FEWS)	0-500	8	0.868	90.1	35.18%
3 ii	Grumosol 2:1 extr. (Flat FEWS)	0-500	7	0.907	68.4	30.91%
3 ii	Sandy Loam, Acidic 2:1 extr. (Flat FEWS)	0-500	7	0.958	45.7	20.64%
3 ii	Grumosol, Acidic 2:1 extr. (Flat FEWS)	0-500	7	0.996	14.5	6.54%
3 iii	Sandy Loam, Saturated Paste, Hamra A1, (ATR)	30-900	30	0.976	41.7	8.97%

¹ the calibration performed for 2 degrees of freedom.

Table A3 – Values of SEE, SEEI, and R^2 , for the simple Cross Correlation procedure applied on nitrate in for several of the examples shown in Table A2.

Experiment Number	Sample Media / Measurement Sensor	single point calibration ¹			cross-correlation calibration ^{1,2}		
		R^2	SEE [mg/l]	SEEI	R^2	SEE [mg/l]	SEEI
2	Water (Flat FEWS)	0.994	2.76	4.77%	0.995	2.58	4.47%
2	Water (ATR)	0.898	29.49	19.66 %	0.926	25.24	16.82%
2	Water (ATR)	0.833	37.82	25.22 %	0.998	4.18	2.79%
3 ii	Sandy Loam Paste (ATR)	0.976	41.70	8.97%	0.999	8.06	1.73%

¹ the calibration performed using 2 degrees of freedom.

² Cross-Correlation performed in the range of 1229 to 1471 cm^{-1} . Two point MAF was applied without optimization.

Figure A2: Spectra of nitrate, bi-carbonate, phosphate, sulphate and ammonium in water – reference set.

Figure A3: – Spectra of Hamra soil in: 2:1 (water/soil) extract, saturated paste, difference of spectra for non-burnt minus burnt soil, and primary and secondary effluent (these are overlapping).

Nitrate in soil and montmorillonite suspension – flattened silver halide fiber

The spectra obtained with the 1% montmorillonite suspensions containing nitrate yielded results quite close to those obtained in water only with the flat FEWS (Table A2). The values of SEE and SEEI were 17.2 and 6.7%, respectively and R^2 was 0.994. The suspended clay particles did not cause significant interference with the nitrate peak. In such systems, possible interference of the clay particles with solution constituents is negligible preassumably due to the relative dilution of particle in suspension.

Nitrate in 10:1 water soil extracts – flattened silver halide fiber

Table A2 indicates that for 10:1 water to soil extracts, the values of R^2 for both soil extracts were the lowest out of all the experiments in Table A2 and the SEE and SEEI values were the largest. The extraction in this case caused significant disturbance to the system. This may also be attributed to the use of de-ionized water, which definitely causes strong dispersion.

Nitrate in 2:1 water soil extracts – flattened silver halide fiber

In this case the water:soil ratio was reduced to 2:1 and thus the interference of solution constituents (e.g. carbonate, sulphate, ammonium and dissolved organic matter) could become more dominant than in the 10:1 suspension. No significant new peaks were identified in this case (Figure A3), implying that the potential for interference at this dilution is small. Moreover the statistical criteria show improved performance as compared to the 10:1 extracts (Table A2). The R^2 were 0.868 and 0.907 for the sandy loam and the grumusol, respectively and the SEEI in the range of 30 to 35% whereas with the 10:1 they were in the range of 63 to 68%. The improvement in this case is attributed to the fact that the extraction was done in 0.05 N CaCl_2 , which preassumably reduced or prevented dispersion of clay or OM particles.

The acidification of the system further improved the results and reduced the noise and interference in the system yielding even better values of R^2 and SEE or SEEI (Table A2). The effect in this case can be both attributed to reduced dispersion and to lower solubilization of organic compounds.

In spectra obtained for pastes there are about six peaks around 1050, 1100, 1250, 1400-1450, 1600 and 1750 cm^{-1} (Figure A3), which do not correspond with nitrate. Part of these may be attributed to soluble organic constituents (Wander & Traina 1996; Ellerbrock et al., 1999), ammonium (around 1450 cm^{-1}), phosphate or colloidal particles. Most of these peaks, and particularly the prominent ones at wave numbers below 1450 cm^{-1} do not appear in the 2:1 and 10:1 water:soil extracts.

As shown in Table A4 the interference caused by the soil constituents in the paste is indeed larger than in the 2:1 water:soil extracts and thus for some of the soils very poor results were obtained with the single point calibration in terms of R^2 , SEE and SEEI. This was particularly so with the more basic and high calcium carbonate soils: the Calcareous Grumusol, the Grumusol and the Loess resulting in R^2 values of 0.342, 0.555 and 0.763, respectively. Accordingly the SEEI values for these soils were in the range of 35 to 46%. Surprisingly, the results obtained with the Sandy loam paste and particularly with the non-agricultural (Hamra A1, lower clay and lower water holding capacity) were very good with the single point calibration (Table A4) with R^2 0.976 and SEEI of 9%. Good results were also obtained with the peat medium (Table A4), which had a relatively low pH (about 4.5) and only a little amount of suspended particles.

A dramatic improvement was obtained in all cases when the simple mode of the cross correlation method was used. Even the poor results obtained with the Calcareous Grumusol became reasonable and R^2 was increased from 0.342 to 0.732 and the SEEI was reduced from 46% to 29%. The results obtained for the two Sandy loam soils, the peat and the volcanic soil were practically very good, with R^2 of 0.998-0.999 and SEEI values ranging between 1.7 to 5.5 %. The values of the SEE for the two Sandy loam soils were 8 and 13 mg N l^{-1} for the pastes. This implies that for these light soils where the moisture was 35 to 38%, the SEE on the dry soil basis should be divided by a factor of three. This practically means that the detection limits of nitrate in this case can be reduced to a few ppm (2.5 to 4).

These results are expected to be further improved by: i. modifying the fibers (flattening or coating), ii. Choosing a stronger IR source, iii. Further reducing soil moisture content, iv. More advanced signal processing techniques.

Spectra of normal vs. burnt Hamra soil

The burning at 550°C is supposed to remove the OM from the soil (Cox et al., 2000). As can be seen in Figure A3, the prominent peaks between 1000 and 1200 cm⁻¹ did not disappear when subtracting the spectrum of burnt from normal soil, indicating that they are associated with organic matter. The area between 1250 to 1500 cm⁻¹, which is the most relevant for nitrate, is almost flat. This implies that the burning did not change significantly the region where significant interference is expected for nitrate. Attention should be paid to the possibility that the far edge of the peak near 1200 cm⁻¹ which is associated with OM may interfere with nitrate, since it is orders of magnitude higher than the peak corresponding with a few tens or even 100 mg N-NO₃ l⁻¹.

Table A4 : Values of SEE, SEEI, F, R², for linear regression, obtained for “single point calibration curves” and for the Cross Correlation method applied to 8 “saturated pastes” of different soils spiked with nitrate. Determinations were done with ZnSe ATR crystal.

Description of medium/soil	Concentration Range [ppm-N]	Number of Samples	single point calibration ²			Cross-correlation calibration ^{2,3}		
			R ²	SEE [mg/l]	SEEI	R ²	SEE [mg/l]	SEEI
Sandy Loam (A1) ⁴	30-900	30	0.976	41.70	8.97%	0.999	8.06	1.73%
Calcareous Grumusol	100-1001	11	0.342	255.78	46.43%	0.732	163.27	29.64%
Acidic Silt	133-1097	11	0.762	164.50	26.70%	0.985	41.33	6.72%
Grumusol	21-942	11	0.554	215.02	44.66%	0.929	85.76	17.81%
Sandy Loam I	0-981	11	0.814	147.99	30.16%	0.998	13.17	2.68%
Loess	13-969	11	0.733	172.68	35.18%	0.769	160.65	32.73%
Peat	0-953	11	0.967	60.58	12.72%	0.998	20.47	4.30%
Volcanic ash	45-925	11	0.903	95.82	19.76%	0.998	26.96	5.56%

¹ all the samples are from experimental set 3 iii.

² the calibration was performed using two degrees of freedom.

³ Cross-Correlation was performed in the range of 1229 to 1471cm⁻¹. Two point MAF was used. No optimization was used.

⁴ This soil served as a validation set

Determination of anion concentration on ion-exchange membranes

A typical energy transmission spectrum of the OH^- loaded anion exchange membrane (BDH) is given in Figure A4 showing the regions in the MIR, which can be effective for detection of mid-IR responsive species or molecules. The energy transmission in the region relevant for ion such as nitrate, bicarbonate, sulphate and phosphate (1000 to 1500 cm^{-1}) is partial but reasonable. To improve detection, a MCT detector was used instead of the DTGS one, and to avoid saturation problems an optical band pass filter was applied.

Figures A5 and A6 show the correlation between the absorbance and equivalent fraction of the added ions relative to membrane capacity. Figure A5 shows a linear increase of the absorbance with the percent of nitrate loading to about 60% ($R^2 = 0.988$). At loading higher than 60% two distinct peaks are observed at 1340 and 1380 cm^{-1} . According to Wissbrun & Hannon (1975) this may be attributed to two types of vibrations of the nitrate: each one associated with interaction with different sites on the membrane. Figure A6 shows the change in absorbance of bi-carbonate with its equivalent loading fraction. In this case the scattering starts after 30% loading.

These results demonstrate the possibility of direct determination of nitrate or bi-carbonate concentrations using anion-exchange membranes. The determination can be done via direct transmission of the MIR energy through the membrane. This offers the possibility of remote sensing of such ions by combining the silver halide fibers, as waveguides, with the membranes as sensing elements.

Figure A4: Spectrum of energy transmission through the BDH anion-exchange resin.

Figure A5: Correlation between absorbance difference (1350 to 1200 cm⁻¹) and equivalent percent of nitrate added relative to membrane capacity.

Figure A6: Correlation between absorbance difference and equivalent percent of bicarbonate added relative to membrane capacity.

APPENDIX B: Details of Investigations in US

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Determination of the nitrate concentration in water and soil samples that contain carbonate, bicarbonate and humic acid using infrared (attenuated total reflection) spectroscopy.

Materials and Methods:

1. Experimental Procedure.

Chemicals.

NaNO₃, Na₂CO₃, NaHCO₃ and humic acid (Aldrich) were used as received. Yolo loam soil was pretreated by air heating to 105°C for 24 hours to remove microbial activity. The dry bulk density was determined to 1.09 g cm⁻³. The dried soil was passed over a sieve (75 µm wire mesh) and the fine powder was used for all experiments. Nanopure water with a resistance higher than 17.9 MΩ was obtained from a Barnstead filtration unit operating with four cartridges for the removal of both organic and ionic impurities. NaNO₃, Na₂CO₃, NaHCO₃, humic acid and water or soil solutions were prepared using sample weights measured at approximately 25 °C and later converted to molarity or to the ppm scale where appropriate. A specific gravity value of 2.65 was used for molarity calculations involving Yolo loam soil.

Spectroscopy.

A Mattson Galaxy 3000 RS-1 spectrometer was used for all infrared measurements. The spectrometer was operated at ambient pressures in an environment that had been purged significantly free of CO₂ and atmospheric water (PUREGAS Air Dryer, model CDA1120). The spectrometer was equipped with a Ge/KBr beamsplitter, a mechanical interferometer having cubic mirrors, a water cooled Globar ceramic source and an MCT detector. The ATR cell was an "ARK" cell purchased from SpectraTech. This cell has two operating modes, one for liquid samples and one for solid samples. Each operating mode uses a ZnSe trapezoidal prism with an angle of incidence of the infrared beam fixed at 45°.

All ATR spectra were obtained using 4 cm⁻¹ resolution and calculated by taking the negative logarithm of the ratio of sample and background single beam spectra. The empty ATR cell blanketed with argon gas was used to collect the background spectrum. Calibration of the ATR cell was accomplished with a program (Loring & Fawcett 1999; Loring 2000) that uses the procedure described by Sperline et al. (1986) and Bertie et al. (1995). The ATR spectrum of an optical standard (Toluene) for which the refractive indices are tabulated was collected using s- or p-polarised light. The angle of incidence or number of reflections in the

cell can be determined through a minimization of the sum of the squares of the deviations between the tabulated and measured s- or p-polarised ATR spectra.

Description Solution Samples Tested.

Five types of infrared ATR tests were conducted in this study. They were: (a) Nitrate in Water; (b) Nitrate in Water Containing Carbonate and Humic Acid; (c) Nitrate in Soil (Yolo Loam); (d) Nitrate and Carbonate in Soil (Yolo loam); (e) Nitrate, Bicarbonate and Humic Acid in Soil (Yolo loam).

(a) Solid sodium nitrate was added to nanopure water. The range of the nitrate concentration was $0.0 - 0.007 \text{ mol dm}^{-3}$ and the total number of samples examined was 16.

(b) Solid sodium nitrate, solid sodium carbonate and solid humic acid were added to nanopure water. The concentration ranges for (i) nitrate was $0.0 - 0.0028 \text{ mol dm}^{-3}$; (ii) carbonate was $0.0 - 0.0011 \text{ mol dm}^{-3}$; (iii) humic acid was $0.0 - 1.5 \text{ g L}^{-1}$. The total number of samples examined was 27.

(c) Solid sodium nitrate was added to a known weight of dry soil. To this mixture a known weight of water was added. The range of concentrations for nitrate was $0.0 - 0.30 \text{ mol dm}^{-3}$. A known amount of water was added resulting in a slurry that contained approximately 1:1 water to dry soil. The total number of samples was 55.

(d) Solid sodium nitrate and solid sodium carbonate were added to a known weight of dry soil. To this mixture a known weight of water was added. The range of concentrations for nitrate was $0.0 - 0.30 \text{ mol dm}^{-3}$ and for carbonate $0.0 - 0.03 \text{ mol dm}^{-3}$. A known amount of water was added resulting in a slurry that contained approximately 1:1 water to dry soil. The total number of samples was 17.

(e) Solid sodium nitrate, solid sodium bicarbonate, and solid humic acid were added to a known weight of dry soil. To this mixture a known weight of water was added. The range of concentrations for nitrate was $0.0 - 0.30 \text{ mol dm}^{-3}$; bicarbonate $0.0 - 0.03 \text{ mol dm}^{-3}$; humic acid $0 - 1.8 \text{ g L}^{-1}$. A known amount of water was added resulting in a slurry that contained approximately 1:1 water to dry soil. The total number of samples was 30.

Multiple dimensional curvefits (Loring, 1997-2002) were performed using an SVD and factor analysis routine (Loring, 1997-2002; Malinowski, 1991). The SVD output allows the determination of the number of significant basis spectra for a series of samples. If no prior knowledge of the basis spectra is known then this is an important advantage. The factor analysis routine allows the contribution of each of the basis spectra to the measured spectrum to be determined. The significance of the basis spectra was evaluated numerically by its percent variance. A basis spectrum was considered insignificant if it accounted for less than 0.01 % of the variance. The spectra with percent of variance below 0.1 were attributed to noise and baseline drift.

Single dimensional curve fits were also performed using a factor analysis routine. The measured spectra that has known constituents but at unknown concentrations can be curve fitted using a series the individual spectra for each species present. That is, the spectra of a sample that has an unknown composition can be curve fitted using the spectra of the individual components in the system. Single dimensional curve fit were performed using the "Linkfit" program developed at UC Davis (Loring, 1997-2002).

The SVD and factor analysis allows for the user to input the known concentrations for each species in the spectra into the model and thereby obtaining the individual spectra for each of those species and their contribution to each spectrum. Linkfit allows the user to fit the spectra of unknown solution concentrations provided that each component present is known and a spectrum for those components are known independently. A detailed description of all the software used in this analysis has been published elsewhere (Loring & Fawcett, 1999).

The Vibrational Spectrum of the Nitrate Ion.

The nitrate ion (NO_3^-) is a planar molecule with D_{3h} point group symmetry. The number of fundamental vibrational modes is 4, ($\Gamma_{\text{vib}} = A_1' + 2E' + A_2''$) and are shown in Schematic B1. The NO_3^- vibrational mode of interest in this ATR study is the ν_3 asymmetric stretching mode.

Schematic B1. The fundamental vibrational modes of NO_3^- .

Results and Discussion:

2. Nitrate in Water.

ATR spectroscopy is a useful technique for observing the infrared vibrational spectrum of aqueous solutions (Mirabella, 1993). The large hydrogen bond density of liquid water is highly absorbing in the infrared spectrum and transmission cell techniques require extremely short pathlengths in order to avoid saturation effects. For ATR spectroscopy, the effective sample pathlength (penetration depth of the evanescent wave) is a function of the optical properties of the system, the wavelength and the angle of incidence of the infrared light. Thus the pathlength of the evanescent wave in most typical ATR cells is the order of microns, which is more suitable for infrared spectroscopy of aqueous solutions or other highly absorbing environments. For this reason, the ATR method is increasingly used to examine the molecular structure of pure water and solutions where water is a major component. Additionally, the ATR spectrum is not a linear absorbance spectrum and therefore contains no useful information regarding molar absorptivities. The spectra presented here are ATR spectra that have not been converted to absorbance spectra.

Figure B1 (part a) shows the infrared spectrum of pure liquid water. The broad intense bands that appear between 2800 and 3800 cm^{-1} are due to the νOH (stretching) vibrational modes. The sharp, intense band centered at 1640 cm^{-1} is the δOH (bending) vibrational mode. The other bands that appear in the spectrum at 2100, 730 and the plateau region between 1640 and 730 cm^{-1} are related to water overtone and librational modes. The intensity and broadness of the water bands make the determination of other species present at low concentration difficult. To illustrate this, Figure B1 (parts b-d) are the spectra of water that contains nitrate at 500, 1000 and 5000 ppm. Water librational modes are intense in the region where the NO_3^- ν_3 vibrational mode occurs and this restricts the effective concentration range where NO_3^- can

be observed to the order of hundreds of ppm. Spectral subtraction techniques are then required in order to observe the NO_3^- vibration below 1000 ppm. For this reason, all ATR spectra have had the water component removed prior to the analysis of those spectra. In addition, each spectrum was baseline corrected and offset to zero absorbance. The spectrometer drift was removed from the spectra by subtracting a specific spectral file that contains the spectrometer response as a function of time. This last correction was not required for almost all experiments; however, it was used for a small number that had long collection times. The result of the water subtraction and baseline corrections can be seen in Figure B2 that shows the infrared vibrational band for NO_3^- in water at 388 ppm ($6.251 \times 10^{-3} \text{ mol dm}^{-3}$). Removing the water contribution to the spectrum improves the observed detection limit for NO_3^- down to approximately 50 ppm. However, this is still not satisfactory for the purposes of determining the NO_3^- concentration of soils, where NO_3^- concentrations as low as 5 ppm are of interest.

The behavior of the nitrate band for a range of concentrations in pure liquid water was examined. Four individual experiments containing a total of 16 samples were performed to collect the data. For each experiment, a known quantity of NaNO_3 was added to a known quantity of water. The result for the intensity at 1395 cm^{-1} is shown in Figure B3. This frequency was chosen because the contribution to the infrared spectrum from the species other than nitrate when present (such as carbonate and bicarbonate that have bands close to that of nitrate) could be minimized while maintaining the contribution from nitrate somewhat high and measurable above the background noise. Hence all of the spectral intensity information given are with respect to the 1395 cm^{-1} frequency. The result shows the intensity of the nitrate band with respect to nitrate concentration is a linear relationship as expected from the Beer-Lambert law of infrared spectroscopy. A regression analysis of the intensity values are given in Table B1.

3. Nitrate in Water That Contains Carbonate and Humic Acid.

Since the behavior of nitrate is predicable and linear in water, the spectral behavior in the presence of contaminants such as carbonate and organic matter simulated by using humic acid was investigated [Note: The structure of HA is dependent upon the place of origin. The elemental composition of the HA used here was C (39.03 %), H (4.43 %), O (0.68 %), Na (7670 ppm), S (2500 ppm), Fe (1300 ppm), Ca (1200 ppm), Mg (1091 ppm), P (215 ppm) and Li (3 ppm)].

Figure B4 compares the infrared spectrum of NO_3^- (388 ppm) with that of HCO_3^- (357 ppm), CO_3^{2-} (103 ppm) and humic acid (0.981 g L^{-1}). The HCO_3^- band maximum is at 1361 cm^{-1} and has a intense shoulder appearing at 1312 cm^{-1} . The CO_3^{2-} vibrational band maximum appears at 1405 cm^{-1} and the HA band maximum is at 1376 cm^{-1} . It is evident that the carbonates and HA have spectral features that significantly overlap with those of nitrate. This is a potentially serious problem if the concentration of nitrate is very low or the concentration of either bicarbonate, carbonate or HA is high.

When more than just one component is present in solution, to identify the contribution to each measured spectrum from the individual components that make up that spectrum (i.e. nitrate, carbonate, HA), a regression analysis procedure is required. While a number of possible methods and models may be applicable to this system, one method in particular was chosen. The method of multiple regression analysis (Singular Value Decomposition or SVD) and factor analysis was outlined in the experimental section.

The hypothesis that is used to define the model of this system relies on several factors: (a) The intensity of the absorbance band(s) in the measured spectrum is a linear combination of the individual component band(s) of each species that contribute to that spectrum: (b) It is reasonable to assume that nitrate, carbonate and HA would not significantly associate with the other species aside from water. This is an important assumption, as interactions such as dimerizations would create additional basis spectra that the model does not account for. (c) Water was not included in this model since the spectra used for the regression analysis have had water removed.

Twenty-seven spectra taken from three experiments, each containing nitrate, carbonate and HA, were used in the SVD analysis. The results from the SVD indicated that three significant basis spectra were present and accounted for 99.766 % of the variance. The fourth largest basis spectrum that accounted for 0.091 % of the variance was deemed to be modeling the noise and / or drift in the spectra.

Figure B5 shows a multiple dimensional deconvolution result (or SVD and factor analysis) for one sample and Figure B6 is a plot of the deconvoluted band intensities at 1395 cm^{-1} for each nitrate spectral component against the nitrate concentration for that sample. The plot shown in Figure B6 has one data point that is well removed from all the other points (a possible outlier). This data point is more than three standard deviations away from the average and is considered an outlier. Figure B7 compares the nitrate results at 1395 cm^{-1} determined from the SVD and factor analysis (Figure B6) to those from the nitrate in water only (Figure B3). The plots in Figure B7 show the SVD and factor analysis is quite powerful in predicting

the nitrate concentration in the presence of interfering effects such as carbonate and humic acid. It is worth noting that when only nitrate is present in the water, the R^2 value from the regression was slightly lower. This was because when only nitrate was present in the water, the absorbance values corresponding to two wavenumbers (1396 to 1394 cm^{-1}) near the nitrate peak (1395 cm^{-1}) were used in the analysis whereas the whole spectra in the range of 1245 to 1540 cm^{-1} was used when interfering chemicals were present. Use of the whole spectra assists in minimizing experimental noise and hence improves the predictive ability.

4. Nitrate in Soil (Yolo loam).

Examination of the nitrate content in soils (Eshani et al., 2001) was initially achieved using a diffuse reflectance infrared spectroscopic technique. The results showed that nitrate could be detected at high concentrations and it was speculated (Eshani et al., 2001) that ATR spectroscopy is potentially able to improve upon the detection limit for nitrate in soils. However, the ATR method applied to powdered (dry) samples was found to be inadequate. The intensity of the band signals was poor unless very high concentrations of nitrate, carbonate and bicarbonate were added. This effect is documented in the literature and arises in part from the poor contact that the sample makes with the ATR prism. Attempts to improve that contact included grinding the powdered samples to micrometer particle dimensions, pressing the samples on the ATR prism surface, wetting the powdered samples with a volatile solvent so that an even and coherent layer could be deposited onto the ATR prism (with subsequent evaporation of the solvent to leave the dry sample) all failed to significantly improve the poor signal. Further, the attempts to duplicate a soil system by adding nitrate to an inert matrix such as NaCl, which has no infrared spectral bands in the region of interest, also gave poor band intensities. In soil samples it would seem desirable to have no (or very little) water present, however, it was found that a paste/slurry of water and soil provided the necessary good contact between the particles of the sample and the ATR prism. The improved infrared signal for component species such as nitrate and soil possibly arises not only from good contact with the prism, but also from the dissolution of the component into the water phase, i.e. a concentrating effect.

The effect of the water content on the infrared signal for nitrate-soil slurry was investigated and the results are shown graphically in Figure B8 (filled circles). Water was added to the soil in quantities from approximately 70 -110 % of the total weight of the system. Regardless of the amount of water added within this range, to remove water from the

measured spectral results, a subtraction factor of 1:1 was determined to be good for all soil slurry mixtures within this percentile range. The scattering of the data points is due to the soil that has a non-zero contribution to the infrared spectrum in the region of the nitrate band. The data was then subjected to SVD and factor analysis to determine the contribution to the spectrum from nitrate alone and the results are also graphed in Figure B8 (open circles). Clearly the SVD and factor analysis was able to uniquely identify the contribution to the spectrum from the soil and subsequently remove that contribution.

To establish whether the nitrate spectra determined from the SVD and factor analysis from the nitrate-soil slurry compares with that determined in water, a plot of the data from these two situations have been constructed and shown in Figure B9. Also included in Figure B9 are the results from two additional experiments that contained nitrate-soil slurry mixtures. The total number of samples from three nitrate-soil slurry experiments was 55. The regression analysis of the data shown graphically the Figure B9 is tabulated in Table B1.

5. Nitrate and Carbonate in Soil (Yolo loam).

The results of the SVD and factor analysis on a series of samples that contained both nitrate and carbonate in soil-water slurries was not conclusive. The SVD results indicate the number of significant basis spectra exceeded the number of components believed to be present in the sample. As such, the model used for the factor analysis was incorrect and attempting to predict the nitrate contribution to the measured spectra using the existing model failed. The failure arises because the concentration of all species present is no longer known. An attempt to model the spectra using an alternative curve fitting routine that does not rely on concentration data was performed (Linkfit) and the results are shown in Figure B10 (filled circles), $R^2 = 0.765$ in Table B1. Clearly the ability to predict nitrate was again poor and a closer examination of the infrared spectra of a soil-water slurry mixture that contained nitrate and carbonate (one sample represented in Figure B11) shows an additional band is present that does not represent either the nitrate or carbonate spectrum. In fact the composition of the band shown in Figure B11 resembles that of bicarbonate (compare Figure B4), nitrate, soil and possibly some residual carbonate. To test this hypothesis, Linkfit was used to again fit the data but in this case with the addition of the spectrum for bicarbonate into the curve fitting procedure. The results are plotted in Figure B10 for the prediction of the nitrate concentration (open circles). The results show the hypothesis to be correct and a significant improvement for nitrate prediction was achieved ($R^2 = 0.986$). For bicarbonate to be present upon addition

of carbonate to the sample indicates the soil pH is a factor that influences the equilibrium between carbonate and bicarbonate and cannot be ignored. The carbonate-bicarbonate pH relationships are given below in terms of the relevant pK's for the pertinent reactions involved.

Therefore the addition of carbonate to soil that has a pH value greater than 6.4 but less than 10.33 will give bicarbonate. The Yolo loam soil pH was not measured but was expected to be in the range of 6-6.8. This would account for the presence of bicarbonate in the samples examined. Taking into account the bicarbonate in solution, the nitrate concentration predicted using Linkfit was good.

6. Nitrate, Bicarbonate and Humic Acid in Soil (Yolo loam).

Given the pH considerations described above, the prediction of the nitrate concentration in soil-water slurries that also contained bicarbonate and HA was attempted. The sample mixture containing these additives is more in keeping with conditions expected to prevail in the field. Given that all species added to the soil-water slurry are in known amounts, the SVD and factor analysis identified the correct number of component spectra believed to be present. However, the prediction of the nitrate concentration while accurate was not coincident with previous results. The slope of the regression line was 1.1692 (Table B1) and is significantly different to all other results obtained thus far. Graphically this has been shown in Figure B12 (filled circles) along with the plots for nitrate in soil-water slurries (open circles). The number of samples used in this analysis was 30.

The total number of samples used over all experiments that contained nitrate (in both water and soil-water slurries, but not including the data from part 6 above) was 150. From this set of 150 spectra, 50 samples were chosen at random and the SVD and factor analysis was performed. The results from this random selection are shown graphically in Figure B13 (filled circles) and the regression results given in Table B1. From the remaining 100 spectra a further 50 were randomly selected, thus leaving behind 50 spectra. Both sets of 50 spectra were used as the validation sets. Each set was subject to SVD and factor analysis and those results are also found in Figure B13 (open symbols) and Table B1. All three sets of data (random and

validation sets) indicate the prediction of the nitrate concentration was similar, although the slope of the random and two validation sets lie intermediate between that determined from the soil-water slurry with nitrate, bicarbonate and HA and that from the remaining data.

7. Detection Limit and Sensitivity.

The concentration of nitrate in the samples is relatively high for the purposes of testing the SVD and factor analysis. A comparison of the spectra for nitrate in water to that in soil-water slurry extracted from the SVD and factor analysis is shown in Figure B14 for nitrate at 99 and 95 ppm; respectively. The signal due to nitrate in a sample containing the soil-water slurry can be observed more readily for the soil-water slurry systems.

The detection limit and sensitivity of the signal in this system depends on several factors, most of which can be improved upon in the experimental design. Firstly, the ZnSe prism used here utilizes approximately 12 reflections. Enhancing the nitrate signal can be achieved by increasing the number of reflections in the first instance. This objective can be met using small filament fibers that have many more reflections depending on the length of the fiber. Additionally, the judicious choice of the fiber material (or ATR prism material) and the angle of incidence of the infrared beam at the interface of the prism and sample will also improve the sensitivity by effectively increasing the sampling pathlength at each reflection. It is evident that the infrared spectra resulting from the SVD and factor analysis has reduced noise levels. This filtering effect inherent in the nature of the analysis further improved the signal.

Given these considerations, the projected sensitivity using ATR in a standard setup is feasibly in the 20 ppm range. However, fiber optics and fast detectors such as the MCT (Mercury-Cadmium-Telluride) have enormous potential to further improve upon that limit. Our Israeli collaborators who had access to such ATR fibers have demonstrated that detection level down to 2 to 5 ppm is possible especially when flat FEWS technique was used.

8. Calculations.

To convert from the molarity scale to the ppm scale:

$$\text{Concentration (ppm)} = \text{Concentration (mol dm}^{-3}) \times \text{Molecular weight (g mol}^{-1}) \times 1000 \text{ (mg g}^{-1})$$

$$(\text{Molecular weight for NO}_3^- = 62.0049 \text{ g mol}^{-1})$$

Table B1. Regression results from the analysis of the nitrate band from the infrared spectra in various solutions. Results are for Figures given in text.

System	Figure	Number of Samples	Concentration Range of Nitrate (mol dm ⁻³)	Regression Analysis for the Nitrate Peak at 1395 cm ⁻¹ .		
				Slope	Intercept	R ²
NO ₃ ⁻ in water	3	16	0 - 0.007	0.6050	-0.0002	0.967
NO ₃ ⁻ + CO ₃ ²⁻ + HA in water ¹	6	27	0 - 0.0028	0.5073	0	1
NO ₃ ⁻ in soil-water slurry ²	8	20	0 - 0.30	0.8740	0.0006	0.970
NO ₃ ⁻ in soil-water slurry ³	8	20	0 - 0.30	0.8672	0	1
NO ₃ ⁻ in soil-water slurry ⁴	9	35	0 - 0.15	0.7637	-0.0003	0.999
NO ₃ ⁻ + CO ₃ ²⁻ in soil-water slurry ⁵	10	17	0 - 0.03	0.7588	0.0016	0.765
NO ₃ ⁻ + CO ₃ ²⁻ in soil-water slurry ⁶	10	17	0 - 0.03	0.6962	0.0009	0.986
NO ₃ ⁻ + HCO ₃ ²⁻ + HA in soil-water slurry ⁶	12	30	0 - 0.05	1.1692	0	0.999
NO ₃ ⁻ in soil-water slurry and in water only ⁷	12	68	0 - 0.042	0.7656	-0.0005	0.999
Random set	13	50	0 - 0.05	0.8634	0	1
Validation set	13	50	0 - 0.05	0.8003	0	1
Validation set	13	50	0 - 0.05	0.8315	0	1

¹Results excluding the data point lying 3 st.dev. outside the average.

²Original data not subjected to SVD or factor analysis.

³Data determined from the SVD and factor analysis.

⁴All soil-water slurries containing only nitrate.

⁵Original data without considering the soil contribution to the spectrum.

⁶Data determined from the SVD and factor analysis.

⁷Combined result for all nitrate in soil-water or water only samples.

Figure B1.

The infrared (ATR) spectra of NaNO₃ in water; (a) pure liquid water; (b) 500 ppm nitrate; (c) 1000 ppm nitrate; (d) 5000 ppm nitrate. The spectra have been offset from zero absorbance.

Figure B2.

The ν_3 infrared fundamental vibrational mode of NO_3^- (388 ppm) in water.

Figure B3.

The intensity of the nitrate band at 1395 cm^{-1} as a function of nitrate concentration in water.

Figure B4.

Comparison of the infrared spectra for NO_3^- , HCO_3^- , CO_3^{2-} and Humic Acid.

Figure B5.

The SVD and factor analysis result for one sample.

Figure B6.

The intensity of the NO_3^- band at 1395 cm^{-1} determined from the SVD and factor analysis.

Figure B7.

The intensity of the nitrate band at 1395 cm^{-1} as a function of the nitrate concentration in water and that determined by factor analysis of a solution containing carbonate & humic acid.

Figure B8.

The intensity of the nitrate band at 1395 cm⁻¹ as a function of the nitrate concentration in soil and water slurries. Comparison of SVD & factor analysis results with observed results.

Figure B9.

A comparison of the intensity of the nitrate band at 1395 cm^{-1} as a function of the nitrate concentration in water and soil-water slurries.

Figure B10.

Plot of the nitrate band intensity at 1395 cm^{-1} for a soil-water slurry containing carbonate. Linkfit without bicarbonate and with bicarbonate.

Figure B11.

The infrared of NO_3^- and CO_3^{2-} in soil.

Figure B12.

Graph of the nitrate band intensity at 1395 cm⁻¹ for soil-water slurry solutions containing (i) nitrate and (ii) nitrate + bicarbonate + humic acid.

Figure B13.

Graph of the nitrate band intensity at 1395 cm⁻¹ for all soil-water slurry solutions. (i) Random selection of 50 samples and (ii) two validation sets each having 50 randomly selected samples.

Figure B14.

Comparison of the infrared ATR spectra of the nitrate band in (a) water (at 99 ppm) and (b) soil-water slurry (at 95 ppm) from the SVD and factor analysis.

APPENDIX C: References

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