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Estimation of nitrite concentration in nitrified urine by means of UV spectrophotometry

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INTRODUCTION

Separating urine at the source allows for recovery of nutrients and subsequent production of valuable products such as fertilizers [5]. This, however, requires temporary storage of urine, which is challenging due to malodor and loss of ammonia. Collected urine can be stabilized through nitrification, a biological process in which bacteria convert ammonia to nitrate via nitrite [8]. The resulting ammonia-nitratesolution can be stored safely until further processing.

The nitrification process is vulnerable to changes in the influent load. Under normal conditions, the nitrite concentration remains near zero as it is consumed as quickly as it is produced. However, a suddenly increased flow rate may cause an increased nitrite production by the ammonia oxidizing bacteria, in turn inhibiting the nitrite oxidizing bacteria, causing an even higher accumulation of nitrite. If no action is taken within a span of hours, the continued buildup of nitrite can lead to an irreversible failure of the entire process [7]. Thus, monitoring nitrite is essential for preventing reactor failure. Currently, a direct and affordable online nitrite measurement is not available for this process; accurate measurements are only possible by sample analyses. Ultraviolet (UV) spectrophotometry is a promising option for automated monitoring of the nitrification reactor [6]. Since nitrite absorbs light in theUV range, it is theoretically possible to determine its concentration by in situ positioning of the sensor. Although the peak absorbances of nitrite are known and are clearly observed when measured in water, spectrophotometric determination in urine is still challenging. Not only does urine contain other compounds that absorb light in the UV range (most importantly nitrate), but the presence of suspended particles could cause backscattering and interfere with the absorbance. Moreover, the concentrations of nitrite and nitrate in a failing urine nitrification reactor are much higher than in any conventional wastewater treatment plant, possibly causing saturation of absorbed light, in practice a loss of signal. The above mentioned disturbances could lead to potentially unreliable measurements.

Chemometrics is a popular method for information extraction from large-scaledata sets. It relies on the construction of mathematical models that establish empirical relationships between input signals, such as absorbance spectra, and output signals, such as compound concentrations [1]. Assuming a linear relationship, such reconstructions can be achieved through linear regression techniques. In cases where the input signals are multivariate, as with spectral data, additional methods could be applied to reduce the data dimensionality while retaining the most relevant information. One such method is Principal Component Regression (PCR), in which a Principal Component Analysis (PCA) is performed to reduce the dimensionality, followed by linear regression [3].

In this work, the potential of a UV spectrophotometer to measure nitrite in nitrified urine is studied for the first time. This contribution focuses on the study of interferences from suspended particles and saturation effects.

MATERIALS AND METHODS

At Eawag in Dübendorf, Switzerland a moving bed biofilm reactor is operated at pilot scale for the nitrification of source-separated urine [2]. The experiments presented in this work were performed offline through sample collection from the reactor. The submersible insitu UV sensor used is an:can spectro::lyser with online data reading in the range 220-399nm. Its measuring path length is 0.5 mm, which is rather short for these devices.

Urine samples were collected three times per week during 11 weeks and analyzed with the UV sensor in a laboratory setup. Each sample was initially subjected to sedimentation in Imhoff cones from which the supernatant was collected after 1 h. Thereafter, the liquid was split into two parts one filtered

through 0.7 µm and one remained unfiltered. From each part an additional, 1:10 diluted solution was prepared, resulting in foursolutions in total. Different nitrite stock solutions were added to ensure a varied nitrite concentration. UV measurements, in replicates of five, were obtained from all solutions during constant mixing. Reference measurements with Hach-Lange tests determined the nitrite concentration in all urine samples.
The collected 180-variatespectra were reduced to lower dimensions with PCA after which a linear regression was performed. Leave-one-outcross validation was used for model selection. The final model was selected as the least complex model (i.e. containing the smallest number of principal components) whose root mean square error (RMSE) was within one standard deviation of the best/lowest RMSE. All computations were programmed and executed in Matlab.

RESULTS AND DISCUSSION

Evaluation of spectral data corresponding to the most ideal case – filtered and diluted – shows that a very simple model containing only one principal component (PC) can be used to estimate nitrite to a most satisfying degree (Fig 1a). When compared with the results obtained for the unfiltered and diluted nitrified urine (Fig 1b), almost no difference in fit can be observed. This indicates that the interference of suspended particles is negligible, a sit does not affect the model performance. Studying the results from the filtered undiluted case (Fig 2a), it seems necessary to use a more complex model containing 15 PCs to obtain a good fit between the estimated and measured nitrite concentrations. From this result it can be concluded that there is a considerable difference between diluted and undiluted solutions, suggesting that saturation severely affects the model performance.

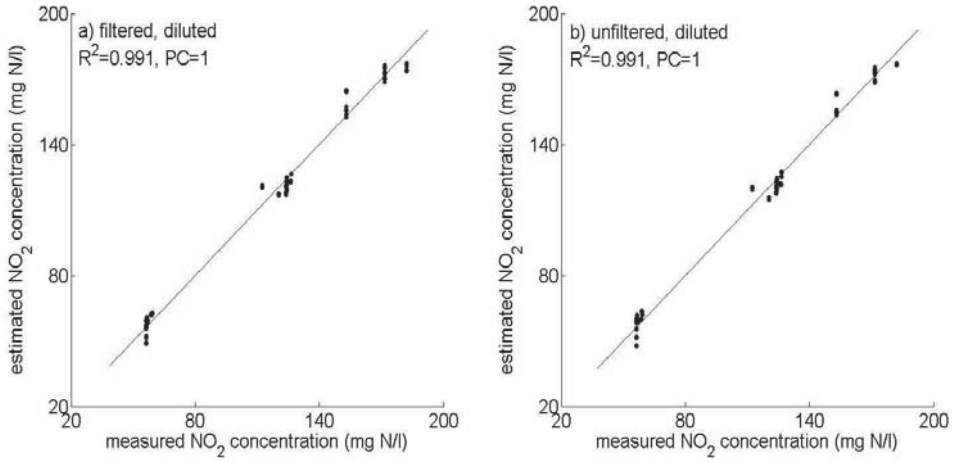

Figure 1. Estimated vs. measured nitrite (mg N/L) for (a) filtered/diluted, and (b) unfiltered/ diluted urine.

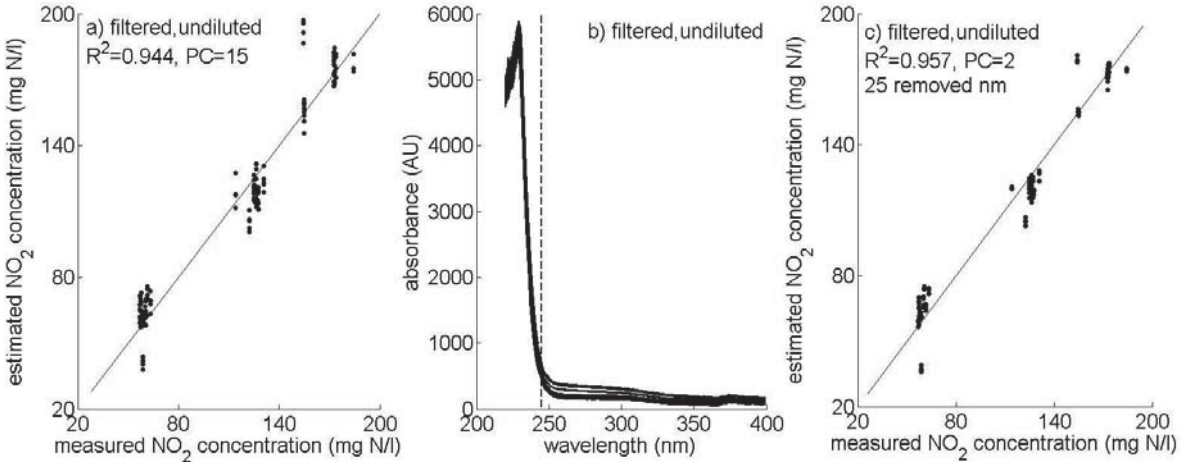

Figure 2.(a) Estimated vs. measured nitrite (mg N/L) for filtered/undiluted urine; (b) the UV absorbance spectra; (c) estimated vs. measured nitrite for filtered/undiluted urine based on wavelength selection.

Saturation in nitrified urine is mostly caused by high concentrations of nitrate, which has a very intense absorption band in the low UV range with a maximum at 201 nm; nitrite absorbs strongly around 220 nm, i.e. they both absorb intensely in the beginning of the UV range of the sensor (Fig 2b). However, both compounds have additional, weaker absorbance peaks: nitrate at around 302 nm, nitrite at around 354 nm [4]. Thus, additional studies were performed to investigate whether only a part of the spectrum (by removing shorter wavelengths from the left-hand side in Fig 2b) would contain sufficient information and could be used for evaluation of saturated spectral data. The model selection was based on the same procedure as before, now additionally removing one wavelength at a time. Results obtained for the filtered undiluted case (Fig 2c) show that a very good fit has been established with a much simpler model than in Fig 2a, now using only 2 PCs. The spectral data used in this case have been shortened by 25 wavelengths, containing absorbance information for the range 245-399nm (marked by a vertical dashed line in Fig 2b). Thus, saturated absorbance spectra can be analyzed by removing the saturated part of the spectra and using the remainder with a simple chemometric model, achieving a credible estimation of the nitrite concentration.

CONCLUSIONS

In this work, the potential use of a UV sensor as a tool in combination with chemometrics to estimate nitrite concentrations in nitrified source-separated urine has been studied. Results show that the effect of suspended particles on the collected and analyzed absorbance spectra is negligible. A credible estimation of nitrite can be obtained with a simple chemometric model. Saturation due to high concentrations of nitrite and nitrate affects the spectral data and model complexity severely. This can, however, be mitigated by a reduction of the absorbance spectra through removal of the saturated, lower end of the UV absorbance spectra. Subsequent analyses show that nitrite can be estimated with a relatively simple model even for saturated data. These results are promising for the eventual use of the UV sensor as an online nitrite measurement.

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