A full Ocean Depth UV-Spectrophotometer for Nitrate Measurements

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***Abstract*- The instrument presented here, named SUV-6, uses the well-known method of UV-absorption measurement for the determination of nitrate concentrations in seawater. To account for the presence of other constituents that show absorption in the UV portion of the light spectrum (e.g. bromide and bisulfite) the absorption is measured in six wavelength bands from 205 nm to 280 nm. While the original instrument, developed in the 1990's suffered from drift due to temperature changes and changes in the spectrum emitted by the light source, the new SUV-6 compensates for these drifts by employing an internal reference path.**

The instrument consists of a Xe-flashlamp as light source, collimating optics, pressure window and retroreflection prism, a ruled grating and a photodiode array. It is microprocessor controlled and allows the user to select either RS-232 or analog outputs. The fast response time of 1 s makes it suitable for use on towed vehicles, such as SeaSoar (at a tow speed of 8 knots 1 Hz results in a spatial resolution of 4 m), autonomous underwater vehicles and for CTD casts. Results of laboratory calibrations and first field tests will be presented.

I. INTRODUCTION

Chemical oceanography is in some cases limited by the ability to make measurements on the appropriate temporal and spatial scales. Most oceanographic sensors for dissolved chemical species in seawater are still based on wet-chemical analyser technologies that have slow response times (typically in the order of minutes) and a deployment period that is limited by the deployed volume of necessary reagents and their degrading. This type of chemical sensors therefore is not suitable for use on fast platforms such as CTD's, towed vehicles or AUV's. This limitation led to the search of methods to detect chemical species in the sea more directly, without the need for reagents. The method of nitrate determination in water using UV absorption measurements is well known for more than 40 years (e.g. [1],[2]). The instrument discussed here, however, was to our knowledge the first UV-absorption based nitrate sensor for oceanographic applications [3],[4]. Recently new oceanographic instruments using this method have become commercially available (e.g. [5]), employing miniature spectrometers. Measurements of nitrate concentrations with the same temporal resolution as CTD sensors could, for example, give valuable additional information about constraints of plankton growth in the water column and aid biogeochemical process studies.

Field trials with the SUV-6 revealed a significant drift with changing ambient temperatures. One of the reasons for this drift was identified to be the changes of the light spectrum of the flash lamp with changes in temperature. An additional drift, albeit on much longer timescales, is anticipated by ageing of the light source. To be able to record these changes in the light spectrum, an additional, internal light path was introduced. This internal reference path can be enabled alternately with the measurement path and then allows to compensate for spectral changes of the light source in the post processing of the data.

II. INSTRUMENT DESIGN

A. Optics

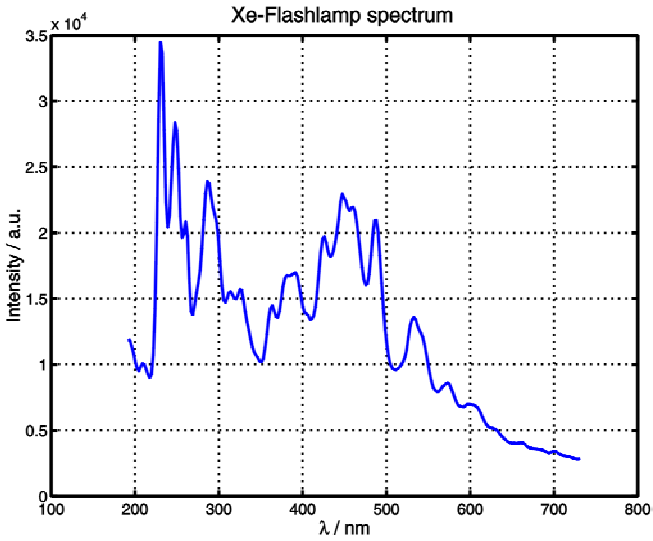

Fig. 1: Output spectrum of Xenon flash lamp.

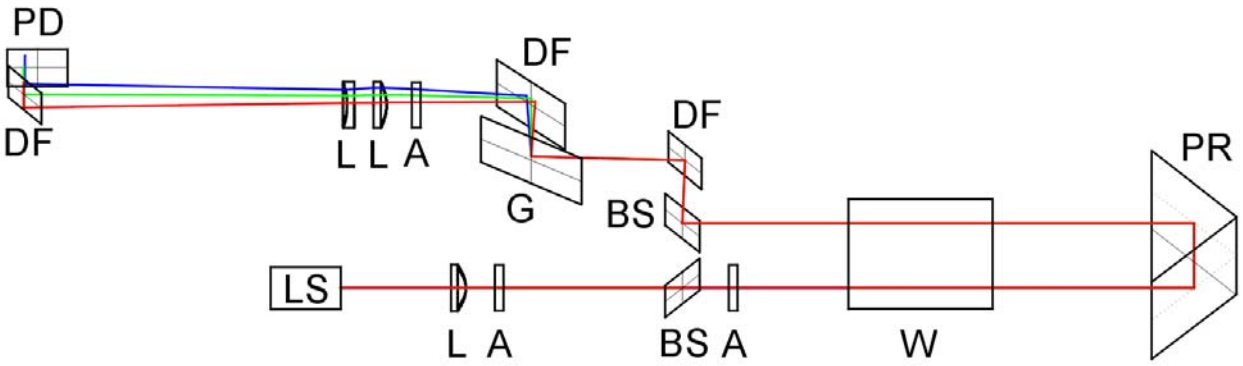

Fig. 2: Schematic of the optical setup of the SUV-6. LS: light source; L: lens; A: aperture; BS: beamsplitter; W: window; PR: prism; DF: dichroic filter; G: diffraction grating; PD: photodiode array.

The SUV-6 uses a Xenon flash lamp with a repetition rate of 8 Hz as light source. A relative spectral distribution of the light output is shown in Fig. 1. The optical layout of the instrument is shown in Fig. 2 and can be described as follows: A single lens collimates light from the flash lamp that, after passing an aperture, is split in two beams, the measurement beam and the reference beam, by a beamsplitter. The measurement beam passes through this first beamsplitter and a further aperture with shutter and the quartz pressure window into the measurement volume. After a pathlength of 3.3 cm the measurement beam enters a prism; it is then reflected and offset by 17 mm and passes through the measurement volume again before entering the pressure window. After being reflected on a second beamsplitter and a dichroic filter, it hits the grating, the dispersive element of the spectrometer. The first order reflections from the grating are reflected once more on a dichroic filter and enter the imaging optics that focus the spectral components on to six elements of a photodiode line array, thus gaining signals for six wavelength bands centered at 205 nm, 220 nm, 235 nm, 250 nm, 265 nm and 280 nm with a bandwidth of 7.5 nm for each band.

After a 90° reflection on the first beamsplitter the reference beam passes through an aperture with shutter and the second beamsplitter, from where it follows the same path as the measurement beam. A solenoid driven mechanism opens the two shutters for measurement and reference been alternately as to select either measurement or reference operation.

B. Electronics

The current of the six photodiode array elements is converted to a voltage using a transimpedance amplifier for each photodiode. This voltage is further amplified in a second amplifier stage with digitally controlled gain. This gain control is used to compensate for the different intensities of the Xenon flash lamp in the six wavelength bands. The output voltages of these second stage amplifiers are then converted into digital values by a 12-bit A/D-converter.

The instruments electronics is controlled by a microcontroller that allows the user to adjust a variety of parameters. A full six channel spectrum can be output via a RS-232 connection (or via analog output lines) every 0.5 s or 1 s. The RS-232 output consists of ASCII strings representing either the A/D-converter output in mV for all six channels or the output in mV of one of the six channels and the relative values for the other five channels.

The user can set the frequency and duration of the internal reference measurement, used to monitor changes in the lamp spectrum over time.

C. Mechanics

The main optical bench is constructed either side of a stable metal plate, with the flash lamp and collimating optics on one side and the grating, imaging optics and photodetectors on the other side. This layout provides a good shielding of the high impedance photodetectors from the high voltage pulses used to drive the flash lamp. The instrument is about 43 cm long and has a pressure housing diameter of 114 mm. The prism housing is connected to the main housing by three bolts that can be exchanged to change the path length of the measurement path. The deep water housing for the SUV-6 is rated to 6000 m, a prerequisite for routine use on CTD's, allowing to leave the instrument in the CTD package even for deep casts.

III. INSTRUMENT PERFORMANCE

A. Stability

After introduction of the additional internal reference path first measurements were made to establish the stability of the instruments output. Fig. 3 shows the results of a one-hour measurement in air. The standard deviations of the 30 s intervals normalised by the mean over one hour range from $2.5 \cdot 10^{-3}$ to $6.7 \cdot 10^{-3}$ for the measurement path and from $2.2 \cdot 10^{-3}$ to $5.3 \cdot 10^{-3}$ for the reference path. A further test in MilliQ-water yielded similar results.

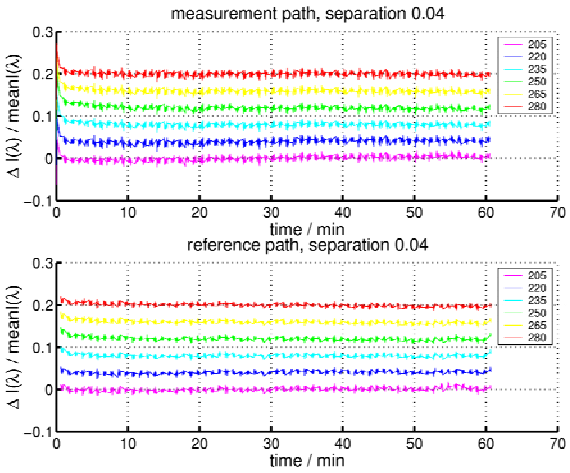

Fig. 3: One hour measurement in air. 30 1 Hz samples at measurement path (upper panel) were alternated with 30 1 Hz samples at reference path (lower panel). The graphs show deviations from the one hour mean scaled by the one hour mean. Channels 1 to 6 are shown from bottom to top with a separation of 0.04.

B. Calibration in pure water

A calibration in 1.5 l of pure water (MilliQ) was carried out, adding aliquots of 300 µl of 5 mM/l solution of NO_3, resulting in concentration steps of 1 µM/l for the concentration range from 1 µM/l to 20 µM/l. Two further concentration steps of 2 µM/l were made, yielding concentrations of 22 µM/l and 24 µM/l. After introducing the solution the concentration was held constant for 3 consecutive 30 s measurement intervals of the instrument before introducing the next aliquot of NO_3 solution. The measurement intervals were alternated with reference intervals of 30 s duration. Fig. 4 shows the result of the calibration for channel 1 (centered at 205 nm) and channel 2 (centered at 220 nm). Three measurements, in pure water, at half maximum concentration and at highest concentration were used to calculate the offset of the channels. A linear regression then was carried out for the absorbances resulting from the measurements. To get a first estimate for the resolution of the instrument, the calibration coefficients were subsequently applied to the measurements carried out during the calibration itself. It should be noted that this does not give any indication concerning the precision or accuracy of the instrument. The resulting concentrations from channel 2 (centered at 220 nm) are shown in Fig. 5. The concentrations resulting from applying the same procedure to the measurements from channel 1 (centered at 205 nm) look similar with a slightly higher 'noise' at the high concentration end. The useful resolution at the low concentration end can be estimated from this to be better than 0.2 µM/l.

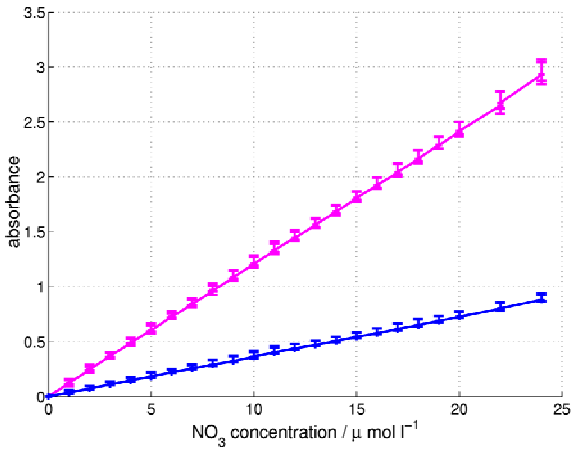

Fig. 4. Calibration in pure water. Error bars indicate standard deviations of 30 s measurement intervals. Upper line: channel 1 (205 nm); lower line: channel 2 (220 nm).

IV. CONCLUSION

The SUV-6 has been tested on a number of platforms, such as CTD, SeaSoar and the Autosub UAV and already delivered useful results in spite of the existing problems with temperature dependent drifts. The introduction of an internal reference path allows to compensate for these drifts and therefore improves the data quality. A full characterisation of the improved instrument is underway and field trials will follow to demonstrate the capabilities of the SUV-6.

Acknowledgments

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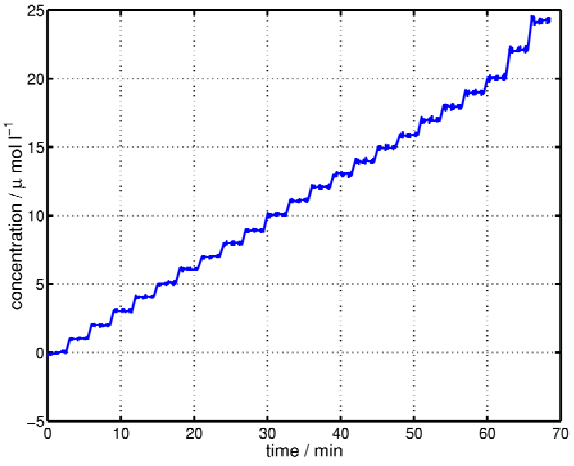

Fig. 3: Concentrations calculated by applying the calibration coefficients to the measurements taking during the calibration for channel 2 (centered at 220 nm).

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