Monolithic DFB laser diodes emitting at 785 nm for *in situ* SER Spectroscopy

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ABSTRACT

A distributed feedback (DFB) laser diode emitting at 785 nm was used as light source for Raman spectroscopy. An *in situ* surface enhanced Raman spectroscopic (SERS) sensor was developed to detect polycyclic aromatic hydrocarbons (PAHs) in marine environment at concentration levels down to nmol/l. The DFB diode used in our SERS experiments had an output power of 150 mW at 785 nm and a spectral linewidth of 3 MHz. The wavelength stability of this laser was ± 0.004 nm over 12 hours. A side mode suppression ratio up to 45 dB was determined. For trace detection of chemicals in marine environment, SERS active substrates were employed based on silver colloids encapsulated in a sol-gel derived matrix. The resulting spectra and a limit of detection (LOD) of phenathrene (34 nmol/l) as an example for PAHs in seawater are presented. A concentration of 1 nmol/l of pyrene was detected.

Keywords: DFB laser, Raman, SERS, PAH, *in situ* monitoring, seawater, marine environment

1. INTRODUCTION

For identification and quantification of chemical compounds Raman spectroscopy is well established. Food analysis[1], medical applications[2], and sensors for environmental monitoring[3] are examples for fields were Raman spectroscopy is being increasingly used.

Available Raman spectroscopic setups have a spectral resolutions varying from 20 cm^{-1} for low resolution of typical hand held sensors to < 1 cm^{-1} for high resolution laboratory setups. Therefore excitation light sources had to be used with a spectral linewidth significantly smaller than the spectral resolution of the Raman setup. Typical laser sources used in laboratory for dispersive Raman systems were gas lasers such as Kr^+ (e.g. at 647.1 nm), Ar^+ (488.0 nm, 514.5 nm), and He-Ne-laser (632.8 nm) respectively. The necessary output power is in the range from 25 mW to several Watts. Solid state lasers, e.g. frequency-doubled Nd:YAG lasers emitting at 532 nm are possible alternatives.

A more compact solution is based on semiconductor lasers, which have a drastically reduced size and are easily implementable into integrated Raman spectroscopic setups. For Raman measurements diode lasers in an external cavity configuration (ECL) are established. They are available at 785 nm with an optical output power of hundreds of mW and fulfil most of the conditions for an excitation light source in Raman spectroscopy[4]. In any case for an application in compact mobile measurement systems ECLs have some disadvantages. These devices need precise mechanical alignment. Therefore their application in harsh environments, e.g. in deep sea applications needs sophisticated mounting technology.

On the other hand recent developments in the field of semiconductor laser devices with internal grating offer new possibilities. High power distributed feedback (DFB) laser were developed. Their design and functionality was demonstrated[5,6]. They have sufficient high optical output power up to 400 mW[6] in a single-mode operation with a high side-mode suppression ratio of more than 40 dB. This avoids unwanted light and improves the signal-to-noise ratio (SNR). The very small spectral linewidth < 10 MHz is superior to other solid state and gas lasers. These features

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together with the compact size offer new possibilities in Raman spectroscopy for mobile measurement systems and for high resolution Raman spectroscopy.

Surface enhanced Raman spectroscopy (SERS) offers a drastically increase in sensitivity enlarging the weak Raman effect[7,8,9]. SERS measurements of chemicals in seawater were performed by our group[10,11]. Limits of detection (LOD) e.g. naphthalene dissolved in seawater down to 3.4 µmol/l[12] were reached limited by SERS substrates sensitivity. To test the substrates a laboratory setup was developed using a DL 100 ECL diode laser (Toptica) as an excitation source. To perform underwater measurements a SERS optode was developed based on the approved laboratory setup[13,14,15]. The ECL laser was replaced with a DFB laser to reduce size for further implementations into small sensor systems.

In this paper, we present the application of a DFB diode laser emitting at 785 nm with an optical output power of 150 mW as an excitation light source for surface enhanced Raman spectroscopic (SERS) measurements of polycyclic aromatic hydrocarbons (PAH) in seawater. The laser diode is employed in a special developed Raman spectroscopic setup of a field operable device. The relevant features of the DFB laser regarding the application in Raman spectroscopy will be presented in section 2. It will be shown, that the device is suitable for the application in a marinised Raman system. This setup containing the specially developed SERS optode and the instrumentation (spectrograph, CCD detector) will be shown. With these components, SER spectra and calibration curves of PAHs were recorded. In section 3 results concerning resolution and sensitivity will be given. Limits of detection (LOD) were determined for phenanthrene.

2. INSTRUMENTATION

2.1 DFB Laser

A schematic view of a DFB diode laser is presented in Figure 1. The layer structure was fabricated with metal organic vapour phase epitaxy (MOVPE). Using a two step epitaxial process realised by holographic lithography and wet-chemical etching[6] a second order grating with a period of 235 nm and a coupling coefficient of about 2 cm^{-1} was manufactured. This grating is embedded into the semiconductor layer structure to obtain an emitting wavelength of 785 nm. The schematic view shows the design of the high power DFB laser with a resonator length L of 1.5 mm with a W = 3 µm wide ridge waveguide.

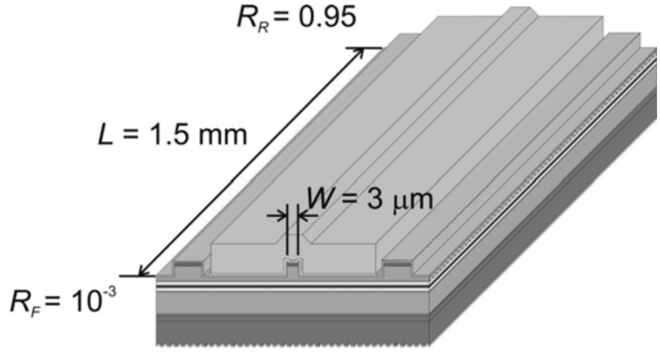

Figure 1: Schematic view of a high power 785 nm DFB laser.

The front- and rear facet are anti- ($R_F = 10^{-3}$) and high ($R_R = 0.95$) reflection coated, respectively. The device is mounted p-side up on an AlN submount in a SOT 148 package on a copper heatsink.

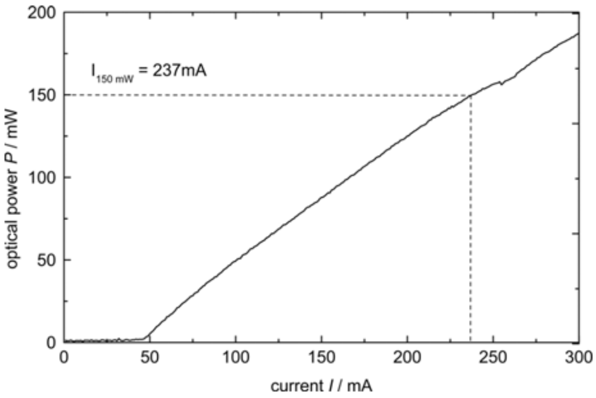

Figure2: Continuous wave power current characteristic of a typical DFB laser emitting at 785 nm at $T = 35°C$.

Figure 2 shows the optical output power P of the laser versus the operating current I for a DFB laser measured at 35°C heatsink temperature. The threshold current I_{th} is 45 mA and the slope efficiency S is 0.63 W/A. The laser achieves a maximum power of 158 mW before a first kink appears.

The side-mode suppression the optical spectra were measured with a spectrometer Q8384 of Advantest. This spectrometer has a dynamic range of more than 60 dB and a spectral resolution of 0.01 nm. Optical spectra were measured at optical output powers of 88 mW, 125 mW and 156 mW at a constant heatsink temperature of 35 °C. The data are presented in Figure 3. They show a single mode operation of the DFB laser from 784.8 nm to 785.2 nm up to 156 mW. The Fabry-Perot (FP) modes suppression ratio of more than 45 dB is sufficient high for Raman measurements. The wavelength shift of 0.2 nm (3.2 cm^{-1}) from 88 mW to 125 mW and 0.22 nm (3.6 cm^{-1}) from 125 mW to 156 mW is caused by Joule heating. Typical wavelength shifts for DFB lasers are 0.06 nm/K (1 cm^{-1}/K) at constant injection current and 0.004 nm/mA (0.06 cm^{-1}/mA) at constant heatsink temperature.

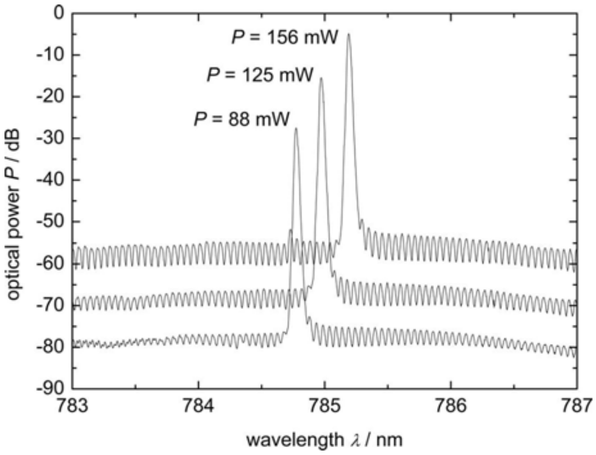

Figure 3: Spectra of a DFB laser measured at $T = 35$ °C and different optical output powers. Spectra offset for clarity.

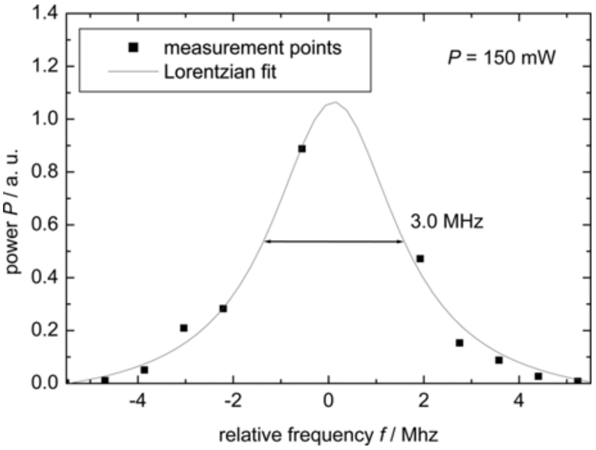

Figure 4: Spectral linewidth of a DFB laser emitting
at 785 nm, 150 mW optical output power and *T* = 30°C.

The spectral linewidth of the DFB laser measured with a homodyne fibre interferometer[16] designed for single mode diode lasers is presented in Figure 4. The maximum resolution of this system is 2 MHz. A laser diode driver ILX 39400 with an output stability of ± 4 µA and a temperature controller ILX 39032 with a short term stability ± 0.004 K over one hour was used for these measurements. The squares represent the measured data. A Lorentzian fit of the measurement points were used to simulate the natural linewidth. A spectral linewidth of 3.0 MHz was calculated at FWHM which corresponds to 10^{-4} cm^{-1}.

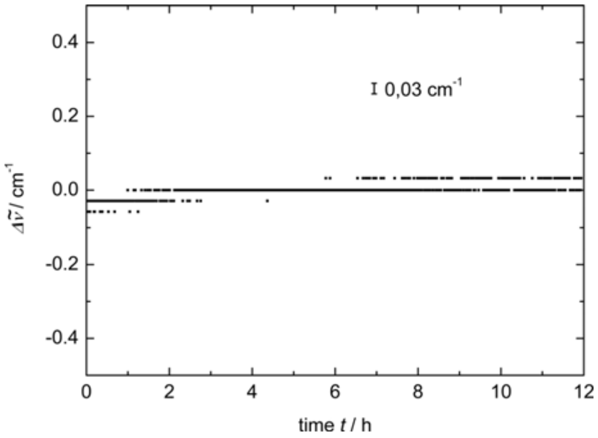

Figure 5: Long term stability over 12 hours in laser frequency of a typical
DFB laser emitting at 785 nm at *T* = 30°C

As mentioned above Raman spectroscopy needs excitation light sources with long term stability in laser frequency. This stability guarantees positions of spectral lines for reproducible Raman measurements over hours. Therefore the measurement of stability in laser frequency of a typical DFB laser emitting at 785 nm were done using a spectrograph Q8347 of Advantest with a spectral resolution of 0.002 nm (0.03 cm^{-1}). The result is presented in Figure 5. The heatsink temperature was stabilised using a temperature controller LDC 3724B of ILX Ligthwave with a long term stability better than 10 mK. To measure the temperature of the laser a thermistor was used. The distance of this thermistor to the laser was about 1 cm placed at heatsink. Using a 5030 laser diode driver of Newport an output current accuracy of ± 135 µA at 150 mA was guaranteed. Over a time of 12 hours optical spectra of the DFB laser were measured every minute. A frequency shift to higher relative wavenumbers is recognizable in Figure 5. The shift is smaller than

± 0.06 cm^{-1} (± 0.004 nm). This effect correlates to a shift of ± 67 mK at the heatsink temperature or a current fluctuation of ± 1 mA. These values are larger than expected from the long term stability of the temperature controller and current accuracy of the laser diode driver. We suppose that a drift of environmental conditions shift the temperature difference between the sensor and the active layer of the laser.

However summarizing the results, it can be stated that the DFB laser emitting a 785 nm with an optical output power of 150 mW, a linewidth below 10^{-4} cm^{-1} and a wavelength stability better ± 0.06 cm^{-1} is well suited for Raman spectroscopy. This will allow measurements in harsh environment but also in high resolution systems.

2.2 Raman setup

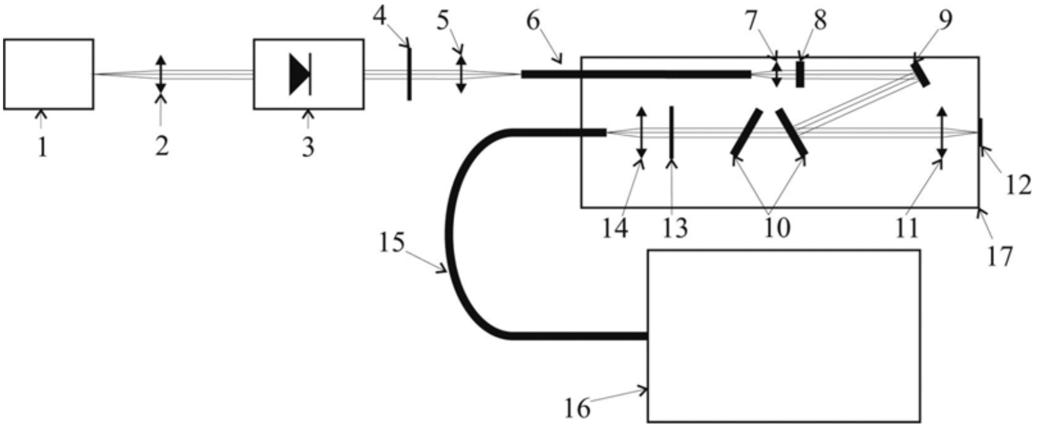

Figure 6: Experimental setup with marinised SERS optode: 1) DFB laser, 2) Lens L1, 3) Optical isolator, 4) Grey filter, 5) Lens L2, 6) Excitation fibre, 7) Lens L3, 8) Bandpass filter, 9) Mirror, 10) Dielectric edge filters, 11) Lens L4, 12) Quartz window with SERS substrate, 13) Red filter, 14) Lens L5, 15) Collection fibre, 16) Spectrograph, 17) Pressure tested housing up to 200 bar.

Based on the measured features of the DFB laser this laser was used for laboratory measurements with a setup designed for marine environment. The sensor head was described in detail by Murphy *et al.*[13,14]. A scheme of the SERS optode is given in Figure 6.

The laser light is collimated by an aspheric lens L1 (2) with a focal length of 8 mm and focused by lens L2 (4) into a multimode fibre (5) with a core diameter of 50 µm. This fibre is positioned inside the sensor head. An optical isolator (3) (> 60 dB) was used to avoid destabilisation of the DFB laser by feedback. The intensity of the light was reduced for all further measurements to 25 mW at the sample by using a grey filter (4) to protect the SERS substrate. A lens L3 (7) with a focal length of 6 mm collimates the laser beam inside the sensor head. This beam is directed through a bandpass filter (8) with 90 % transmission at 785 nm and a bandwidth of 8 nm (FWHM). Over a mirror (9) and one of the two dielectric edge filters (10) the beam is focussed by lens L4 (11) with a focal length of 16 mm. The edge filters are designed to reflect the light at 785 nm with > 99.99 % reflection and have a cut on wavelength at 810 nm with 50 % transmission. The focus of the laser beam lies on top of a SERS substrate which is fixed outside the optode in front of the quartz window (12). The backscattered light is collected by lens L4 and directed to the edge filters (10) to eliminate the laser light from the Raman signal. After passing both edge filters and a red filter (13), the Raman light is focussed by lens L5 (14) into a collection fibre with a core diameter of 50 µm and is transported to the spectrograph (16).

The spectrograph is a custom made axial spectrometer (Horiba Jobin Yvon) with TE-cooled CCD chip detecting the NIR region (800-950 nm). The spectral resolution of this system is 12 cm^{-1}. The dispersive element is a prism combined with a grating so called "GRISM". The input slit is composed of an optical fibres comb arrangement on one end of a 2 m long fibre bundle with 50 fibres with a core diameter of 50 µm. A high resolution image of the chromatic dispersion of each individual fibre projected on a front illuminated CCD chip with 2048 x 512 pixels. The 2048 columns on the CCD chip correspond to the dispersed wavelength while the 512 rows are for the input channels for each fibre. This spectrograph was embedded in a marinised housing for deep sea application so called "Core Instrument".

3. EXPERIMENTAL RESULTS

3.1 Raman spectra

The setup described above together with the DFB laser was tested in surface enhanced Raman spectroscopic (SERS) experiments.

In all experiments the optical output power of the DFB laser emitting at 785 nm was 150 mW at $T = 33°C$. At first a wavelength calibration of the system was performed. For this purpose polystyrene was used as reference standard. As shown in Figure 7 five Raman lines of polystyrene were taken in the region from 400 cm^{-1} to 1800 cm^{-1} to fit the wavelength positions in numbers of pixels to the corresponding relative wavenumbers known from literature[17]. Therefore a second order polynomial function was used. This calibration was used in all further measurements.

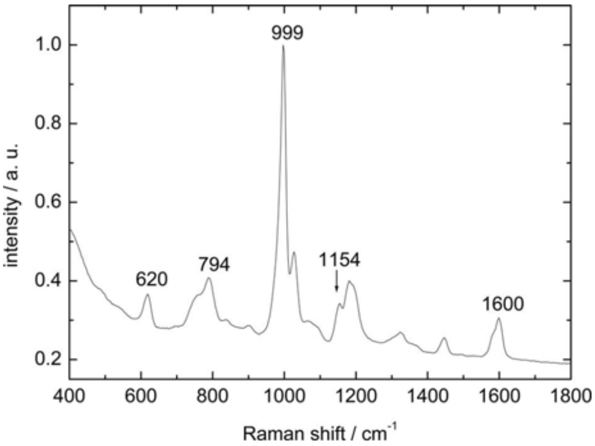

Figure 7: Raman spectrum of polystyrene with the DFB laser emitting at 785 nm, 25 mW at the sample and an integration time of 1s.

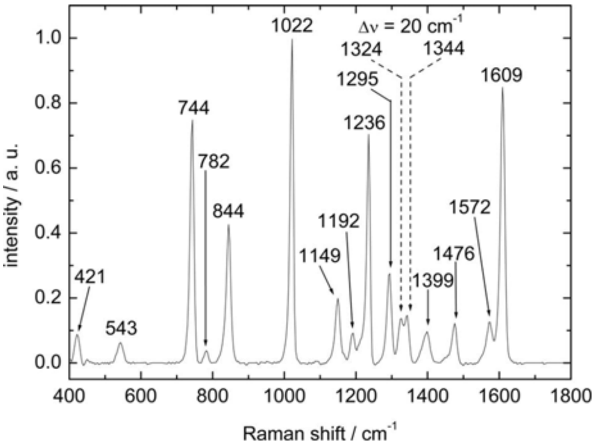

Figure 8: Raman spectrum of fluorene with a DFB laser emitting at 785 nm, 25 mW at sample and an integration time of 10s.

For the generation of reference spectra and to verify the resolution of the system, Raman spectra of PAHs were measured in solid phase. In Figure 8 a Raman spectrum of fluorene as an example of a PAH is presented. It is measured with an integration time of 10 seconds. The Raman spectrum in the 400 cm^{-1} to 1800 cm^{-1} range shows a multitude of peaks of fluorene some of which are not fully resolved. Two Raman lines marked out by dashed arrows are separated by 20 cm^{-1}. This correlates to the resolution of the spectrometer.

3.2 SER spectra and calibration curves

SER spectra were measured of PAHs in artificial seawater using sol-gel-based substrates[12]. These SERS substrates are reversible and can be used for several measurements. Based on the results of Lucht *et al.* an optimised process towards the SERS substrates sensitivity was carried out. For the described experiments a substrate was selected with a high sensitivity.

The sensitivity calibration was made using PAHs dissolved in artificial seawater at different concentration down to the level of nmol/l. Dependencies of the signal intensity on the concentration of the PAH in seawater can be fitted with a Langmuir-isotherm[12] of the strongest Raman peaks. Using a linear fit in the low concentration region of the calibration curve and a prescribed statistical procedure the limit of detection (LOD) for the sensor system one determined. This LOD is limited by the signal-to-noise ratio (SNR). A Raman line applies as detectable if the signal intensity is 3 times the standard deviation σ of background noise[18].

As an example a background subtracted SER spectrum with an integration time of 10 s of phenanthrene dissolved in seawater is shown in Figure 9. The therefore used background spectrum is a SER spectrum of artifical seawater.

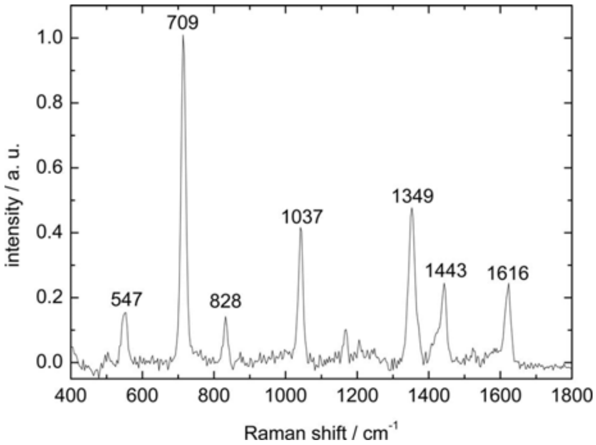

Figure 9: Background subtracted SER spectrum of phenanthrene in seawater with a DFB laser emitting at 785 nm, 25 mW at sample and an integration time of 10s.

The concentration of phenanthrene in seawater was 3960 nmol/l which is equal to the saturation concentration of this compound in seawater. The most intensive peak at 709 cm^{-1} is used for the determination of the limit of detection (LOD) for phenanthrene in seawater. The experimental data fitted by using a Langmuir-isotherm is presented in Figure 10. The inset shows a linear fit of the measurement points in the low concentration range.

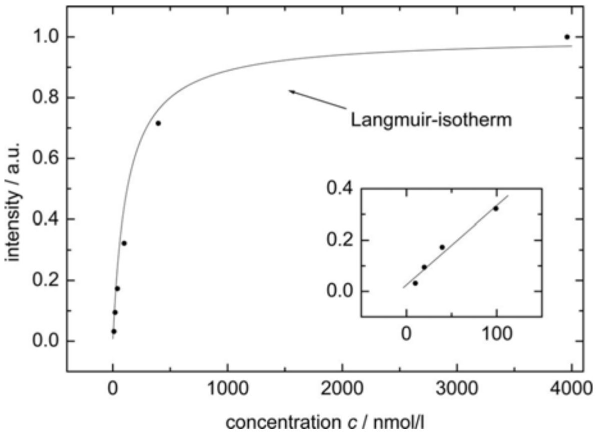

Figure 10: Calibration curve of phenanthrene in seawater using the Raman line at 709 cm^{-1}.

The LOD of 34 nmol/l for phenanthrene in seawater is calculated by using the prescription DIN 32645[19] based on the 3 σ criterium.

In Figure 11 two SER spectra of pyrene dissolved in artificial seawater are shown. The integration time was 10 s. Comparison between the concentration at 430 nmol/l (saturation concentration) and 1 nmol/l of pyrene in seawater are presented. It is obvious that a concentration of pyrene down to 1 nmol/l in seawater is visible.

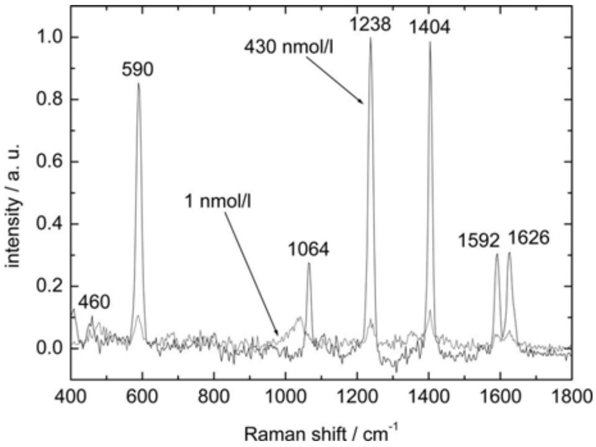

Figure 11: SER spectra of pyrene in seawater measured with the core unit and the DFB laser emitting at 785 nm with 25 mW at sample and an integration time of 10s.

Using these sol-gel-based substrates naphthalene and phenathrene are comparable analytes. Our results using the highly active substrates have compared to Lucht *et al.* a 100 times smaller LOD for selected and comparable PAHs dissolved in seawater.

4. CONCLUSIONS

It is shown that a single mode DFB laser emitting at 785 nm with an optical output power of 150 mW and a narrow spectral linewidth of 10^{-4} cm^{-1} is well suited for the application of Raman spectroscopy and SERS as an excitation light source and fulfil all requirements. The high wavelength stability of ± 0.004 nm over 12 hours allows using a DFB laser for long time Raman measurements for environmental monitoring or process control in industries. The small dimension of a DFB laser diode is ideal to integrate this light source into handheld sensors for outdoor spectroscopic applications. The whole sensor system including the highly active SERS substrates is sensitive enough to detect PAHs in seawater at trace level concentrations e. g. pyrene down to 1 nmol/l. Field experiments using the DFB laser as excitation source in SERS are planned.

5. ACKNOWLEDGMENT

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