



Detection of Manganese in Sea Water using Laser Induced Breakdown Spectroscopy

Application Note

Abstract

Levels of dissolved manganese in different water samples like distilled water and sea water with an increase from 30 mg/l to 90 mg/l are measured using emission spectroscopy. Optical emission spectroscopic methods tend to be insensitive in liquids due to strong quenching processes. Laser induced breakdown spectroscopy (LIBS) within a cavitation bubble overcomes this restriction. The output of a double pulsed Q-switched Nd:YAG laser system (wavelength @ 532 nm) is coupled to an optical fibre. This fibre guides the laser pulses to a silicon target immersed in a water sample contaminated with manganese. The cavitation process is initiated at the first laser pulse. At maximum bubble expansion the second laser pulse ignites the plasma in the vapour/gas filled cavitation bubble. Emission is collected by a further optical fibre in the bubble. Characteristic spectral line intensities of manganese are recorded and correlated to an internal calibration standard. Spectral analysis and data acquisition is carried out using an image-intensified optical multi-channel analyser.

Introduction

The aim of this investigation is the development of a LIBS methodology to determine the manganese concentration in coastal flat tidal waters of the North Sea. There are several reasons why this determination is important. Large changes in concentration of this element appear during tides and seasons due to the binding of manganese with mineral particles in suspension or precipitation in sediment [3]. Primary organic particle production and micro-organisms are responsible for re-mineralisation. They have a specific influence on the heavy metal budget of the water and on mineral material in suspension.

The relatively high manganese concentration may also be influenced by seasonal and other mobilisations e.g. reduction of organic material. Supply of freshwater contributed via flood gates may also have a strong influence on tidal flat conditions. The tidal flats between the terrestrial (freshwater) and the marine (North Sea) realm contain between 88 $\mu\text{g/l}$ and 0.5 $\mu\text{g/l}$ manganese [1]. Former investigations have shown levels of dissolved manganese in water samples of concentrations down to 80 $\mu\text{g/l}$ within a cavitation bubble [2].

Experimental setup

A double pulse, Q-switched Nd:YAG laser beam is coupled by a biconvex BK7 lens with a focal length of $f = 40$ mm to a quartz fibre with core diameter $d = 600$ μm . The laser is set to provide 6 ns pulses at the second harmonic wavelength of 532 nm with a repetition rate of 5 Hz. The laser peak irradiance at the fibre tip is 7 MW/cm² for the first laser pulse and 6.2 MW/cm² for the second. A sketch of the experimental setup is shown in Fig. 1.

The fibre is guided to a silicon target and ensures that plasma emission occurs at a fixed location. The silicon target is fixed on an aluminium support, held by an x-y-adjustment to allow horizontal movement of the target, necessary after every sample measurement. The first laser pulse induces a cavitation bubble in the solution containing manganese and strontium as an internal standard. The second laser pulse induces a breakdown within the maximum expansion of the cavitation bubble, i.e., after approx. 80 μs . Plasma emission is collected directly by a 1.2 mm quartz fibre perpendicular to the target. The sample cell is a glass cuvette 20 x 20 x 10 mm³.

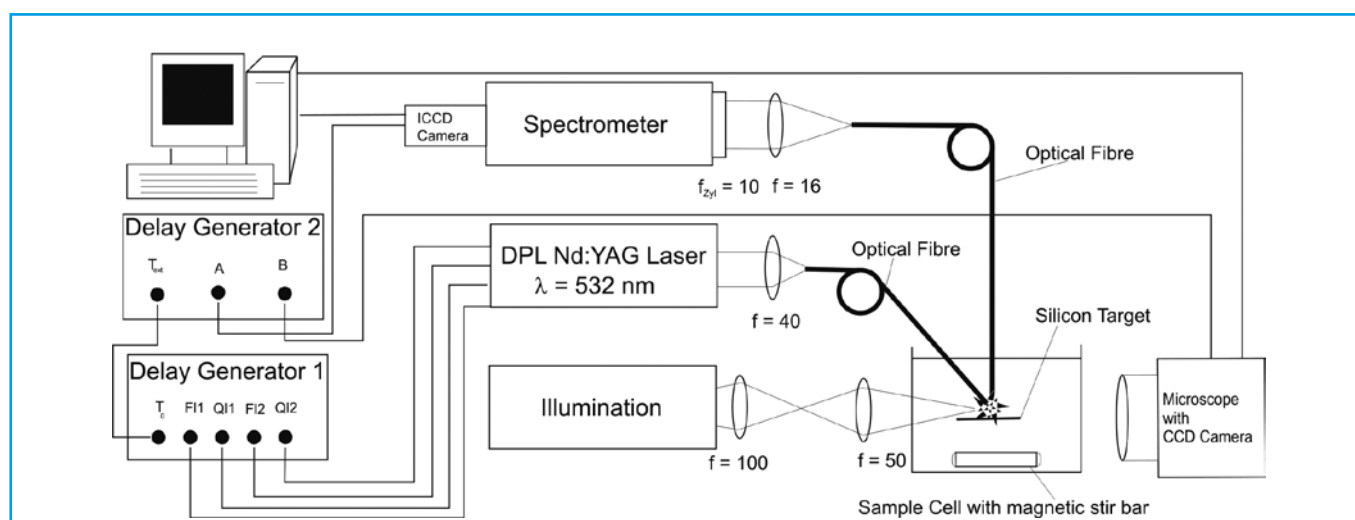


Fig. 1. Scheme of the experimental setup for LIBS by Nd:YAG Double Pulse Laser system (DPL).

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A magnetic stirrer avoids the deposition of the ablated silicon on the target surface. During the experiments, the positioning of the fibre with regard to the target is kept constant. The cuvette itself is moved only to allow changing of sample fluid. A microscope fitted with CCD camera (VGA, 640 x 480 Pixel, 9 x 9 μm) is used to observe bubble expansion and plasma. The camera was used to detect shadow images at an exposure time of 20 μs . The fast photography illumination necessary for observation of the positioning of fibre to target relation is provided by a lamp which is focussed on the target using two BK7 lenses ($f_1 = 100$, $f_2 = 50$). The spectroscopic fibre is adjusted to approx. 1 mm above the surface of the cavitation bubble. This allows to protect the analysis fibre from any damage due to ablation pulse, debris and shock wave effects. The numerical aperture of the sampling fibre is matched by a biconvex lens, $f = 16$ mm, and a cylindrical lens, $f = 10$ mm, to an Acton Research SpectraPro spectrograph. This Czerny-Turner spectrograph with a focal length of 275 mm is used with a grating of 1200 lines/mm blazed at 500 nm. An intensified CCD detector (Andor iStar DH734, 1024 x 1024 Pixel, 13x13 μm , Gen II intensifier) records the signal. Triggering of the gated ICCD camera is set with a delay of 450 ns and 600 ns respectively. The longer delay times improve the signal, especially for lower concentrations. The measuring gate width varies between 1 μs and 10 μs . Continuous background plasma emission is reduced effectively by the given delay times. Control of delay and synchronisation is performed by a delay/gate generator (Stanford Research Systems DG 535). Please see Koch et al. [2] for further details.

Sample preparation

The sample ablation and atomisation are complex processes which depend upon many experimental parameters such as the amount of ablated sample material and the related plasma temperature. The varying parameters are difficult to control and to measure during an analysis. To overcome this restriction an internal standard is favourable to be used. The internal standard is a known concentration of strontium added to the unknown concentration of the analyte manganese. The signal from the analyte is compared with the signal from the internal standard to determine how much analyte is present. For the analysis, the background corrected peak area of the manganese intensity is normalised to the peak area of strontium. A dilution series contains between 30 mg/l Mn and 90 mg/l Mn and 50 mg/l Sr. The solvent is distilled water, fresh water (filtered) and sea water (filtered and unfiltered) with an increasing amount of salt in this order. 0.45 μm SFCA syringe filters are used for filtration.

Results and Conclusion

The quantitative analysis of manganese is carried out using the spectral line triplet at 403.075 nm, 403.306 nm and 403.448 nm of Mn I normalised to the ionic line of strontium at 407.77 nm chosen as an internal standard. When using an internal standard the diversity of parameters like plasma temperature, amount of ablated material, bubble size and also the phase of bubble oscillation have almost no influence on the signal intensity as the internal standard as well as the manganese concentration are effected identically.

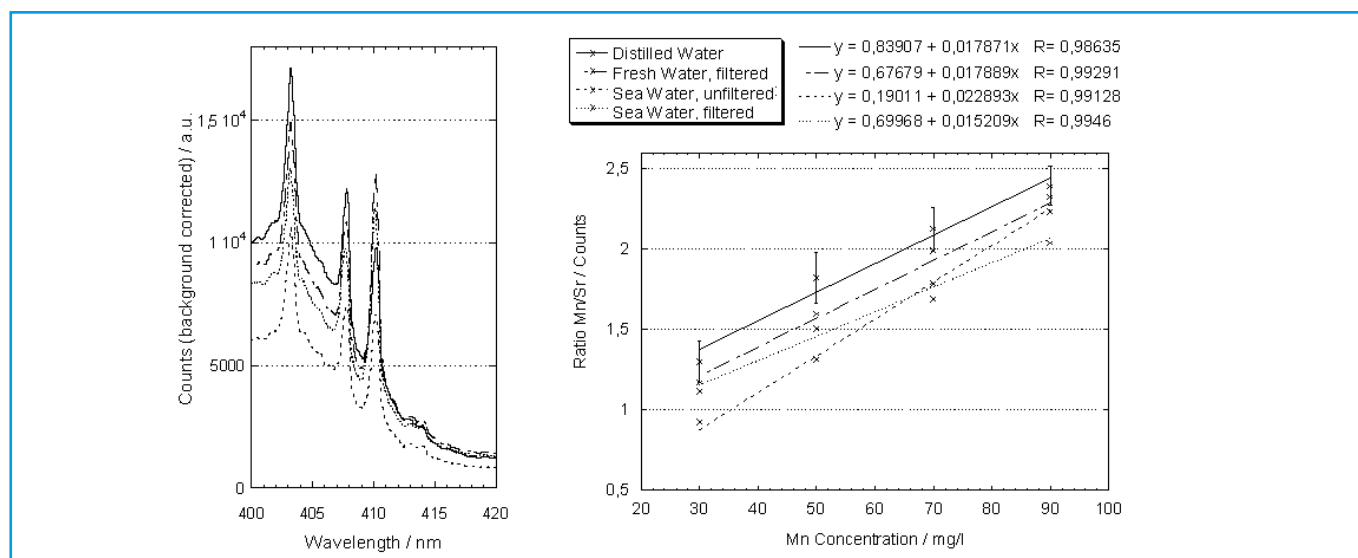


Fig. 2. Calibration series of different water samples



The correlation with strontium as an internal standard is excellent with regression values between 0.986 and 0.994 (Fig. 2). Due to the LOD of 80 µg/l reached in former investigations it is not possible to detect the natural content of Mn in sea water (0.5 – 88 µg/l). The equations of the different calibration curves may vary due to the influence of matrix effects, namely caused by sea salt and suspended particles. Unfiltered sea water with the biggest matrix containing the highest amount of salt and particles are found to be having the lowest number of counts and the steepest slope of the calibration curve. Our results show the feasibility of successfully carrying out LIBS in water within a cavitation bubble. The fluctuation of all measurement parameters is outruled by using strontium as the internal standard.

References

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