

Thermal Lens Spectrometric Detection of Mn^{2+} In Aqueous Solutions

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Summary:

Manganese (Mn^{2+}) is an essential trace element required for normal body functions, but high levels can be toxic to organs as it can damage liver and heart or introduce disorders to fetus and cause dysfunctionality of reproductive system [1]. Thus, it is of high importance to monitor its amounts in the environment. In the work the thermal lens spectrometry (TLS) was applied to detect the trace amounts of Mn^{2+} in water [2]. The detection is based on the adsorption of Mn^{2+} ions onto the surface of silver nanoparticles (Ag^0 NPs), which were synthesized by the reduction of Ag^+ ions to Ag^0 using BH_4^- as a reducing agent and a stabilizer. Manganese solutions with concentrations ranging from 0.5 μM to 10 μM were prepared. The calibration curve showed good linearity over the examined concentration range (Fig. 1). The obtained limit of detection (LOD) and limit of quantification (LOQ) were 20 and 68 nM, respectively and confirmed high sensitivity of the method. Furthermore, the method shows both good repeatability and reproducibility, as well as high precision and accuracy with RSD not exceeding 3%. The maximum contamination level (MCL) of Mn^{2+} in water is 0.91 μM (0.05 mg/L), which indicates values higher than LOD [3]. The results indicate that the proposed TLS-based method is a simple and reliable technique for determination of metal ions in water.

Keywords: Thermal lens spectrometry (TLS), Manganese Mn^{2+} , silver nanoparticles (Ag^0 NPs).

Evaluating manganese concentrations in water is an important environmental and public health issue since Mn^{2+} has direct impact on water quality. Manganese plays an important role in the process of bone growth, functionality of nervous system, maintenance of immune system, regulation of sugar level in blood, as well as the prevention of blood clotting disorders. However, excessive concentrations of Mn^{2+} can be dangerous, negatively affecting the body and causing health problems such as neurological disorders, Parkinson's disease, and manganism [1]. Various analytical methods have been reported for detection of Mn^{2+} in liquids, including voltammetry, inductively coupled plasma atomic emission spectrometry, atomic absorption spectroscopy, UV-Vis spectrometry, and ion chromatography that requires complicated sample preparation procedure, are expensive in use or do not provide high enough LOD [1,4]. Thus, there is a need of developing techniques that overcome these limitations. In this work, we employed a TLS technique for the detection of manganese in water that is highly

sensitive, enabling the detection of concentrations at the level of 10^{-7} a.u..

Material and Method

The silver colloids (Ag^0 NPs) were prepared at room temperature by adding the reducing agent sodium borohydride (0.6 mM) to a solution of $AgNO_3$. The Ag^+ solution (1 mg/mL) was prepared by dissolving 15.74 mg of $AgNO_3$ in 10 mL of water. For the reducing solution, a NaOH solution was first prepared by dissolving 5 g of NaOH in 95 mL of water; then, 8.2 mL of this NaOH solution was diluted with 500 mL of water to obtain a NaOH solution at pH 12.5. By mixing the two prepared solutions at room temperature, a bright yellow color was immediately obtained, which indicates the formation of Ag^0 NPs. The prepared Ag^0 NPs solution was subsequently used for detection of Mn^{2+} that is based on MnO_2 formation which further coats the Ag^0 NPs. For that purpose, 5 mL of Ag^0 NPs solution was mixed with Mn^{2+} solutions (different concentrations of Mn^{2+} (0.5 μM to 10 μM) with a volume above 100 μL . The color of the solution changed from yellow to gray.

In the TLS experimental setup, the excitation beam is the Kr laser beam (407 nm and 70 mW) whereas the probe beam is He-Ne laser (632.8 nm and 2 mW) (Fig. 1). Changes in the probe beam intensity after interaction with the sample were detected using a photodetector THORLABS, MODEL PDA 36A-EC) equipped with an interference filter (MELLE GRIOT, LASER LINE FILTER, CWL 632,8 nm) and connected to a lock-in amplifier (STANFORD RESEARCH INSTRUMENTS, SR830 DSP).

The pump beam was modulated at 5 Hz using a mechanical chopper (SCITEC INSTRUMENTS, 310CD). The excitation beam was focused by a lens of 5 mm focal length (EDMUND OPTICS), while the probe beam was collimated using a pair of lenses of focal lengths 1 mm and 5 mm, respectively (EDMUND OPTICS). Collinear propagation of the focused excitation and probe beams through the sample cell was achieved using a dichroic mirror (MELLES GRIOT).

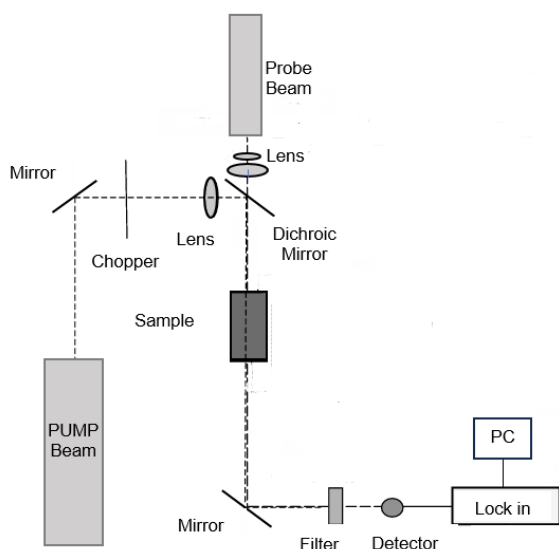


Fig. 1. TLS experimental setup used in the studies.

Results

The TLS method was applied to detect trace amounts of Mn^{2+} in water by introducing varying concentrations of Mn^{2+} (0.5 μM to 10 μM) into a solution containing Ag^0NPs . By plotting the TLS signal as a function of Mn^{2+} concentration, a strong linear relationship was observed (Fig. 1), with a correlation coefficient (R^2) of 0.999. This result indicates that the aggregation behavior of Ag^0NPs is dependent on the Mn^{2+} concentration. The limit of detection (LOD) of the method was calculated to be 20 nM, while the limit of quantification (LOQ) was 68 nM, demonstrating its high sensitivity. The method also exhibited good repeatability and reproducibility, with high precision and accuracy, as indicated by relative standard deviations (RSD) not exceeding 3%. Notably, the achieved LOD (20 nM) is much

lower than the maximum contaminant level (MCL) 0.91 μM (0.05 mg/L) for Mn^{2+} in water. Overall, these results suggest that the proposed method is a simple, reliable, and effective technique for the determination of Mn^{2+} in water.

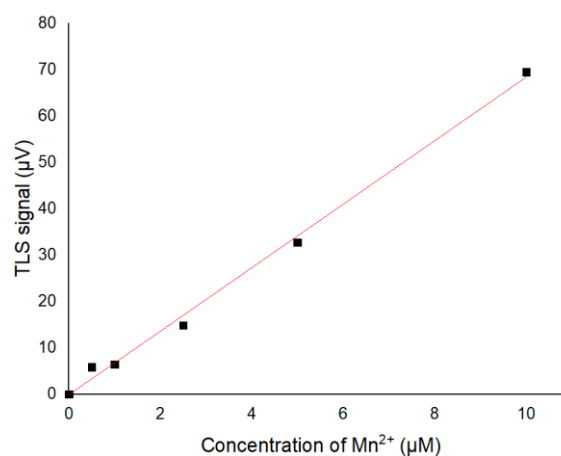


Fig. 2. The calibration curve for determination of Mn^{2+} in water.

Conclusion

In this work, we confirmed the feasibility of highly sensitive detection of Mn^{2+} using the TLS technique. The achieved limit of detection (20 nM) is lower than the maximum contaminant level (0.91 μM) for manganese in water, demonstrating that TLS is a sensitive and simple method for monitoring water quality.

References

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