Determination of colloid silver in drinking water by flow injection analysis with TLS spectrometric UV detection

D. Korte Kobylinska\textsuperscript{a}, M. C. Bruzzoniti\textsuperscript{b}, C. Sarzanini\textsuperscript{b}, Mladen Franko\textsuperscript{a}

\textsuperscript{a} Laboratory of Environmental Research, University of Nova Gorica, Vipavska 13, SI-5000 Nova Gorica, Slovenia
\textsuperscript{b} Department of Analytical Chemistry, University of Torino, Via Pietro Giuria 5, 1-10125 Torino, Italy

E-mail: Mladen.Franko@p-ng.si

Abstract. In this work flow injection analysis coupled to collinear dual beam thermal lens spectrometric UV detection was used for determination of silver in water. The detection is based on the increase in absorbance resulting from the formation of colloidal elemental silver due to reduction of Ag\textsuperscript{+} after reaction with BH\textsubscript{4}-. The optimal performance of the experimental setup was achieved with 500 µL sample injection loops or larger and the flow rate of 0.6 mL/min. The estimated limit of detection (LOD) for silver in water was 0.01 mg/L what compares favorably with the maximum contaminant level (MCL) for silver in drinking water.

1. Introduction
Because of its antibacterial effects, colloid silver is widely used for disinfection of drinking water supplies on international airlines and space craft, whereas definition of "colloidal silver" includes products that contain various concentrations of ionic silver, silver colloids, ionic silver compounds or silver proteins in purified water.

Currently drinking water is produced for aircraft and space missions by disinfection using iodine or ionic colloidal silver. Such technology has been in development for decades by the National Aeronautic and Space Administration (NASA) and European Space Agency (ESA) \cite{1}, but a sensitive water quality monitoring system is also needed for effective utilization of such technology in practice.

There are several methods that enable determination and characterization of colloid silver solutions. Among them, the most frequently used are UV-Vis spectrometry \cite{2}, transmission electron microscopy (TEM) \cite{2} or surface-enhanced Raman spectroscopy (SERS) \cite{3}. While UV-Vis spectrometry lacks in sensitivity, the other two techniques require much too complex and expensive instrumentation to be suitable for continuous and on-line monitoring of water quality in air or space.

Recently the flow injection analysis (FIA) with absorbance detection became one of the most versatile analytical tools for chemical analysis owing to the advantage of using small volumes of reagents or samples, which are injected into a flowing carrier stream \cite{4}. This makes it possible to perform on-line chemical analysis and monitor a variety of chemical processes. To provide a more sensitive detection of analytes than by conventional absorbance measurements, thermal lens spectrometric detection (TLS) \cite{5} was recently introduced in FIA applications as well. This technique is highly sensitive and provides low limits of detection as demonstrated for determination of chromate and various pesticides \cite{6–8}.
In this paper the first application of FIA with dual beam TLS detection method to monitor the quality of drinking water samples is presented for determination of silver.

2. Sample preparation
Colloid silver was produced by the reduction of aqueous solution of silver nitrate (99.8%, CARLO ERBA), following the reaction:

$$2\text{AgNO}_3 + 2\text{NaBH}_4 + 6\text{H}_2\text{O} = 2\text{Ag} + 7\text{H}_2 + 2\text{NaNO}_3 + 2\text{H}_3\text{BO}_3$$

0.6 mM sodium borohydride (98%, ACROS), which served as reductant, was prepared by dissolving 0.095 g NaBH₄ in 25 mL of aqueous solution of NaOH (pH 12.5) and diluting 3 mL of such solution further by the addition of 500 mL of NaOH solution (pH 12.5).

Stock standard solution of AgNO₃ (1 mg/mL of Ag) was prepared by dissolving 15.744 mg of AgNO₃ in 10 mL of water. The stock standard solution was diluted daily to 10 mg/L working standard solution, which was used to prepare solutions for constructing the calibration line (0.05 – 0.70 mg/L) by appropriate dilutions in water.

All solutions were prepared using double-deionized H₂O (18 MΩ/cm) which also served as the FIA carrier for AgNO₃ samples. The colloid silver was produced in flowing NaBH₄ solution (0.6 mM). The AgNO₃ samples injected into carrier were mixed with the reductant in the mixing coil producing Ag⁰. The flow rate of both NaBH₄ and the carrier was 0.3 mL/min.

3. Experimental setup
To determine the presence of colloid silver in water a home built FIA system with a dual-beam TLS UV detection unit was used. The instrumental set-up is schematically presented on Fig. 1.

![Figure 1. FIA setup with TLS detection unit.](image_url)
3.1. Flow-injection analysis set-up

The FIA manifold consists of two HPLC pumps (Shimadzu LC10Ai and KNAUER), one injection valve (Rheodyne model 7725) with replaceable 10, 50, 200, 500 and 1000 μL sample loops and a 50 cm long reaction coil of 1 mm internal diameter made from teflon tubing. With the increase of the volume of sample loop the TLS signal increases but also longer reaction coil is required to provide the proper mixing. Furthermore, higher volume of injected sample increase the time of peak formation what increases the time of colloid silver detection (Fig. 2) without significant increase in LOD. Therefore an injection coil volume of 500 μL was chosen for further experiments.

The carrier and the reductant are pumped through the system by separate pumps at 0.3 mL/min flow rate each. To determine the presence of colloid silver in water, the samples of silver nitrate standard solutions are injected through the injection valve. Silver particles are synthesized in the reaction coil and carried by the carrier further into the flow through detection cell.

3.2. Thermal lens spectrometric detection unit

An Argon-ion laser (Coherent, CR4) operating at 351.4 nm emission line (30 mW) was used as the excitation beam source and a He-Ne laser (Uniphase, Model 1103P) provided the probe beam (632.8 nm, 2 mW). The changes in probe-beam intensity after passing the flow cell (sample) were monitored by a photodiode connected to a lock-in amplifier (Model SR830 DSP) and a PC.

4. Results

The presented data were obtained under optimal experimental conditions (flow rate = 0.3 mL/min for the carrier and the reductant, injection loop = 500 μL and 12.5 pH 0.3 mM concentration of NaBH₄, modulation frequency of excitation beam f = 40 Hz) which were determined previously (Fig. 2).

![Figure 2. TLS signals obtained with different injection loops (silver concentration 0.5 mg/mL).](image)

The TLS signals for on-line generation of Ag⁰ resulting from triplicate injections of different concentrations of silver in water and a corresponding calibration curve are presented in Fig. 3. Signals show a relative standard deviation of less than 2 % and a linear increase with the concentration for the selected concentration range (0.05 – 0.70 mg/mL), which is also reflected in calibration curve ($r^2 = 0.9947$) shown on Fig. 3. The calculated LOD for signal to noise ratio of 3 was 0.01 mg/L. This is sufficiently lower than the maximum contaminant level (MCL) for silver in water, which varies from 0.05 mg/L to 0.10 mg/L in different countries and 0.2-0.5 mg/L in case of space missions.

5. Conclusion

This study confirmed the feasibility of highly sensitive detection of ionic and colloidal silver by on line generation of silver colloids through chemical reduction of ionic silver with sodium borohydride
in a FIA system and its detection by dual beam TLS. The achieved LOD (0.01 mg/L) is much lower than the MCL for silver in water, demonstrating that FIA with TLS detection is a sensitive and simple method for monitoring the quality of water.

![TLS signal calibration curve](image)

**Figure 3.** TLS signals (a) and calibration curve (b) for on-line production of colloid silver.

The sensitivity of TLS technique can be further increased by increasing the laser power of the pump beam and/or changing its wavelength to such a range for which the absorption of blank (0.3 mM NaBH$_4$) is lower, but higher for the analyte. Under such conditions the increase of laser power does not increase the background noise but increases the sensitivity, and consequently results in lower LOD.

### References

[1] K. Pickering, M. Anderson, L. Carter, B. Motil, M. Flynn, J. Garland, 44th AIAA Aerospace Sciences Meeting and Exhibit, **AIAA**, 141 (2006).

[2] H. J. Hah, S. M. Koo, S. H. Lee, Journal of Sol-Gel Science and Technology **26**, 467 (2003).

[3] J. Neddersen, G. Chumanov, T. M. Cotton, Applied Spectroscopy 17, 1059 (1993).

[4] E. H. Hansen, Talanta **64**, 1076 (2004).

[5] M. Franko, Applied Spectroscopy Reviews **43**, 358 (2008).

[6] A. Madžgalj, M. L. Baesso, M. Franko, The European Physical Journal-Special Topics **153**, 503 (2008).

[7] L. Pogačnik M. Franko, Biosensors and Bioelectronics, **18**, 1 (2003).

[8] M. Bavcon Kralj, P. Trebše, M. Franko, TrAC - Trends in Analytical Chemistry **26**, 1020 (2007).