Detection of colloidal silver chloride near solubility limit

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Abstract. Detection of nanoparticles in solution has been made possible by several means; one of them is laser-induced breakdown detection (LIBD). LIBD is able to distinguish colloids of various sizes and concentrations. This technique has been used in several solubility studies. In this study, the formation of colloids in a mixed system of silver nitrate and sodium chloride was observed by acoustic LIBD. Silver chloride has low solubility limit, therefore LIBD measurement is appropriate. Silver and chloride solutions with equal concentrations, set at below and above the solubility of silver chloride as the expected solid product, were mixed and the resulting colloids were observed. The result of LIBD measurement showed that larger particles were present as more silver and chloride introduced. However, once the concentrations exceeded the solubility limit of silver chloride, the detected particle size seemed to be decreasing, hence suggested the occurrence of coprecipitation process. This phenomenon indicated that the ability of LIBD to detect even small changes in colloid amounts might be a useful tool in study on formation and stability of colloids, i.e. to confirm whether nanoparticles synthesis has been successfully performed and whether the system is stable or not.

1. Introduction
Detection of nanoparticles presences in liquid medium can be achieved by applying laser-induced breakdown detection (LIBD). LIBD is a sensitive characterization technique developed especially for detecting colloids with small size and low concentration [1, 2]. The liquid samples subjected to LIBD measurement need no specific treatment for preparation, i.e. it can be measured as it is [3]. Previous study has shown that LIBD can detect nanoparticles as small as few nanometers and down to several part per trillion (ppt) [4], while also can be applied both in situ or online monitoring system [5 – 7].

Some studies related to solubility had applied LIBD to detect solid formation more precisely [8 – 17]. Most of the samples were oxides and optical LIBD was often employed [8 – 10, 12, 13]. Applications of acoustic LIBD in solubility study are somewhat less often. Meanwhile, solubility of metal salt is also interesting to be studied, since it can be an unwanted product in a chemical process. Some metal salts might be formed due to excess amount of precursors added during metal nanoparticle synthesis, e.g. formation of silver chloride (AgCl) precipitate when silver nitrate (AgNO₃) is introduced to chloroauric acid (H AuCl₄) at concentrations beyond the solubility limit of AgCl [18].

This research aimed to study the use of acoustic LIBD in solubility study, particularly in detecting the formation of colloidal AgCl as a reaction product of AgNO₃ and NaCl while observing its
evolution near solubility limit. AgCl has low solubility, i.e. colloids are form at low concentration of Ag and Cl, and therefore it is appropriate for LIBD measurement.

2. Experimental method
Silver chloride (AgCl) samples were prepared by introducing sodium chloride (NaCl) solution into silver nitrate (AgNO₃) solution. The concentrations of Ag and Cl after mixing were set equally at 5×10⁻⁶ mol/L, 10⁻⁶ mol/L, 1.2×10⁻⁵ mol/L, 1.5×10⁻⁵ mol/L, and 2×10⁻⁵ mol/L. As stock solutions, 0.5 mol/L AgNO₃ and 0.5 mol/L NaCl were prepared by proper dissolution of AgNO₃ powder and NaCl powder in distilled water. Each sample was placed in a 10 ml glass container. Two other samples containing only AgNO₃ and only NaCl were also prepared to provide data comparisons.

The experimental setup for acoustic LIBD used in this study is shown in figure 1. Pulsed laser beam from nanosecond Nd:YAG laser (Q-smart 850, Quantel) at 532 nm wavelength and 10 Hz frequency was focused into the aqueous sample in glass container. Upon interaction between laser beam and colloid passing by the focused area, a breakdown was occurred following plasma formation. The acoustic signal was then detected by a microphone-recorder system and saved as an audio file. Each file, which contained data for one measurement, was processed and analyzed using a homemade processing program [19].

In this experiment, each sample was measured by LIBD technique at increasing laser energies, which were set from 0 to 5 mJ. The pulsed laser energy setting were carried out with considering the attenuation by a glass cover which was put on top of the glass container to minimize contamination. For statistical purpose, three measurements were done for each condition. Breakdown occurrences from 1000 laser shots were observed in every measurement.

3. Result and discussion
AgCl was expected to be formed from an exchange reaction between AgNO₃ and NaCl, as shown in equation 1 [20].

$$\text{AgNO}_3(aq) + \text{NaCl}(aq) \rightarrow \text{AgCl}(s) + \text{NaNO}_3(aq)$$ (1)

When AgNO₃ was dissolved in distilled water below its solubility, it dissociated into Ag⁺ and NO₃⁻ ions. In the presence of Cl⁻ from NaCl, Ag⁺ formed the insoluble AgCl. Such reaction is called coprecipitation, where an ion brings down another to precipitate. Na⁺ and NO₃⁻ were present as
spectator ions, because they do not participate in the reaction [20]. Therefore the mixed sample was simply mentioned as AgCl sample.

Figure 2 shows the LIBD measurement result of AgNO₃, NaCl, and AgCl samples. The homemade processing program processed the recorded signal by dividing it into blocks of signal with equal width [19]. The block width was set so that it represent the time gap between two consecutive laser shots. A breakdown was expected to generate within this gap, if any. To count the breakdown, the processing system detected any acoustic signal which exceeded the predetermined intensity threshold. The number of breakdowns generated for a certain number of laser shots was called breakdown probability. The breakdown probabilities increased with increasing pulsed laser energy, hence the so-called S-curve. The S-curve of AgCl was positioned more to the left compared to those of AgNO₃ and NaCl. This might indicate the formation of AgCl colloids as reaction product of AgNO₃ and NaCl. The dotted lines are precursor solutions before mixing and the solid line signifies the mixed solution. A closer look to the breakdown threshold energies suggested the similar colloidal size of AgNO₃ and AgCl, however the steeper slope of the mixed solution hinted that more colloids were present. The breakdown threshold energy was the pulsed laser energy needed to induce breakdown probability of 0.01. In LIBD analysis, breakdown threshold energy corresponds to colloidal size, while S-curve slope correlates to colloidal concentration. The lower the breakdown threshold energy, the larger the colloidal size; while the steeper the slope, the more concentrated the colloids [4].

![Figure 2](image_url)

**Figure 2.** The shift in S-curves implied the formation of AgCl through coprecipitation process.

Further experiment was carried out to see the evolution of colloidal AgCl near the solubility limit. The solubility product constant (Ksp) of AgCl is $1.66 \times 10^{-10}$, thus giving the solubility value of AgCl as low as $1.33 \times 10^{-5}$ mol/L. Three of the AgCl samples prepared had Ag and Cl concentrations below AgCl solubility limit, whilst the others were above it. Figure 3a shows the LIBD results for AgCl with various concentrations of Ag and Cl. Curves with solid lines represent mixed solutions in which the Ag and Cl concentrations were below AgCl solubility limit, whereas the dotted lines represent mixed solution with Ag and Cl concentrations above AgCl solubility limit. As Ag and Cl concentrations increased, the S-curve shifted to the left; yet it was back to the right when the concentrations exceeded the solubility limit of AgCl.

A clearer detail on breakdown threshold energy is shown by figure 3b. For the three samples with Ag and Cl concentrations below AgCl solubility limit, the breakdown threshold energy values decreased as concentrations increased. It indicated that larger particles were formed as Ag and Cl
concentrations increased. However, once Ag and Cl concentrations in the mixed sample exceeded AgCl solubility value, i.e. at $1.5 \times 10^{-5}$ mol/L, the breakdown threshold energy rose again, which implied the presence of smaller particles in the sample. Further increase in Ag and Cl concentrations, i.e. at $2 \times 10^{-5}$ mol/L, caused the breakdown threshold energy to decrease, suggesting that larger particles had been formed again. It was the same trend with those of below AgCl solubility. From this result, it implied that LIBD might be useful to detect when solubility limit has been exceeded.

Figure 3. An increase in Ag and Cl concentration affected the (a) S-curves and (b) breakdown threshold energy. The dotted red line in the right figure represents the solubility value of AgCl.

4. Conclusion
Formation of colloidal AgCl and its evolution near solubility limit was observed by means of acoustic LIBD. Introduction of NaCl into Ag solution resulted in higher concentration of colloids observed due to the formation of AgCl colloid. For Ag and Cl concentrations below AgCl solubility limit, larger particles were detected when higher concentrations of Ag and Cl were given. Once the solubility limit was exceeded, the colloidal size decreased. It rose again when more Ag and Cl were added. This phenomenon indicated that the ability of acoustic LIBD to detect small changes in colloid amount might be useful in studying solubility of a substance, including metal salt. It can signify the formation of reaction product in a mixed sample and detect the solubility limit. It might also be useful for study on colloidal stability. However, to get more pronounced trend and clear solubility value, more detailed research with more variation of Ag and Cl concentration near solubility limit is needed.

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References
[1] Thang N M, Knopp R, Geckeis H, Kim J I and Beck P 2000 Anal. Chem. 72 1
[2] Bundschuh T, Yun J-I and Knopp R 2001 Fresenius J. Anal. Chem. 371 1063
[3] Walther C, Bitea C, Hauser W, Kim J I and Scherbaum F J 2002 Nucl. Instr. and Meth. in Phys. Res. B 195 374
[4] Kim J I and Walther C 2006 Laser-induced breakdown detection *Environmental Colloids and Particles: Behaviour, Separation, and Characterisation* vol 10 eds K J Wilkinson and J R Lead (Chichester: John Wiley & Sons) chapter 12 pp 555-612

[5] Hauser W, Geckeis H, Kim J I and Fierz Th 2002 *Colloids Surf. A* 203 37

[6] Zanker H 2010 In situ measurements on suspended nanoparticles with visible laser light, infrared light, and x-rays *Nanoparticles in the Water Cycle* eds F H Frimmel and R Nießer chapter 8 pp 117-138

[7] Jung E C, Cho H R, Park M R and Baik M H 2011 *J. Kor. Rad. Waste Soc.* 9 41

[8] Bundschuh T, Knopp R, Müller R, Kim J I, Neck V and Fanghänel Th 2000 *Radiochim. Acta* 88 625

[9] Neck V, Müller R, Bouby M, Altmann M, Denecke M A and Kim J I 2002 *Radiochim. Acta* 90 485

[10] Bitea C, Walther C, Kim J I, Geckeis H, Rabung T, Scherbaum F J and Cacuci D G 2003 *Colloids Surf. A* 215 55

[11] Bitea C, Müller R, Neck V, Walther C and Kim J I 2003 *Colloids Surf. A* 217 63

[12] Walther C 2003 *Colloids Surf. A* 217 81

[13] Bouby M, Geckeis H, Manh T N, Yun J-I, Dardenne K, Schäfer T, Walther C and Kim J-I 2004 *J. Chromatogr. A* 1040 97

[14] Cho H R, Walther C, Rothe J, Neck V, Denecke M A, Dardenne K and Fanghänel Th 2005 *Anal. Bioanal. Chem.* 383 28

[15] Cho H R, Park K K, Jung E C and Jee K Y 2007 *J. Kor. Rad. Waste Soc.* 5 189

[16] Rothe J, Walther C, Brendebach B, Büchner S, Fuss M, Denecke M A and Geckeis H 2009 *J. Phys.: Conf. Ser.* 190 012188

[17] Shin Y, Bae S and Lee W 2013 *Adv. Env. Res.* 2 167

[18] Mallin M P and Murphy C J 2002 *Nano Lett.* 2 1235

[19] Putri K Y, Zahar I and Isnaeni 2016 *Prosiding LINOF 2015* (Tangerang Selatan: Pusat Penelitian Fisika LIPI) 102

[20] Kotz J C, Treichel P M and Townsend J R 2009 *Chemistry & Chemical Reactivity*, 7th ed (Belmont: Thomson Brooks/Cole) pp 121-130