Detection of aquatic colloids in drinking water during its distribution via a water pipeline network

T. Wagner*, T. Bundschuh*‡, R. Schick** and R. Köster*

* Forschungszentrum Karlsruhe GmbH, Institute for Technical Chemistry, Water Technology and Geotechnology, P.O. Box 3840, D-76021 Karlsruhe, Germany (E-mail: tobias.wagner@itc-wgt.fzk.de; tobias.bundschuh@itc-wgt.fzk.de; rainer.koester@itc-wgt.fzk.de)

** Zweckverband Bodensee-Wasserversorgung, Water Control and Research Laboratory, Süßenmühle, D-78354 Sipplingen, Germany (E-mail: roland.schick@zvbwv.de)

‡ corresponding author

Abstract Laser-induced Breakdown Detection (LIBD) is a highly sensitive method for the direct detection of nano-particles (colloids). During the detection process plasmas are generated on single particles by a focused laser beam, the resulting plasma light emissions are detected optically. The method is based on the difference in breakdown thresholds of liquid and solid matter, it is lower for solid material. The laser pulse energy is adjusted precisely so that in the pure liquid no breakdown events occur, and only in the presence of colloids is the breakdown threshold in the focal volume exceeded. The spatial distribution of several thousand recorded plasma flashes within the focal volume reveals the mean particle diameter. The evaluation of the number of breakdown events per number of laser pulses results in a breakdown probability, together with the particle size the concentration is calculated using specially-designed computer software. Compared to conventional laser light scattering methods the LIBD is approximately 6 orders of magnitude more sensitive for particles smaller than ca. 0.05 µm. Together with laser light obscuration the LIBD technique has been used successfully for the quantification of aquatic nano-particles during drinking water processing and its distribution via a pipeline network of nearly 1,700 km total length. In addition, the particulate content of several brands of mineral water has been investigated.

Keywords Breakdown detection; colloids; drinking water; laser; particle size; water pipeline

Introduction

Colloids are officially defined by their size; they range from 1 nm to 1 µm (Everett, 1989; Myers, 1991; Buffle and Leppard, 1995). However, this definition does not reflect important functional boundaries. Groundwater scientists often use an upper limit of 10 m that represents the mobile material within groundwater flow. On the other hand, there are humic substances that are smaller than 1 nm and that exhibit polyelectrolyte behavior. Thus, when referring to the term “colloid” it is important to recognize that there is no such thing as a single, rigid definition, and that such a definition would not make much sense in many cases.

Natural colloids are of a very heterogeneous nature regarding parameters like size, chemical composition, shape and surface charge (Hofmann et al., 2003a). They may play a key role in the transport of contaminants in aquatic systems which is of major concern in environmental research (McCarthy and Zachara, 1989; Hofmann, 2001) as well as drinking water purification. Since they are formed out of equilibrium, colloids also have to be taken into account in geochemical models. What is more, they are believed to represent a major fraction of the global carbon budget.

Due to their large surface and sorption capacity colloids may increase the total amount of pollutants in water beyond what can be expected from the thermodynamic solubility product of their respective chemical compounds (McCarthy and Zachara, 1989; Honeyman and Santschi, 1992). Also, they can provide a medium for microbial growth and thus can be
an indication for the presence of disease-causing microorganisms, including bacteria, viruses and parasites (Ryan and Elimelech, 1996; Abbaszadegan et al., 1999). Especially viruses are often responsible for the outbreak of waterborne diseases (US Environmental Protection Agency, 2000). There will be strict impositions regarding both the monitoring of drinking water quality throughout the treatment processes, transport and storage and the protection of its natural sources. Therefore, the efficient removal of particulate water content is and will be of vital importance in water and wastewater treatment.

Quantification of aquatic colloids is associated with considerable difficulties, because they are often found in low concentrations and in a colloid size distribution where small particles with diameters below 0.1 µm predominate (Kim, 1994). For the correct description of aquatic colloids non-invasive methods are preferred (Plaschke et al., 2001; Hofmann et al., 2003b). They do not affect the original colloid population and, thus, do not cause any artifacts during measurement. Light scattering methods allow for a direct, non-invasive quantification of colloids. However, such methods are only suited for determining size distributions of multi-modal dispersions with certain limitations. Light is not only scattered selectively by the colloids to be studied, but also by the solvent or by gas bubbles and scratches on the wall of the sample cell. Also, the detection sensitivity for particles smaller than 0.1 µm in diameter is often not sufficient. In the past years, the Laser-induced Breakdown Detection (LIBD) has been developed as a novel method for quantifying colloids. The method had already been applied for the detection of particles in purest water used by the semiconductor industry (Kitamori et al., 1989; Fujimori et al., 1992) as well as for the characterization of several aquatic colloids (Knopp, 1996; Bundschuh, 1999).

Method
The principle of the LIBD is based on the generation and counting of breakdown events on colloidal particles in liquids. Light of very high intensity can lead to a breakdown of the dielectric property of matter. The necessary power densities can be generated by focusing a pulsed laser beam with pulse energies typically under 1 mJ and pulse lengths of several ns. As a result of the very high electrical field strength (around $10^{11}$ V/m (Bettis, 1992)) the electrons of atoms and molecules are released by multi-photon absorption. The initially released electrons absorb further light quanta and are accelerated within the electrical field of the laser pulse (inverse bremsstrahlung). These electrons in turn knock further electrons out of atoms which in the end leads to an electron avalanche. The ionization increases strongly, and a plasma is generated (Radziemski and Cremers, 1989; Fujimori et al., 1992). During the process described the plasma heats up to several thousand kelvin and expands quickly, resulting in a shock wave. After the end of the laser pulse the plasma cools down, recombination processes and emission of light occur. The minimally required critical power density for plasma generation (breakdown threshold) depends on the state of aggregation of matter. It is highest for gases, lower for liquids and lowest for solids (Bettis, 1992). The LIBD principle is based on this difference of breakdown thresholds between liquid and solid matter. The laser pulse energy is adjusted so that in the pure liquid no breakdown event occurs but in the presence of solids (colloids) the breakdown threshold within the focal area of the focused laser beam is exceeded. The breakdown events can be detected piezo-electrically and/or optically (plasma light emissions) by means of a camera. Figure 1 shows the principle of breakdown generation in aqueous solutions. The number of breakdown events per number of laser pulses is defined as the breakdown probability and is dependent both on particle concentration and size.

In the literature the determination of particle sizes by means of interpretation of photo-acoustic piezo amplitude distributions is described (Kitamori et al., 1988, 1989).
However, such photo-acoustic piezo amplitude distributions depend on both particle size and concentration, just like the breakdown probability. Therefore it is not possible to get any information about particle size by solely recording piezo amplitude distributions. Another approach for particle size analysis using the correlation between the plasma delay times and plasma intensities is found in the literature (Ajiro et al., 1992). It was possible to distinguish 0.04 µm from 3 µm particles, a more precise resolution failed because of the unfavorable spatial distribution of the laser pulse power density and because of the limited time resolution of the photomultiplier used. We followed the approach to determine the spatial distribution of the breakdown events within the focal area by use of an image processing system. From the statistical distribution of the determined local plasma coordinates in the plane of projection of the breakdown events, information about the expansion of the effective focal volume is available. This approach is based on the consideration that the probability for igniting a plasma on a particle depends on the power density of the laser pulse at the location of the particle and on the number of the particle’s weakest bound electrons. This means that an increasing number of these so-called initial electrons are available with increasing particle size. Hence, the bigger a particle, the lower the laser pulse power density that is necessary for the generation of a breakdown. This also means that bigger particles are able to ignite in the energy-depleted areas of the focus. By recording a sufficient number of plasmas, a spatial distribution of breakdown events is obtained that reflects the ignition range of the colloids in the focus. This means that with increasing particle size in a dispersion, an increase in the ignition range in the focus and, hence, in the effective focal length (ignition length) can be observed (Hauser and Bundschuh, 2000; Bundschuh et al., 2001a).

For determination of the ignition length of reference colloids, each sample is measured until a few thousand plasma events have been recorded. Their extension, i.e. the ignition length $L_\text{Z}(P)$, is determined considering 99.7% of all plasma events in the focus. $L_\text{Z}(P)$ of

**Figure 1** Schematic illustration of the breakdown principle with analytical information for LIBD.
the reference colloids is then plotted against the corresponding particle diameters $d$ on a double logarithmic scale. The ignition lengths increase linearly with increasing particle diameter. The relation between the ignition length and the particle diameter is shown in Eq. (1).

$$d = 10 \left( \frac{L_Z(P)}{b} \right)^{-a}.$$  

By fitting this function to the data points the parameters $a$ and $b$ can be calculated. It is then possible to use this calibration function for the determination of the number-weighted mean particle diameter of colloids in unknown samples (Bundschuh, 1999; Hauser and Bundschuh, 2000; Bundschuh et al., 2003).

For the calculation of the particle concentration, the effective focal volume is computed (Knopp, 1996; Scherbaum et al., 1996) using the mean particle diameter derived from the ignition length. The relation between the effective focal volume and the observed breakdown probability (Knopp, 1996; Scherbaum et al., 1996; Bundschuh, 1999) allows the determination of the particle concentration according to Eq. (2) (Bundschuh, 1999; Hauser and Bundschuh, 2000; Bundschuh et al., 2001b).

$$c_P = \left( 1 - W_{Bd} \frac{V_p}{V_{F, eff}(P)} \right) \cdot \frac{1}{V_p}$$  

with $c_P$ = colloid concentration
$W_{Bd}$ = breakdown probability
$V_p$ = volume of a colloid particle
$V_{F, eff}(P)$ = effective focal volume

The experimental setup of an LIBD instrumentation is illustrated schematically in Figure 2. A frequency doubled, pulsed Nd:YAG laser (Continuum Surelite I) is used at a wavelength $\lambda_{em.} = 532$ nm and a repetition rate of 20 Hz. After passing a servo-motor controlled variable attenuator controlling the laser pulse energy, the laser beam is focused by a plano-convex lens of 60 mm focal length into the sample dispersion in a rectangular cuvette with a volume of 3.5 mL. The incident laser pulse energy is monitored by a calibrated pyroelectric detector (Newport 818J-09B) and adjusted just below the breakdown threshold of ultra pure water (MilliQ synthesis A10, UF-module with 5 kD cut-off, UV-module). The plasma light emissions generated during the breakdown process are magnified by a microscope (Leica) and recorded by means of a triggered CCD camera (Basler A302fs). The images are transmitted to a personal computer for data storage and evaluation. The average laser pulse energy and the $x,z$-coordinates of each plasma event are determined using a newly designed, fully automatic image processing software and are subjected to further data processing.

![Figure 2](https://iwaponline.com/wst/article-pdf/50/12/27/419436/27.pdf)
Results and discussion

For calibration of the LIBD instrumentation various diluted polystyrene standard colloid dispersions with particle diameters of about 0.02 µm to about 1 µm are used. The polystyrene particles are dispersed in ultra pure water at the concentration desired and measured in quartz sample cells. After calibration and parameterization of the LIBD system by the procedure described (Bundschuh, 1999; Hauser and Bundschuh, 2000; Bundschuh et al., 2001a,c) the LIBD is used for the characterization of particles in drinking water during processing (Bundschuh et al., 2001b; Wagner et al., 2002) and distribution via a water pipeline network of approximately 1,700 km total length.

The main obligations of water purification plants are water purification, supply and continuous quality inspection. The distribution and storage of the drinking water are additional tasks assigned to water suppliers. During the purification process of raw water the particulate content must be effectively reduced in order to minimize the risk of contamination by toxic substances as well as the risk of germination of microorganisms. For an efficient removal of bacteria, viruses, and parasites, it is important that colloidal particles are held back equally well as the larger suspended particles (typically > 1 µm). Also, during the distribution over a pipeline network there must be no colloid generation, e.g. by bacterial growth. Therefore, it is of major importance that both the size and the number of particles in the colloidal size range are monitored.

The water taken from Lake Constance at a depth of 60 m already meets the legal requirements regarding chemical and physical quality parameters. Therefore, water treatment at the processing plant Sipplingen Berg mainly aims at a reliable deactivation and removal of pathogenic germs and any particulate water content. In the first step of water purification the water from Lake Constance is pumped from a depth of 60 m below sea level and micro-strained (15 µm cut-off). The following oxidation step using ozone (1.0-1.2 mg/L) is designed for disinfection and oxidation of solid matter in the water. Next a small amount of FeCl₃ (0.1 mg/L) is added before filtration through rapid sand filters. Finally, chlorine is added for disinfection. The purified water is then stored in tanks and distributed via two main lines. An illustration of the different steps of water purification as performed by the Bodensee-Wasserversorgung is shown in Figure 3.

The Bodensee-Wasserversorgung supplies many communities in Southern Germany with drinking water form Lake Constance. A pipeline network of 1,700 km total length with mainly large-calibre pipes is used for this purpose. The pipe diameters range from 0.1 m (small supply pipe) up to 1.6 m directly after the water processing plant Sipplingen Berg. Two water mains form the skeleton structure of the water pipeline system. They are made of reinforced or prestressed concrete. Additional water tanks, pumping stations and turbines are part of the distribution system.
The 1st main line leads towards Tuttlingen and across the mountains of the Schwäbische Alb. Next is the water deficiency area Baarhochfläche, the line then continues to Villingen-Schwenningen, Rottweil, Albstadt and Balingen into the area Reutlingen/Tübingen, then Böblingen and Sindelfingen, through Stuttgart, Kornwestheim and Ludwigsburg as far as Bietigheim. The 2nd main line directly leads to the area of the Neckar (main service area) and north of it. Near Tübingen the 1st and 2nd main meet and continue as far as the Mosbach area. The pipeline network has some elevated tanks for temporary storage. A map of the whole pipeline network of the Bodensee-Wasserversorgung along with the sampling points and the different elevated tanks is shown in Figure 4. The local distribution to the consumer is managed by the respective community.

For examination of the purification process the suspended matter (particles > 1 µm in diameter) has been quantified with laser light obscuration. Particles in the colloidal size range and in lower concentrations as in natural waters or drinking water cannot be detected with this method since it is not sensitive enough. The same applies to the photon correlation spectroscopy (see Figure 7). Therefore, the water samples taken after different steps of water purification and at various points of the pipeline network have also been analyzed by LIBD.

It has been shown by a perennial (Schick et al., 2002) research project that suspended matter is effectively removed by addition of small amounts of iron(III) salts ($\beta_{Fe} = 0.1$ mg/L) before filtration through rapid sand filters. It is no conventional flocculation precipitation, but the small amount of iron leads to the formation of iron hydroxide colloids of

![Figure 4](https://iwaponline.com/wst/article-pdf/50/12/27/419436/27.pdf)
0.1 to 0.8 µm in size. They are partly covered with NOM (natural organic matter) and have a high surface affinity to the filter medium which leads to a coating layer on the sand grains. This conditioning of the filter medium in turn accounts for a better attachment of the particulate water content and explains the high efficacy of the Fe(III)-assisted filtration (see Winzenbacher (2000) for a more detailed description).

The concentration of suspended particulate matter (particles with a diameter typically above 1 µm) in the drinking water was reduced from 5,000–30,000 (typically around 15,000) to merely 50–150 particles per mL (Schick et al., 2002), widely independent of seasonal fluctuations of the particulate content of the lake water. By using LIBD analysis it could be shown that the Fe(III)-assisted filtration step is highly effective for the removal of the much smaller colloidal water content, too. After micro-straining, but before the filtration step, $5 \times 10^5 - 8 \times 10^8$ colloids per mL were found depending on the time of year, and the number-weighted mean diameter ranged from 0.02 µm to 0.7 µm with a volume concentration of $10^{-7}$ to $10^{-9}$ m³/m³. After the filtration step the values had decreased to only 1 to 10% (removal rate: 90–99%) of the original values (Wagner et al., 2002).

In order to find out about possible changes in the particle population of the purified water from Lake Constance during transport and storage, investigations on the particulate content have been carried out at several points of the pipeline network since late 2001. It was found that both the number and the size of colloids and particles $> 1$ µm remains quite constant, even if the water is transported and stored for up to 15 days in total. There was no sign of an increase (e.g. by smashing of aggregates/agglomerates, precipitation and flocculation phenomena, germination) or a decrease (e.g. by precipitation, biological decomposition, adsorption) in particulate water content. The values at all sampling points were very similar to the ones directly after the water purification plant Sipplinger Berg. This may be due to the fact that the whole distribution system is inspected and maintained on a regular basis. Table 1 lists the concentrations of particles $> 1$ µm and of colloids at the different sampling points over the whole pipeline system. They have been examined both by laser light obscuration and Laser-induced Breakdown Detection. In addition, the remains of iron from the Fe(III)-assisted filtration are listed. Figure 5 illustrates the colloid concentrations: as is obvious the concentrations in the water samples were all similar to that of “fresh” drinking water right after purification. The colloid number densities varied from $4.7 \times 10^6$ to $6.6 \times 10^6$ mL⁻¹, and even the elevated tanks which are farthest from the processing plant, Rehberg and Hardhof, showed with $6.3 \times 10^6$ and $4.7 \times 10^6$ mL⁻¹ only a slight increase of colloid concentration over the number density of drinking water at the processing plant, which was $3.1 \times 10^6$ mL⁻¹.

To get an idea of the low colloid concentration in drinking water from Lake Constance

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Particle concentration $\text{[part./mL]}$</th>
<th>Colloid concentration $\text{[coll./mL]}$</th>
<th>Iron concentration $\text{[µg/L]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processing plant Sipplinger Berg</td>
<td>50–150</td>
<td>$3.1 \times 10^6$</td>
<td>4.5–5.5</td>
</tr>
<tr>
<td>Tunnel inflow cistern Büttnau</td>
<td>80–110</td>
<td>$5.0 \times 10^6$</td>
<td>5.0–5.1</td>
</tr>
<tr>
<td>Elevated tank Rohr</td>
<td>100–296</td>
<td>$5.9 \times 10^6$</td>
<td>4.4–5.5</td>
</tr>
<tr>
<td>Elevated tank Wimsheim</td>
<td>110–213</td>
<td>$6.6 \times 10^6$</td>
<td>4.4–8.1</td>
</tr>
<tr>
<td>Elevated tank Stromberg</td>
<td>150–224</td>
<td>$5.9 \times 10^6$</td>
<td>4.2–6.5</td>
</tr>
<tr>
<td>Elevated tank Schweinsberg</td>
<td>110–211</td>
<td>$5.1 \times 10^6$</td>
<td>4.1–4.6</td>
</tr>
<tr>
<td>Elevated tank Hardhof</td>
<td>140–194</td>
<td>$4.7 \times 10^6$</td>
<td>5.1</td>
</tr>
<tr>
<td>Elevated tank Rehberg</td>
<td>150–210</td>
<td>$6.3 \times 10^6$</td>
<td>4.9–5.4</td>
</tr>
</tbody>
</table>
several brands of commercially available carbonated and non-carbonated mineral waters have been examined by means of LIBD. The mineral waters came in glass and plastic bottles. To ensure identical measurement conditions the carbonated waters have been degassed before investigation by shaking and opening the bottles carefully multiple times. The results can be seen in Table 2, for a better comparison they are shown graphically in Figure 6. The colloid densities found were typically in the range of $10^6$ to $10^8$ mL$^{-1}$, the corresponding sizes ranged from 0.015 to 0.773 µm. It seems that the mineral waters that come in glass bottles contain more and bigger colloids. One reason for this might be a formation of colloids by polynucleation of silicic acid released from the glass walls of the bottles, even though this process is slow and normally found at a pH value of about 9 or higher. In summary the colloidal content of commercially available mineral waters is often equal to or higher than that of drinking water coming from Lake Constance.

Conclusions
Both the laser light obscuration and the rather novel Laser-induced Breakdown Detection as a highly sensitive tool for the direct, non-invasive characterization of aquatic colloids.

<table>
<thead>
<tr>
<th>Brand of mineral water</th>
<th>Colloid diameter [µm]</th>
<th>Colloid concentration [coll./mL]</th>
<th>Colloid concentration [µg/L]</th>
<th>Type of water/bottle</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Volvic”</td>
<td>0.049</td>
<td>$3.8 \times 10^6$</td>
<td>0.24</td>
<td>Non-carbonate/plastic</td>
</tr>
<tr>
<td>“Evian”</td>
<td>0.062</td>
<td>$1.7 \times 10^7$</td>
<td>2.23</td>
<td>Non-carbonated/plastic</td>
</tr>
<tr>
<td>“Vittel”</td>
<td>0.020</td>
<td>$2.0 \times 10^6$</td>
<td>0.01</td>
<td>Non-carbonated/plastic</td>
</tr>
<tr>
<td>“Gerolsteiner”</td>
<td>0.026</td>
<td>$2.5 \times 10^7$</td>
<td>0.25</td>
<td>Carbonated/plastic</td>
</tr>
<tr>
<td>“Römer classic”</td>
<td>0.028</td>
<td>$1.2 \times 10^8$</td>
<td>1.52</td>
<td>Carbonated/plastic</td>
</tr>
<tr>
<td>“Apolinarias”</td>
<td>0.015</td>
<td>$6.1 \times 10^6$</td>
<td>0.01</td>
<td>Carbonated/plastic</td>
</tr>
<tr>
<td>“Alwa classic”</td>
<td>0.017</td>
<td>$3.2 \times 10^7$</td>
<td>0.09</td>
<td>Carbonated/plastic</td>
</tr>
<tr>
<td>“Griesbacher”</td>
<td>0.021</td>
<td>$2.9 \times 10^8$</td>
<td>6.27</td>
<td>Carbonated/glass</td>
</tr>
<tr>
<td>“Krumbacher”</td>
<td>0.208</td>
<td>$1.7 \times 10^7$</td>
<td>85.5</td>
<td>Carbonated/glass</td>
</tr>
<tr>
<td>“K3 Sprudel”</td>
<td>0.069</td>
<td>$4.1 \times 10^7$</td>
<td>7.34</td>
<td>Carbonated/glass</td>
</tr>
<tr>
<td>“Selters”</td>
<td>0.133</td>
<td>$2.0 \times 10^7$</td>
<td>16.2</td>
<td>Carbonated/glass</td>
</tr>
<tr>
<td>“Bad Vilbeler”</td>
<td>0.189</td>
<td>$1.2 \times 10^7$</td>
<td>45.4</td>
<td>Carbonated/glass</td>
</tr>
<tr>
<td>“Hirschquelle”</td>
<td>0.134</td>
<td>$2.2 \times 10^7$</td>
<td>29.6</td>
<td>Carbonated/glass</td>
</tr>
<tr>
<td>“Ensinger Sport”</td>
<td>0.773</td>
<td>$3.2 \times 10^5$</td>
<td>80.6</td>
<td>Carbonated/glass</td>
</tr>
</tbody>
</table>

Figure 5 Colloid concentrations in drinking water samples during the distribution via the water pipeline network.
Figure 6 Mean colloid size (a) and mean mass concentration (b) in different brands of mineral water.

Figure 7 Limits of detection of photon correlation spectroscopy (PCS) compared to Laser-induced Breakdown Detection (LIBD).
have been used successfully to prove the efficiency of the water purification procedure used by the Bodensee-Wasserversorgung for treatment of water from Lake Constance. While the laser light obscuration was useful for the determination of the particle number density of larger particles (d > 1 m), it was not capable of detecting colloids with diameters typically < 1 m. This was, however, no problem for the LIBD method that gives a number-weighted mean particle diameter of all the particles in the sample (see Figure 7 for detection limits). Within those restrictions, both methods have proved useful for the examination of the particle population during transport and storage of drinking water. Although the pipeline system of the Bodensee-Wasserversorgung mainly consists of reinforced or prestressed concrete, neither an increase nor a decrease in the number of particles was found, even though the water sometimes remained in the pipes or tanks for several days. This also means that the supplied drinking water is stable from a microbiological point of view (no germination or biological decomposition).

The LIBD has also been used to determine the particulate content of several brands of mineral water, both carbonated and non-carbonated. It seemed that water coming in glass bottles generally contained more particles than water in plastic bottles. It was interesting that the water supplied by the Bodensee-Wasserversorgung contained as many or even fewer particles than the commercially available mineral waters investigated.

References


