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Laser-Induced Breakdown System for Colloid Characterization in Dilute Aqueous Suspensions

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Colloids / Laser-Induced Breakdown Spectroscopy / Americium

Summary

Detection and sizing of colloids by acoustic detection of laser-induced breakdown and elemental analysis of colloids by laser-induced breakdown spectroscopy are investigated in dilute aqueous suspensions. Development and testing of the methods are performed with standard polystyrene suspensions and prepared suspensions of defined composition and particle size. Application of the methods to analysis of field and laboratory samples is discussed. Am atomic emission lines are observed by laser-induced breakdown spectroscopy of an Am hydroxycarbonate suspension.

Introduction

Colloids may enhance the groundwater transport of low-solubility actinides and fission products [1]. Analyses of the concentration, size distribution and composition of colloidal particles are essential in understanding the role of colloid-facilitated transport in a particular water. In some groundwaters colloid concentrations are below the detection limits of common characterization techniques such as light scattering. Thus we have investigated a particle counting method for dilute suspensions based on acoustic detection

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of laser-induced breakdown [2-4]. We have also investigated the use of laser-induced breakdown spectroscopy (LIBS) for elemental analysis of particles in suspensions [5-7]. In this paper we discuss results obtained with standard, prepared and "real world" suspensions.

Experimental Methods

Acoustic detection of laser-induced breakdown: The experimental setup is shown in Figure 1. The second harmonic (532 nm wavelength) of a 10 Hz pulsed Nd:YAG laser (GCR-190, Spectra Physics) was focused at the center of a quartz sample cuvette by a combination of two concave lenses with effective focal length 25 mm. The applied laser energy was adjusted under computer control using a motor-controlled attenuator (Model 935-5, Newport Corporation). A beamsplitter reflected a portion of the incident laser beam onto a photodiode to measure the laser pulse energy. The photodiode was calibrated against a laser power meter (Scientech). The acoustic sensor was a piezoelectric PVDF foil mounted inside an aluminum box which was coupled to the cuvette using double-sided adhesive tape. The electrical signals of the preamplified piezofoil and the photodiode were sampled with boxcar amplifiers and an A/D interface to a PC (Stanford Research Systems). For each measurement the applied laser energy was varied over the threshhold range for breakdown in the sample. The breakdown probability at a given laser energy was determined by sampling 250 to 1000 laser shots. The method was tested and calibrated using standard polystyrene spheres with diameters from 20 nm to 895 nm (Duke Scientific).

Laser-induced breakdown spectroscopy: Breakdown was initiated using the laser and optics as decribed above. Light from the laser spark was collected at 90° and focused onto the entrance slit of a spectrograph (Spectra Pro -300i, Acton Research Corp.) with an ICCD detector (DH520-25F-01, Andor Technology). Spectra were recorded using a slitwidth of 0.1 mm and a 600 g/mm or 1200 g/mm diffraction grating which resulted in a spectral resolution of 0.4 or 0.2 nm. Measurements were performed in time-gated mode and were triggered using the advance Q-switch pulse from the laser. After an initial study of emission line intensity dependence on gate width and delay, LIBS data was typically collected using a gate width of 300 ns and a delay of 100 ns relative to the laser pulse. Assignment of observed lines was based on the NIST atomic spectral database [8].

Monodisperse $Eu(OH)CO_3$ suspensions were prepared by controlled hydrolysis of solutions of $EuCl_3$ and urea at 86-88°C [9]. Previous studies have indicated that amorphous spherical particles are produced under these conditions [9,10]. A sample was dried and dispersed in a CsI pellet to record the infrared spectrum in an FTIR spectrometer (Mattson Galaxy 5300). The particle size distribution of each suspension was determined by photon correlation spectroscopy (Malvern 4700), then an aliquot was immediately diluted for LIBS. Following the LIBS measurements the sample was acidified with HCl to dissolve the particles and the Eu concentration was determined by fluorescence emission spectroscopy (SPEX Fluorolog 2) using standard additions.

Results and Discussion

I. Acoustic detection of laser-induced breakdown

The background was determined using deionized water from a Milli-Q system (Millipore). The breakdown probability curve is shown in Figure 2. Breakdown events are not observed in the water sample at laser energies below 6.5 mJ/pulse. In this paper, the laser pulse energies at the sample are given, i.e., they have been corrected for reflection at the quartz-air surfaces.

As an example of results obtained with polystyrene standard suspensions, the breakdown probability curves for 496 nm particles are shown in figure 2. The breakdown probability (BDP) is related to the laser pulse energy E by the empirical function:

$$BDP = \frac{E^n}{k^n + E^n}$$

Here E is the laser energy in mJ/pulse, n is a sample specific parameter and k is the laser energy at 50% breakdown probability.

The parameter k is used to characterize the sample. In Figure 3 the observed k values are plotted as a function of particle size and concentration. The distribution of the parameter k for a given particle size indicates the method is most sensitive at low particle concentrations. At high particle concentrations light scattering is significant and accounts for the minimum observed in the curve for 895 nm particles. The concentration detection limits of the laser-induced breakdown method are at levels appropriate to direct particle counting in dilute groundwater samples.

The breakdown probability has been modeled as a function of particle size and concentration in the literature [4]. However, we found the model difficult to apply to natural systems containing nonspherical particles (e.g. clay minerals) and polymodal

particle size distributions. In the approach used here, breakdown is used as a sensitive method of colloid detection and must be combined with a size separation method such as serial filtration or field-flow fractionation to determine particle size distributions. Our current instrumentation allows sensitive qualitative detection of trace particles in aqueous systems and has been applied to colloids in groundwater samples, particle breakthrough in core flow experiments, and investigation of precipitation kinetics.

II. Laser-Induced Breakdown Spectroscopy

Eu LIBS spectra were investigated using $EuCl_3$ solutions at pH 3-4 containing standard polystyrene particles of 200 nm diameter. The laser energy was 2.5 mJ/pulse to ensure that breakdown was initiated by particles. Several Eu I and Eu II lines were observed, and further analyses were made using the strong Eu I peaks at 459.9, 463.2 and 466.6 nm. The peak heights were directly proportional to Eu concentration over the range 0.4 to 20 mM. This indicates that a constant volume of solution was sampled by the breakdown plasma. In certain cases, it may be possible to use a dissolved standard to quantify particulate elemental concentrations.

The infrared spectrum of the Eu colloids was similar to that of $Eu(OH)CO_3(cr)$ [11], but band broadening was significant and consistent with an amorphous solid. Observed absorption band maxima (cm^{-1}) were: 3400 (broad), 1504 (strong), 1402 (strong), 1076 (medium), 843 (medium), 729 (medium), and 687 (medium).

LIBS results for $Eu(OH)CO_3$ colloids of different size are listed in Table 1. In these measurements the probability of having two or more particles in the focal volume was

extremely small, thus the emission peak height is correlated with particle size rather than the average Eu concentration. However, the peak height increases as roughly the square of the particle diameter. A cubic relation is expected if the particles are spherical and the entire particle contributes to the observed signal. The particles may be nonspherical, or the entire particle may not be vaporized during the breakdown event.

First results for LIBS of Am are shown in Figure 4. The Am I lines at 351.0, 356.9, 367.3, 426.6, 428.9, 466.3 and 468.2 nm were observed. The sample was prepared with a total Am concentration of 9.8×10^{-5} M in a 0.12 M $NaHCO_3$ solution. A visible solid was not present, but the sample was supersaturated with respect to $Am(OH)CO_3$, and the laser energy of 2 mJ/pulse indicates that breakdown was initiated by particles.

We found it difficult to observe U or Pu lines in laser-induced plasmas produced within the volume of U or Pu hydrous oxide suspensions. This is consistent with LIBS results for U solutions [12]. The absence of strong lines in the atomic spectra or rapid formation of metal-oxygen bonds during cooling of the laser plasma may lead to weak emission under these conditions.

Conclusions

A laser-induced breakdown system was developed for colloid detection and sizing in aqueous suspensions. Particle concentration detection limits are appropriate to dilute laboratory samples and natural groundwater systems. Laser-induced breakdown spectroscopy of colloidal suspensions and actinides was investigated. Am atomic

emission lines were observed by LIBS of an aqueous suspension. The laser-induced

breakdown methods are unique tools for investigation of colloids in aqueous media.

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Table 1. LIBS results for Eu(OH)CO$_3$ colloids of different size.

Sample number	Particle Size (nm)	Avg. [Eu] (M)	459.9 nm Eu I Peak Height
021	304 ± 76	1.97 x 10^{-4}	10817
019	389 ± 93	4.74 x 10^{-5}	16229
020	667 ± 278	7.23 x 10^{-5}	38038

Figure Captions

Figure 1.   Scheme of experimental setup (PHS-1: prism harmonic separator, 1: neutral filter, 2: telescope, 3: beamsplitter, 4: attenuator, 5: photodiode, 6: focussing lens, 7: sample cuvette, 8: piezoelectric detector, 9: preamplifier, 10: stepper motor, 11: stepper motor controller, 12: beam dump)

Figure 2.   Breakdown probability as a function of particle number and laser energy (Polystyrene standard particles, diameter 496nm, particle numbers [particle / mL] from a to j: 1.50E+8, 7.50E+7, 3.75E+7, 1.88E+7, 9.36E+6, 4.69E+6, 2.34E+6, 1.17E+6, 2.93E+5, deionized water)

Figure 3.   Critical laser energy (laser energy at 50 % breakdown probability) as a function of particle concentration (polystyrene standards)

Figure 4.   LIBS emission spectra of Am colloids (10000 accumulations, 100 ns delay after laser pulse, 300 ns gatewidth)
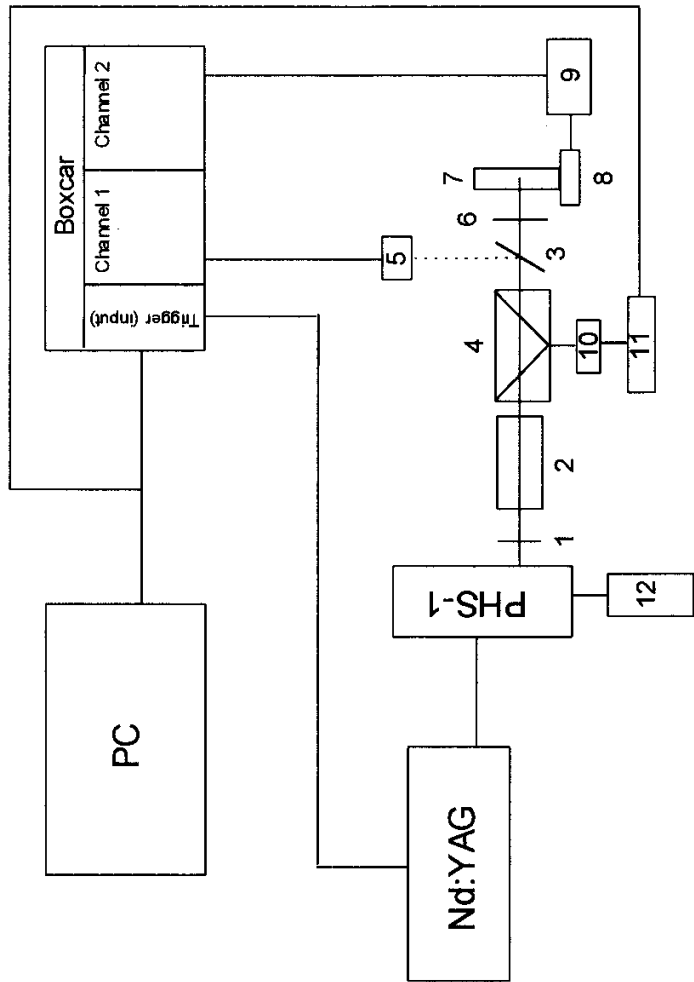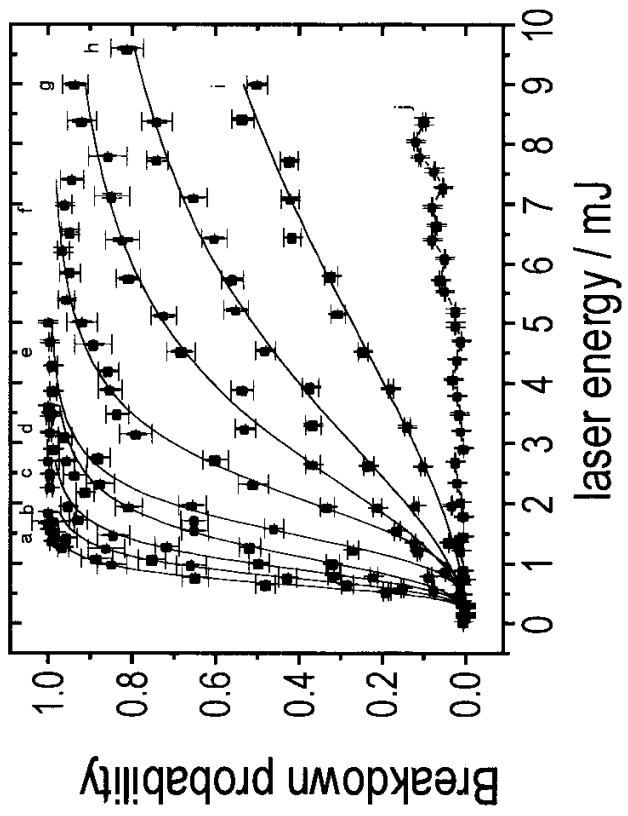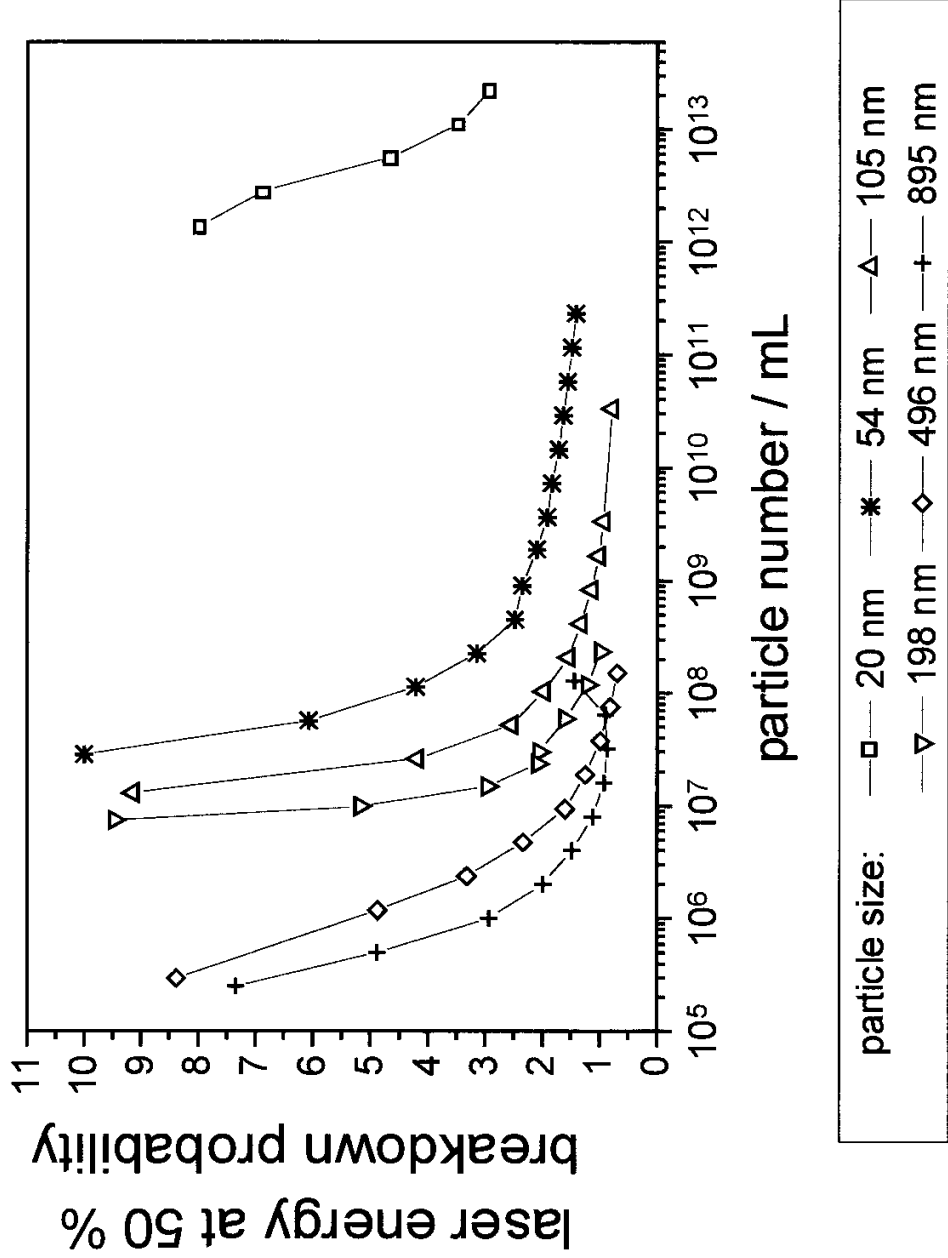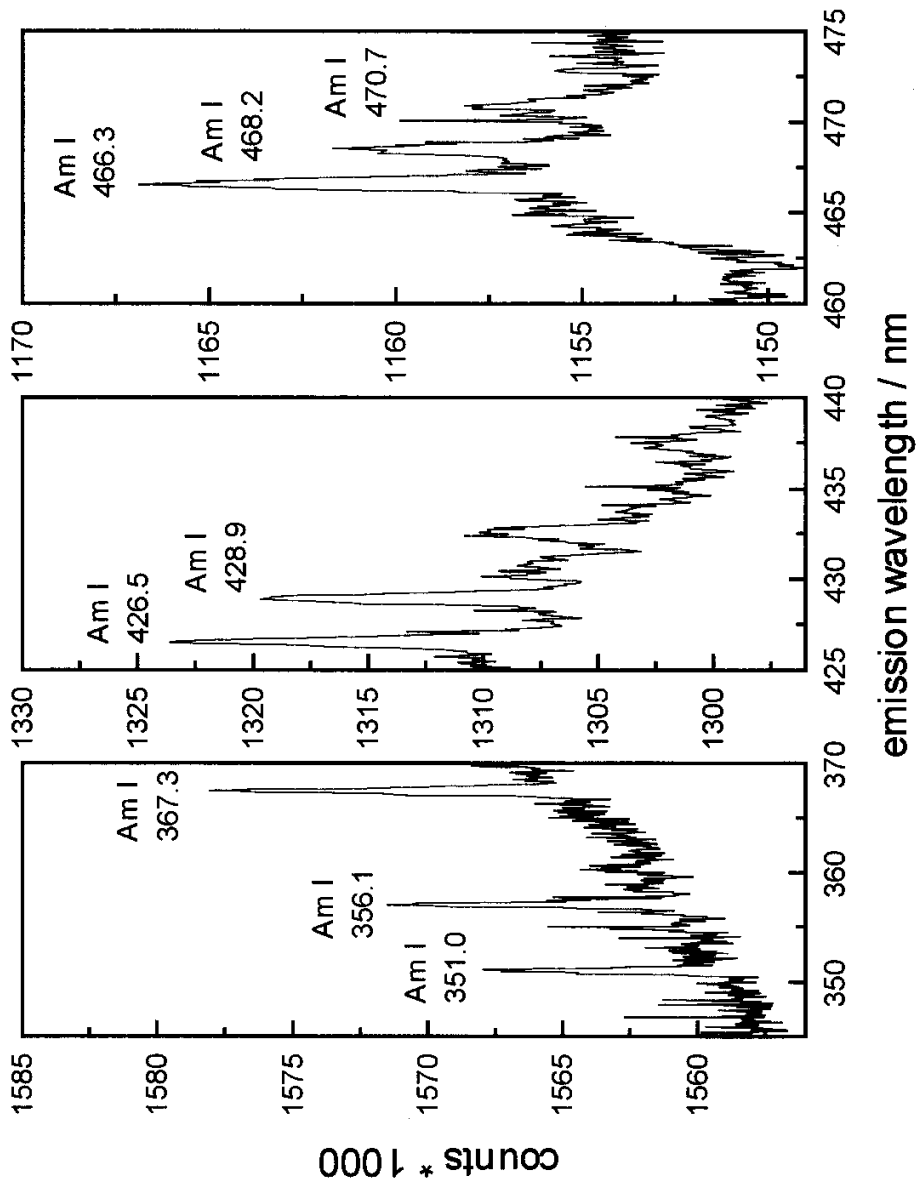
Figure 1

Figure 2

Figure 3

Figure 4