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Use of Sol–Gels as Solid Matrixes for Trace Analysis by UV Laser Ablation and Laser-Enhanced Ionization Detection

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Zirconium and silicon sol–gels were investigated as solid materials for trace elemental analysis of pelletized solid samples by laser ablation and laser-enhanced ionization. The highly homogeneous dispersion of an internal standard spiked in the solid material obtained with the sol–gel formation process leads to a significant improvement in signal repeatability and to an increase in the precision of measurements through better correction of variations in the laser ablation rate. Signal repeatability values of 5–8% RSD were obtained for Pb in NIST 1632c Bituminous Coal sample pellets prepared using both sol–gels, as compared to 9–21% for graphite-based sample pellets. Furthermore, the zirconium sol–gel was shown to offer better resilience to signal bias due to preferential ablation and a more accurate correction of ablation rate using the internal standardization method.

The use of laser ablation for elemental analysis has grown tremendously in popularity over the past few years, stimulated by the advantages it provides for the direct analysis of solid samples.^{1,2} In particular, it allows the direct analysis of solid samples without any sample digestion and very little sample preparation, which results in reduced risks of contamination, lower analysis costs, and higher sample throughput, while facilitating the analysis of refractory solids that do not lend well to dissolution such as coals,³ graphite,⁴ and ceramics.⁵ Furthermore, the limited laser–material interaction area allows spatially resolved analysis of heterogeneous materials.⁶ Laser ablation has been used as a solid sampling method for various detection techniques, such as inductively coupled plasma mass spectrometry (ICPMS) and atomic emission spectrometry,² as well as laser-excited atomic

fluorescence spectrometry,⁷ diode laser atomic absorption spectrometry,⁸ and laser-enhanced ionization spectrometry (LEI).⁹

When the samples to be analyzed are in powdered form, they are generally formed into solid targets prior to laser ablation. Because the fusion techniques¹⁰ developed for X-ray fluorescence analysis require the use of high temperatures that may lead to evaporative losses of volatile analytes, a method of choice for solid target preparation in laser ablation is the hydraulic pelletization of powdered samples, often using a suitable binder. For example, soil samples have been pelletized using cellulose,¹¹ powdered Ag,¹² and even glue¹³ as binders, and coal pellets have been prepared with and without KBr binder.³ Conveniently, the preparation of solid samples from powders allows the correction of analytical signal fluctuations due to the variations in mass removal rate that are inherent to laser ablation, by adding an internal standard to the sample material, either in the form of an aqueous standard solution^{3,11} or as a solid metal oxide.^{12,14} However, to obtain analytical results of acceptable accuracy and precision using this method, the prepared pellets must possess sufficient homogeneity. Baker et al.,¹¹ in their analysis of soil and sediment samples by laser ablation ICPMS, observed significant fluctuations in analytical signal when sampling at a fixed location on the pellets. The authors attributed these deviations to local variations in the homogeneity in the samples, which imposed that the soil pellets be sampled over a large enough portion of the total sample volume to ensure accurate and precise measurements of global concentration. In a similar fashion, Gravel et al.,¹⁵ using laser ablation laser-enhanced ionization (LA-LEI) for the measurement of lead in pelletized graphite and coal samples, showed that large variations in the analyte signal originated from the uneven distribution within

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the samples of the spiked elements. In addition, Borisov et al.,¹⁴ in a report on the analysis of mixed metal oxide pressed pellets by LA ICPMS, suggested that internal standardization may be thwarted by an insufficiently homogeneous distribution of the internal standard in the sample pellets.

The use of sol–gels for the preparation of sample pellets could lead to a more homogeneous dispersion of the internal standard in the sample material and to more precise measurements by laser ablation. In the sol–gel process, a colloidal suspension (sol) is first formed by mixing a liquid metal alkoxide precursor, such as tetramethoxysilane (TMOS) or zirconium *n*-propoxide (TPOZ), water, a cosolvent, and an acid or base catalyst. Alkoxy groups are removed by acid- or base-catalyzed hydrolysis reactions, and networks of O–M–O linkages (gel) are formed in subsequent condensation reactions involving hydroxyl groups.¹⁶ Sol–gels are amorphous and highly homogeneous solids that are finding countless applications in many fields, including analytical chemistry. For example, Davis et al.¹⁷ have recently reported the use of a sol–gel as a solid matrix for the analysis of suspended particulate matter in a thin-film form by radio frequency glow discharge optical emission spectrometry, and Tang et al. have developed novel O₂-sensing materials based on spin-coated *n*-octyltriethoxysilane/tetraethylorthosilane composite sol–gel films.¹⁸ We believe that the intrinsically high homogeneity of sol–gels and the ease with which one can incorporate both the powdered sample material and an aqueous internal standard in the initial precursor mixture¹⁹ could lead to a novel and better performing, yet uncomplicated pelletization procedure for the analysis of powdered samples by laser ablation. To the best of our knowledge, the use of sol–gels for this purpose has not yet been reported.

The objective of the work presented herein was thus to investigate whether the sol–gel process can be used to prepare solid pellets from powdered samples that are more suitable for direct analysis by laser ablation than those prepared using more heterogeneous pelletization procedures. Signal repeatability and detection sensitivity were determined for Pb in NIST Bituminous Coal certified reference material by laser ablation and laser-enhanced ionization, using either graphite or a mixture of graphite + sol–gel as the matrix-matching material. The properties and behavior of two different types of sol–gel-based matrixes (zirconium and silicon based), as well as a high-purity graphite matrix, were compared.

EXPERIMENTAL SECTION

Instrumentation (Laser System) and LEI Conditions. The experimental setup used for the laser ablation of solid samples and the determination of Pb by laser-enhanced ionization has been described in detail elsewhere.^{15,20} Indium was chosen as the internal standard to compensate for variations in the ablation rate

of sample pellets. The signal from indium was corrected to account for its actual concentration in the sample, which can vary slightly from sample to sample depending on the mass of graphite, sol–gel, and NIST certified reference material (CRM) used to make each solid pellet. For all experiments described herein, ablation was performed at 10 separate positions on the sample pellets, and the LEI signals from Pb and In were integrated over the duration of the ablation in each crater (300 ablation laser pulses, $\lambda = 308$ nm) and averaged over the 10 craters. The beam footprint and laser irradiance at the sample surface were estimated at approximately 250 μm and 0.2 GW/cm², respectively. Other experimental parameters such as LEI flame composition, laser excitation schemes, and carrier gas flow rate were set according to the results of the optimization study presented in ref 15.

Sample Preparation. Materials. TMOS (99+%, Aldrich), TPOZ (70% in 1-propanol, Aldrich), trace metal grade methanol (Anachemia), anhydrous ethanol, high-purity concentrated nitric acid (Anachemia), high-purity graphite (99.9999%, Alfa Aesar), Triton X-100 (<3% poly(ethylene glycol), Aldrich), and NIST 1632c Bituminous Coal CRM were used as received. For the silicon-based sol–gels, high-purity concentrated nitric acid (Anachemia) was also diluted to 1.0 N with 18-M Ω deionized water. Aqueous Pb and In solutions were prepared from 1000 $\mu\text{g/mL}$ standard stock solutions (spectrometric grade, SCP Science).

Preparation of Sol–Gel Targets. Several procedures are described in the literature for the synthesis of sol–gel materials.¹⁹ A dried gel obtained by conventional thermal drying under atmospheric pressure is called a xerogel.

Silicon. For silicon-based materials, the synthesis of xerogel monoliths typically extends over a period of ~2 weeks. Thus, an adaptation of the fast sol–gel method¹⁶ followed by an oven drying step has been used for faster solid sample preparation. The fast sol–gel process is a direct reaction of alkoxysilane monomers with water at 70–80 °C and a quick outdistillation of methanol following partial polymerization. This procedure involves running the reaction at 70–80 °C in an open vessel, which accelerates hydrolysis and condensation and reduces the volume of liquid by expelling excess methanol through outdistillation.

To a clean disposable scintillation vial (20 mL, Sarstedt) were added, using microliter pipets, 3.1 mL of methanol, 0.7 mL of deionized water, 1.5 mL of TMOS, and 20 μL of 1 N HNO₃. This corresponds to a methanol/water/TMOS/HNO₃ molar ratio of 8:4:1:0.002. Sol–gel synthesis procedures are quite flexible in the choice of the acidic or base catalyst, and nitric acid was chosen rather than hydrochloric acid in order to minimize the risks of analyte loss to volatilization or precipitation as chlorides. The powdered materials were then incorporated before gelation of the sol–gel started to occur: (i) for the samples prepared from the NIST CRM, 0.75 g of the Bituminous Coal CRM (3.79 $\mu\text{g/g}$ Pb nominal concentration) was added to the mixture; (ii) for the calibration standards, 0.75 g of high-purity graphite was added to the mixture, as well as suitable quantities of a 1000 $\mu\text{g/mL}$ Pb standard solution to obtain concentrations between 0 and 5 $\mu\text{g/g}$ Pb. A 200- μL aliquot of a 1000 $\mu\text{g/mL}$ In standard solution (as internal standard) was added to every mixture, as well as 30 μL of Triton X-100 to ensure complete wetting of the powdered material.

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Table 1. Signal RSD for Pb and In in Calibration Standards and NIST 1632c Coal Bituminous CRM Samples Using Silicon Xerogel, Zirconium Xerogel, and High-Purity Graphite-Based Matrixes

	silicon xerogel		zirconium xerogel		high-purity graphite ¹⁵	
	calibration standards	NIST samples	calibration standards	NIST samples	calibration standards	NIST samples
Pb RSD (%)	5	5	5	5	17	21
In RSD (%)	5	8	5	8	17	9
Pb/In RSD (%)	3	5	2	5	4	11

The vials were suspended on a Styrofoam plate in a thermostated water bath maintained at $\sim 75^\circ\text{C}$ under ultrasonic stirring. The temperature must be kept relatively constant in order to prevent the solvent from evaporating too quickly and the reaction mixture from dehydrating. After 20 min, 2.5 mL of water was added, followed by 1 mL of methanol after 30 min and an additional 1 mL of methanol after 40 min. The exact timing of the above sequence is not critical; care must simply be taken to ensure that dehydration does not occur before gelation takes place. The mixture was then left to stir for ~ 2 h to reach complete gelation. The resulting sol–gels were dried overnight in an oven at 100°C .

Zirconium. The same apparatus was used in the synthesis of zirconium sol–gels. However, since gelation is immediate (within 1 min), heating is not required and the powdered material is deposited first in the scintillation vial. The amounts of powdered materials used for the preparation of calibration standards and NIST samples were the same as those used in the silicon sol–gel fabrication procedure. The remaining reagents were added to the powdered material in the following order: 5.9 mL of ethanol, 50 μL of concentrated HNO_3 , 30 μL of Triton X-100, suitable quantities of a 1000 $\mu\text{g}/\text{mL}$ Pb standard solution to obtain concentrations between 0 and 5 $\mu\text{g}/\text{g}$ Pb, 200 μL of a 1000 $\mu\text{g}/\text{mL}$ In standard solution, and 0.3 mL of deionized water. After 5 min of ultrasonic stirring, 1.8 mL of zirconium propoxide was added dropwise. Formation of a white gel is observed as soon as the alkoxide comes into contact with water. The resulting sol–gels were dried overnight in an oven at 100°C .

Preparation of Graphite Targets. For the preparation of the calibration standards, 0.75 g of high-purity graphite was placed in glass Petri dishes, to which were added 20 mL of 18-M Ω deionized water, a few drops of Triton X-100, and appropriate volumes of In (as internal standard) and Pb standard solutions to obtain Pb concentrations between 0 and 5 $\mu\text{g}/\text{g}$. After meticulous mixing, the blends were left to dry under a hood for 12 h. For the preparation of the CRM samples, the high-purity graphite in the samples was replaced by the CRM material entirely (0.75 g of Bituminous Coal CRM).

Grinding and Pelletization. Prior to pelletization, the sol–gel samples were ground with a mortar. A 0.05-g sample of paraffin was then added to 0.45 g of each sample (10% w/w paraffin concentration), and the resulting mixtures were homogenized for 5 min using polystyrene vials (Spex Certi-Prep, 6133) and metacrylate balls (Spex Certi-Prep, 3112) along with a grinder-mixer (Spex Mixer/Mill, 5100), before final pelletization in a 13-mm die (Macro/Micro KBr die, 0012-2477) at 10 000 lb for 2 min. Note that zirconium xerogels, being softer than silicon xerogels, do not require grinding in a mortar. The mixtures need only to

be homogenized using the grinder–mixer. The graphite pellets were prepared by adding paraffin to the powdered samples (10% w/w paraffin concentration), and 0.5 g aliquots of the resulting mixtures were homogenized and pelletized following the same procedure as described above.

Characterization of Ablated Material and Sample Powders. The ablated particles were collected on Nucleopore polycarbonate membranes (0.1-mm pore size, Structure Probe Inc.) and examined by scanning electron microscopy following the procedure described in ref 20.

RESULTS AND DISCUSSION

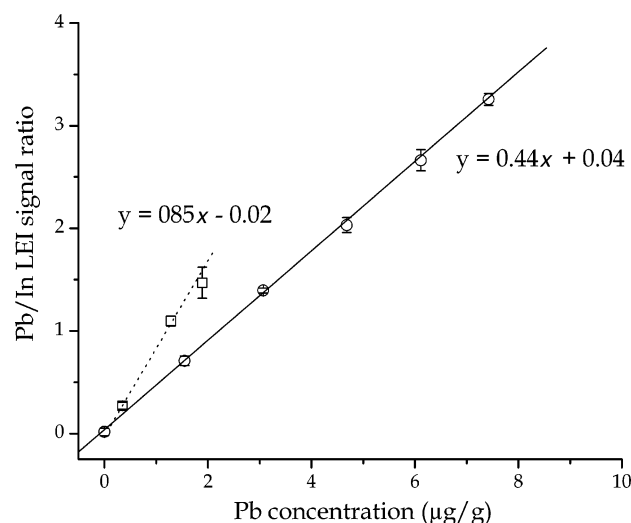
To evaluate how the use of sol–gels for the preparation of matrix-matched pellets can affect sample homogeneity and potentially improve analytical results provided by laser ablation, signal repeatability for In and Pb were recorded for pellets containing NIST 1632c Coal Bituminous CRM as well as matrix-matched calibration pellets, using the three different types of samples under study. The results (Table 1) show an important overall increase in signal repeatability for silicon (SiX) and zirconium (ZrX) xerogel-based pellets, as compared to those prepared using only NIST CRM or high-purity graphite (HPG), i.e., $\sim 6\%$ for the xerogel-based pellets versus $\sim 16\%$ for the HPG-based pellets. This improvement in signal repeatability can be attributed to a more homogeneous dispersion of the analytes within the xerogels. The poorer precision observed for the HPG-only calibration standards reflects the uneven distribution of Pb and In within the pellets, which resulted from their gradual concentration in isolated droplets as water evaporated during the sample drying process.¹⁵ In addition, the greater homogeneity of elements spiked within the xerogels increases the efficiency of the internal standardization method in correcting for the local variations in ablation rates caused by variations in sample compactness, topology, or reflectivity, i.e., RSD values on the Pb/In ratio of 5% for SiX and ZrX xerogel-based NIST CRM samples versus 11% for the other samples.

We have observed a higher detection sensitivity for Pb in SiX-based pellets than in those prepared with either ZrX or HPG (Table 2, row 1), and visual SEM observation of the ablation craters clearly showed evidence of higher mass removal for SiX-based targets. This may result from differences in sample composition or optical properties, but the lower boiling point of amorphous silica (2230°C) than that of zirconium oxide (5500°C) and graphite (4200°C) might be a major factor in the observed difference in mass removal rate.

Likewise, we have observed by SEM a notable increase in mass removal rate in the NIST samples as compared with the calibration standards for the three types of pellets, which has been attributed

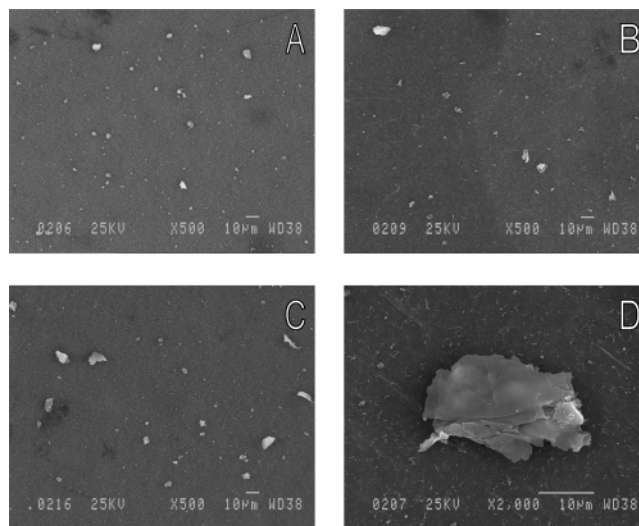
Table 2. Detection Sensitivity for Pb and In in Calibration Standards and NIST 1632c Coal Bituminous CRM Samples Using Silicon Xerogel, Zirconium Xerogel, and High-Purity Graphite-Based Matrixes

	silicon xerogel		zirconium xerogel		high-purity graphite ¹⁵	
	calibration standards	NIST samples	calibration standards	NIST samples	calibration standards	NIST samples
Pb sensitivity ($V/\mu g \cdot g^{-1}$)	1.52	3.67	0.44	1.33	0.72	1.59
In sensitivity ($V/\mu g \cdot g^{-1}$)	0.024	0.028	0.018	0.051	0.083	0.180
Pb sensitivity/ In sensitivity	62	132	24	26	9	9

**Figure 1.** Pb/In sensitivity ratios for silicon xerogel + high-purity graphite calibration standards (open circles) and silicon xerogel + NIST 1632c Bituminous Coal CRM samples (open squares).

to the greater cohesiveness and mechanical strength of the latter. This difference in ablation rate is reflected in the different detection sensitivities measured for Pb in the calibration standards and in the NIST samples. Interestingly, while the internal standardization method corrects well for these variations in the case of the ZrX-based pellets, for which similar Pb/In ratios were measured in the calibration standards versus the NIST samples, it is not so for the SiX-based pellets (Table 2, row 3). This is also illustrated in Figure 1, where three SiX + NIST CRM samples, varying only in the mass of bituminous coal powder present in the pellets, have been plotted against a calibration curve obtained from SiX + HPG standards. Since the Pb/In sensitivity ratio is higher in the CRM samples than in the calibration standards, the Pb/In ratios measured for the CRM samples do not fit the calibration curve, and the internal standardization procedure fails. A possible cause of this behavior may lie in the fact that the internal standard and the analyte are both located, in the case of calibration standards, in the sol-gel component of the matrix-matching sol-gel + HPG mixture, but not in the SiX + NIST samples (in which the analyte is present solely in the NIST sample material while the internal standard is located in the sol-gel component); if, in the latter case, the sol-gel component somehow behaves differently from the NIST material toward ablation, then the Pb/In ratio of the ejected sample material might differ in its final, atomized form in the LEI flame than in the sample pellet.

It was demonstrated in a previous report that the material ablated by the excimer laser and transported to the LEI detector

**Figure 2.** SEM photographs of particles ablated from SiX-based materials and collected on Nucleopore filters. (A) SiX only; (B) SiX-based calibration standard; (C) SiX-based NIST sample; (D) closeup view of a particle ejected from SiX.

exists predominantly in the form of very small particles (<100 nm) aggregated into filaments that are small enough to be efficiently vaporized in the atomization source.²⁰ However, SEM photographs of the material ejected from the pellets show that SiX-based targets also generate a significant number of micrometer-sized particles, flakes, and droplets (Figure 2). These large particles are probably ripped mechanically off the surface of the target or produced by spallation from the melted surface layer²¹ or by explosive phase change.^{22,23} These large particles have been analyzed by energy-dispersive X-ray emission and were shown to be composed mainly of SiO_2 .

Larger particles are more prone to losses by gravitational settling during their transport from the ablation cell to the atomization source. The cutoff in average particle diameter depends on experimental parameters, such as the length and diameter of the transfer line and the carrier gas composition and flow rate; for the present experimental setup, it was determined that particles larger than $2.5 \mu m$ do not reach the LEI detector.²⁴ In the case of the SiX-based calibration standards, Pb and In are both located in the xerogel component of the pellets and will be

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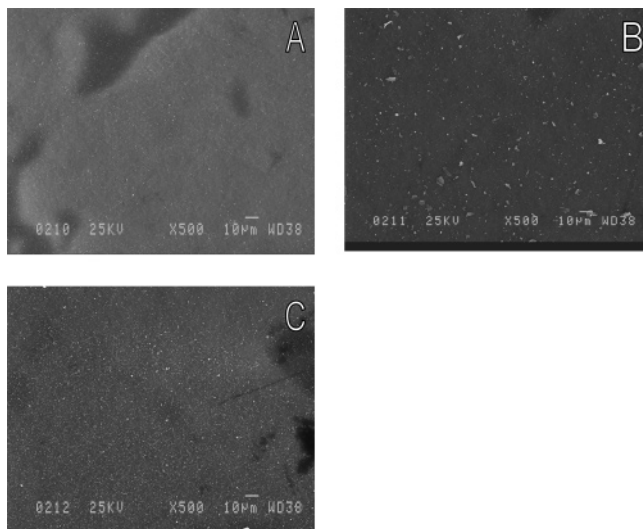


Figure 3. SEM photographs of particles ablated from ZrX-based materials and collected on Nucleopore filters. (A) ZrX only; (B) ZrX-based calibration standard; (C) ZrX-based NIST sample.

lost in equal amounts to gravitational settling of the large SiO_2 particles generated during ablation of SiX-based pellets; therefore, the Pb/In sensitivity ratio will remain unaffected. On the other hand, in the SiX + NIST CRM pellets, indium is contained solely in the xerogel component while Pb is located exclusively in the bituminous coal powdered material. Therefore, these particle losses will affect the detection sensitivity of the internal standard to a greater extent and lead to inaccurate results from the internal standardization procedure.

Examination of SEM of particulate material ejected from the ablation of ZrX-based pellets indicates that the production of large particles is much less severe with ZrX-based pellets (Figure 3) and has been observed only with HPG-containing calibration standards (Figure 3B). This behavior is reflected in the unchanging Pb/In sensitivity ratio measured for ZrX-based calibration standards and ZrX + NIST pellets (Table 2). Zirconium xerogels thus offer the combined advantages of a highly homogeneous dispersion of spiked analytes and of a greater resilience to signal deviations resulting from preferential losses of analytes added as internal standards to the matrix-matching material. Using ZrX-based calibration pellets and indium as the internal standard, the Pb concentration in the NIST 1632c Bituminous Coal CRM sample was measured at $3.72 \mu\text{g}\cdot\text{g}^{-1}$, a 2% deviation from the $3.79 \mu\text{g}\cdot\text{g}^{-1}$ certified value. A 3σ limit of detection of 60 ng/g was calculated

for Pb, which compares well with results obtained in other laboratories by different techniques.^{7,25–29}

CONCLUSION

The reliability of quantitative analysis of refractory powdered materials using laser ablation sampling has long been limited by the signal fluctuations caused by the inhomogeneous dispersion of analytes and internal standard in the sample pellets. With the aim to resolve this long-standing problem, we demonstrated herein how sol–gels, used as a dispersion medium for an internal standard, can be used to develop a novel and better performing pelletization procedure based on the intrinsically high homogeneity of sol–gels and the ease with which one can incorporate both the powdered sample material and an aqueous internal standard in the initial precursor mixture. Since the prepared pellets possess high homogeneity, analytical results of excellent accuracy and precision has been obtained using this method, at the cost of a longer preparation time than that needed by other methods that do not require drying of the samples. The highly homogeneous dispersion of the internal standard in the sample pellet allows the successful correction of variations in the ablation rate of the solid samples. Zirconium-based sol–gels, in particular, were shown to offer excellent resilience to signal bias due to preferential ablation.

Our observations suggest that the sol–gel material chosen should have a boiling point similar to those of both the sample powder and the matrix-matching material. An undeniable advantage of the sol–gel method described in this work is that it makes possible the preparation of highly homogeneous calibration standards in solid form using a simple and straightforward procedure, and the large variety of sol–gel types that can be prepared will facilitate the adaptation of this method to samples of varying chemical and physical properties. Finally, following a report by Guillong et al. on the effect of laser wavelength on the size distribution of particles ablated from silicates,³⁰ additional development work is needed to determine whether the use of shorter laser wavelength could help alleviate the issue of signal bias due to gravitational losses of larger particles in silica-based sol–gels.

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