SUPPLIMENTARY INFORMATION

Supplementary information (S1)

In direct bulk liquid analysis, DI water was filled in a quartz beaker and the laser beam was focused through the wall of the beaker to reduce splashing and sample loss. The LIBS experimental setup for direct bulk analysis is illustrated in Fig. S1(a). When a laser beam propagates through water, it suffers several types of energy losses such as reflection, refraction, scattering, and absorption. The propagation of light through different media is illustrated in Fig. S1(b). When a high-intensity laser pulse is focused on the liquid sample (DI water), the sample breaks down and plasma will be formed. Plasma formation is also accompanied by shock wave emergence and cavitation bubble formation in the case of water [44]. When laser energy is 46 mJ, the length of the laser-induced plume was found to be smaller than that of the same for energy 65 mJ.
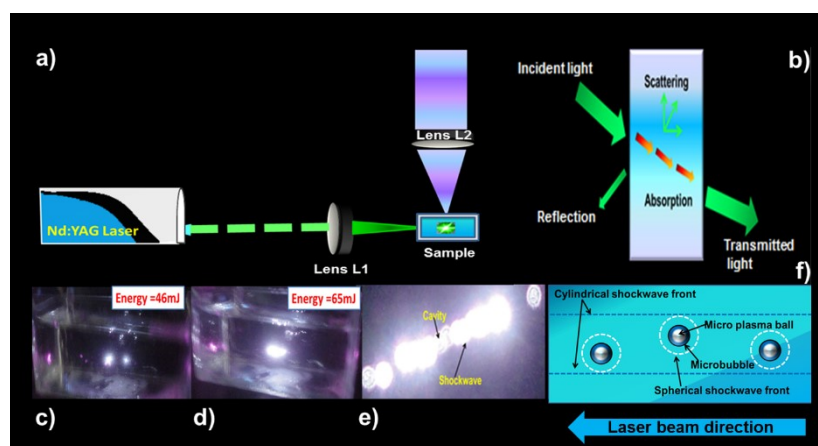

Figure 1 a) Schematic diagram of experimental set up used for the bulk liquid analysis b) Light propagation through different media, c-d) Plasma creation in de-ionized water using different laser energies, e) Photograph of plasma in de-ionized water using energy, E = 50 mJ [45], f) Schematic diagram of laser spark column in the liquid sample.

Another major concern is the propagation of light through different media and the subsequent refraction effects. This is a consequence of different propagation speeds of light through different media having different refractive indices. In the direct bulk, liquid analysis laser light travels from the air→glass→water, and then the plasma emission light travels from

water→glass→air. It is well known that the frequent travel from denser to rarer and vice versa can cause significant alignment issues in the optical scheme as this causes serious concerns on beam focusing and collimation. Also, most of the laser energy is getting wasted in the optical path itself, which at times makes it insufficient for the ablation processes. The aforementioned causes make the direct liquid analysis a challenging task in the back-collection scheme and necessitates the need for alternate strategies. In case of plasma creation in the direct bulk of the analyte solution, we notice that laser-induced plasma was inhibited inside the weakly compressible liquid environment. Therefore, it is imperative to apply a large amount of laser energy to induce plasma inside the liquid sample and create plasma having a very short lifetime. Fig. 1(c-d) show the plasma created inside the liquid sample using the pulsed laser excitation at different energies. Multiple microplasma bubble was created while using lower pulse energies, whereas homogeneous plasma with stronger emissions was observed with higher values of laser energies. Fig. 1(f) depicts that the plasma formation and successive cavitation occur along the direction of laser beam propagation in different sites. In all cases, induced plasma was followed by multiple cavitation bubbles at various places. It is observed that shortly (a few ns) after the laser pulse, the laser spark column is occupied with microplasma balls of smaller size. Various plasma actions were formed near the focal area and along the propagation direction of laser beam which forms the laser spark column. It consists of micro plasma balls, microbubbles, and spherical shockwaves [12]. Fig. 1(e) shows the plasma created inside the DI using 50 mJ energy. In water, a different kind of cylindrical shockwave evolves at longer times: the spherical shockwaves expand and interfere with each other and result in a cylindrical pattern structure called a spherical shockwave cylinder. Even though there are several technical problems such as formation of cavitation bubbles and shorter plasma duration while handling direct liquid analysis, we have optimized the experimental parameter for improving the system sensitivity and reproducibility.

Supplementary information (S2)

Sensitivity and reproducibility of the substrate

The reproducibility of our Teflon substrates has also been evaluated, as shown in Fig. 2(b), the peak intensity of the Cr at 520.6 nm was chosen as a parameter to evaluate the reproducibility of its LIBS spectra. For the higher intense peak at 520.6 nm, the relative standard deviation (RSD) of LIBS spectra from 8 different sites on the Teflon substrate was found to be about 8% (Fig. 2(b)). The consistency of the LIBS spectra of Cr solution confirms the homogeneous property of sample deposition on the Teflon substrate.
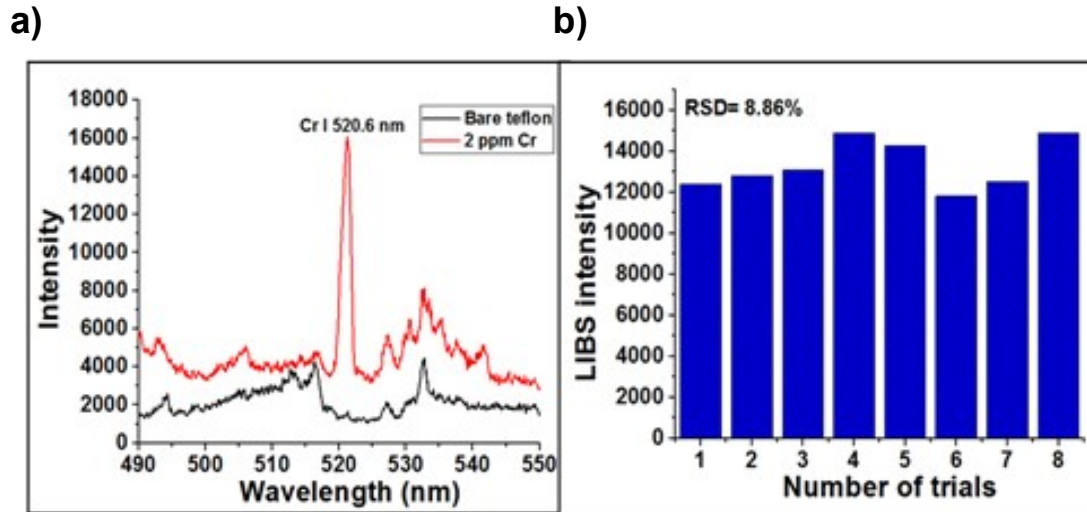
Figure.2 a) LIBS spectra of 2 ppm Cr solution dried on Teflon substrate b) LIBS intensity of 2 ppm Cr solution obtained from random spots on the substrate at the emission peak (520.6 nm).

Supplementary information (S3)

Validation of the results with ICP-OES

The LIBS technique has been previously used on marine sediments, soils, and aerosols from Antarctica to decipher the elemental composition. The lakes of Antarctica are largely pristine and least affected by anthropogenic activities. Therefore, the elements present in the sediments should reflect the composition of the local geology and hence we have employed the developed drop coating deposition method to measure the trace elements level in surface sediments from an East Antarctic Lake (Latitude: 70° 43′ 50″ and 70° 46′ 40″ south; Longitude: 11° 22′ 40″ and 11° 54′ 25″ east) after acid digestion (in liquid form). The same samples were also measured on an Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES; Thermo Scientific, iCAP 7000) to validate the measurement results obtained from the LIBS analysis. We deposited 10 μL of each sample on a Teflon substrate for LIBS analysis. Fig. 3(b) shows the trace element concentrations in the lake sediments. Each LIBS spectrum is an average of five single-shot trials to reduce fluctuations and improve the signal-to-background ratio.
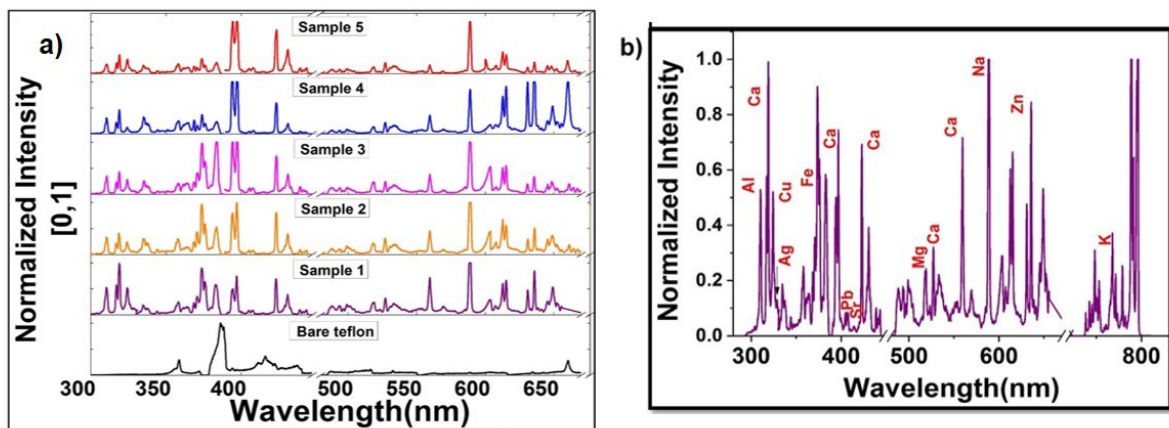
Figure 3 a) LIBS spectra of five surficial sediments from Lake L-55, East Antarctica. b) LIBS spectra of sediment sample-1using solid residue analysis on Teflon substrate.

The recorded LIBS spectra consist of characteristic atomic emissions from different elements with their strength proportional to concentration of that particular element in the sediments. These emission lines have been assigned using NIST (National Institute of standards and Technology) spectral database. As mentioned, the emission line intensity of any particular element is indicative of its concentration in the sample. In view of this, we can arrange the LIBS detected elements based on decreasing order of its concentration as Na<Ca<Fe<Zn<Al<Cu<K<Mg<Pb<Sr<Ag. As shown in Fig. 3(b), Na and Ca lines exhibited higher LIBS intensity, indicating its abundance in the sample and therefore causing the LIBS signal to saturate. Whereas the LIBS intensity of Pb, Sr, Ag was lower in the analyzed samples. This clearly shows the potential of the LIBS method to analyze minor geochemical elements with the solid residue method. A comparison of the data obtained by the LIBS technique and ICP-OES was used to assess the overall potential of the LIBS method for such applications. For this, the lake sediments of Antarctica were digested and analyzed using both methods. The results reveal that the data obtained by the LIBS technique were comparable to those by the ICP-OES method. The comparison of the data obtained by two different methods shows that the LIBS results mainly concur with data of the ICP-OES. This suggests that our solid residue method using a Teflon substrate could be effectively applied on the analysis of trace elemental analysis in liquid samples using 10 μL of sample volume. The results suggest that the LIBS technique can be successfully used on lake sediments from Antarctica.

Table.S1 Elements detected using ICP-OES

Elements	Al	As	B	Ba	Bi	Ca	Cd	Co	Cr	Cu	Fe	Hg
Concentration(ppm)	53469.76	7.41	139.47	766.44	14.10	22654.78	3.75	27.07	61.84	1.65	23097.63	0.954

Elements	Li	Mg	Mn	Ni	Pb	Sr	Zn	Na
Concentration(ppm)	11.49	4676.99	320.94	8.40	17.42	140.68	136.76	20907.48