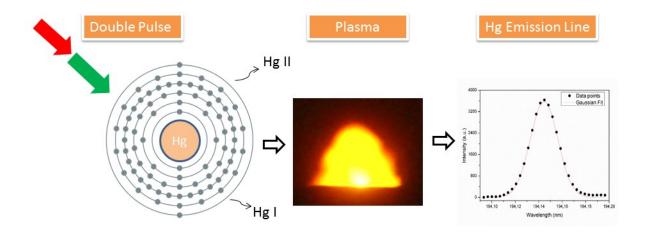


New approach to improve detection of landfill-related pollution

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Targeting a leachate sample with a high-intensity double-pulse laser generates an extremely hot plasma. The light emitted by the plasma is then analyzed to assess the quantity of mercury present in the sample. Credit: Gustavo Nicolodelli, Embrapa Instrumentation



Numerous hazardous substances seep from landfills into soil and groundwater, threatening human health and the environment. However, current methods for monitoring these substances are cumbersome and can create additional hazardous chemicals.

A method known as laser induced breakdown spectroscopy (LIBS) offers a cleaner, faster and simpler approach than existing technologies for detecting contaminants in the fluids coming from landfills, known as leachates. In The Optical Society journal *Applied Optics*, a team of researchers working in the Brazilian company Embrapa Instrumentation report refinements to LIBS technology and confirm that LIBS can be used to detect mercury in leachates.

"LIBS is an environmentally clean technique that is free of chemical residues, compared to standard reference techniques currently used for the same type of analysis," said Carlos Menegatti, University of São Paulo, Brazil, and the paper's first author. "Moreover, LIBS is a much faster technique and does not require pre-preparation of the samples."

Analyzing landfill leachates

As rainwater flows through a <u>landfill</u>, it picks up various kinds of dissolved and suspended contaminants. Landfill managers must collect and treat this fluid before it can carry pollution into the surrounding soil. To know which treatment methods to employ, managers rely on tests that detect the specific contaminants present, which must be reduced below the legal concentration thresholds.

Mercury is one of the most hazardous contaminants found in landfill leachate. It harms wildlife and has been associated with neurological and developmental problems in humans. Most environmental standards require mercury to be reduced below 0.5 parts per million (ppm); it is often found in pre-treatment leachates at concentrations of 0.05 to 160



ppm.

Current techniques for detecting mercury and other metal contaminants in leachates include atomic absorption spectroscopy, x-ray fluorescence, inductively coupled plasma atomic emission spectroscopy and inductively coupled plasma mass spectrometry. Although these techniques are highly precise, they require laborious preparation of samples, making it impossible to acquire real-time test results. Some of these techniques also generate chemical wastes.

The new study is the first to apply LIBS to the detection of mercury in landfill leachate. In LIBS, a sample is targeted with an intense laser pulse, which generates a very hot plasma. The light emitted from this plasma is then captured and measured by a spectrometer, which can be calibrated to detect the chemical signatures of specific contaminants.

Refining the LIBS setup

Conventional LIBS is not sensitive enough to detect mercury at the concentration levels that are relevant to landfill leachate. To overcome this limitation, the researchers used a double-pulse setup in which a series of two laser pulses targets the sample, generating an even more intense plasma. This increases the amount of light emitted by the plasma, which improves the sensing sensitivity.

"This was the first time that the double pulse LIBS was applied to measure mercury in a solid sample," said Menegatti. "It is well established in the literature that double pulse LIBS has more sensitivity than the single pulse LIBS, so we have achieved better detection limits in solid samples than previous work."

The double-pulse approach also made it possible to use a different emission line (the region of the emission spectrum scientists use to



identify a specific chemical of interest) to detect mercury. The emission line near 253 nanometers (nm) is often used to detect mercury, but when iron is also present, the iron emission line can cause interference at 253 nm, necessitating more complex data analysis to separate the mercury fingerprint from that of iron. Using the double-pulse laser makes it possible to observe a different mercury emission line near 194 nm, thus avoiding interference with the iron emission line.

The team tested their system experimentally using leachate that had been laced with mercury. The lowest mercury concentration detectable in their tests was 76 ppm. The researchers said further refinements should allow detection of lower levels of mercury, ultimately to 5 ppm or below, in order for the system to be useful for ensuring compliance with legal standards. In validation experiments, the system showed an average error of about 20 percent, which the researchers said should be satisfactory for quantifying mercury in landfill leachate.

Next steps

The researchers plan to further refine the LIBS instrumentation to improve the ability to detect mercury at lower concentrations and to more accurately quantify the amount of mercury present. In addition, although mercury was the focus for this proof-of-concept demonstration, the system could be calibrated to measure the chemical signatures of contaminants other than <u>mercury</u>.

"This concept can be applied to other chemical elements," said Menegatti. "Depending on the type of sample, you can choose more appropriate lines to avoid interference in the spectrum caused by the emission lines of other elements."

More information: Carlos R. Menegatti et al, Semiquantitative analysis of mercury in landfill leachates using double-pulse laser-induced



breakdown spectroscopy, *Applied Optics* (2017). DOI: 10.1364/AO.56.003730

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