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Direct Electrospray Analysis of Bio-Molecules in Solid Materials

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Abstract

It is reported that organic compounds can be quickly and in situ analysed by combining Electrospray Ionization Mass Spectrometry (ESI-MS) with a newly designed Laser Ablation in Liquid (LAL) sampling technology. A method known as LAL enables laser ablation to be carried out in a liquid media that has organic compounds that have been successfully recovered from solid materials. Three chemical substances valine, alanine, and Benzyl Butyl Phthalate (BBP) were examined.

***Keywords:** Electrospray ionisation, Mass spectrometry, Solid materials; Laser Ablation in Liquid (LAL); Benzyl Butyl Phthalate (BBP)*

Introduction

In-place sampling

Mass spectrometry is now one of the most important analytical methods for detecting organic substances *in situ*, from tiny molecules to big macromolecules. These compounds were measured using various combinations of sampling probes and ion sources.

The most extensively used approach for in situ sampling and imaging analysis of molecules is mass spectrometry coupled with Matrixassisted Laser Desorption/Ionisation Mass Spectrometry (MALDI/MS). The target molecules are extracted into the matrix components in the MALDI technique, and the molecules are then ionised *via* a protonation process, resulting in predominantly protonated ions fragmentation being a minor contributor. Electrospray Ionisation-Mass Spectrometry paired with a Laser Ablation sampling approach (LAESI-MS) is another option for *in situ* investigation of organic molecules. The laser is used to irradiate the sample surface and the induced sample particles or vapour containing the analyte is collected. Ionisation occurs as a result of the collision of sample molecules with the electrospray plume produced by the ESI.

Because laser ablation is performed under air pressure, it is inherently suitable for *in situ* sampling from tissues and living cells. Mass spectrometric investigations of biomolecules can be performed with little sample preparation using LAESI-MS, removing the necessity for time-consuming surface coating of conducting materials or matrix components. Despite these analytical benefits, this approach has two key limitations. The first is that the spatial resolution achieved by the LESA technique (approximately 1 mm) is significantly lower than that achieved by various in situ analytical methods such as MALDI/MS (approximately 5m-30 m), LAESI-MS (approximately 30 m), direct liquid extraction and ionisation technique including liquid micro junction surface sampling probe/electrospray ionisation mass spectrometry (100 m), secondary ion mass spectrometry

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(approx. 5,6,12-15) To enhance the LESA technique's analytical capabilities, more spatial resolution improvements are necessary.

Description

Another issue with the LESA technique is that the target molecules must be soluble in the solvents utilised, which can reduce the sampling efficiency for insoluble substances. Because soluble components can be preferentially sampled, the technique is incapable of simultaneous multicomponent analysis. To address these issues, we created a new sampling approach based on laser ablation in a liquid. As the name implies, the sampling mechanism, including sample heating and aerosol formation of solid materials using the LAL approach, is essentially identical to that of LA. Time resolved shadow pictures also confirmed it. However, because the physical and chemical properties of the gas phase and the liquid phase differ, the methods of laser ablation in these two phases differ to some extent. Laser ablation in the gas or liquid phase is quite similar and occurs within a few picoseconds of the arrival of the laser pulse. However, significant differences are discovered afterwards. In contrast to the gas phase, the liquid phase.

Conclusions

The combination of the LAL approach and ESI-MS has the potential to be a promising analytical method for analysing organic molecules in solid materials. Several findings were made using repeated LAL sampling from in-house solid materials.

- The overall efficiency of transmitting solid materials to ion detectors, including LAL sampling, was determined to be 1.1103% for valine, 8.7103% for caffeine, and 6.7104% for Benzyl Butyl Phthalate (BBP).
- LAL sample recovery for the three analytes was 31% for valine, 45% for caffeine, and 37% for BBP.
- It should be noted that the recovery of water-insoluble compounds (*i.e.*, BBP) was not significantly different from that of soluble compounds (valine and caffeine), implying that the LAL technique might be applied.
- The repeatability of readings was calculated to be 5.8% for valine, 4.1% for caffeine, and 3.6% for BBP using four repeated samples from independent sampling locations. Analytical repeatability was determined by either the heterogeneity of the standard materials used in this investigation or by time dependent changes in ion yields caused by the likely introduction of large sized sample particles into the ESI-mass spectrometer.

The results show that the LAL methodology has the potential to be used as a sampling method for both soluble and insoluble compounds. LAL has the benefit of being quick and can be utilised at atmospheric pressure, eliminating the need for time-consuming and complex sample preparation processes. The obtained samples can be kept for extended periods of time and used in future analyses.