Dry Sample Preparation for MALDI of Derivatised Fullerenes

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One of the most serious problems and limiting factors for the analysis of derivatised fullerenes by matrix-assisted laser desorption/ionisation (MALDI) analyses, is the solubility of the solid analytes. The fact that the analyte and the matrix must be dissolved in appropriate solvents and then be spotted onto the sample holder, can cause severe practical problems in sample preparation and also large errors in the calculation of the molar matrix-to-analyte ratios. For example, if the analyte and/or the matrix do not completely dissolve, or if they completely dissolve in incompatible/immiscible solvents then the results obtained will be greatly impaired. An additional problem, in the cases of mixtures, is that not all components targeted for identification may dissolve thereby producing misleading results. A good example of such compounds are amongst others the highly hydroxylated fullerenes (fullerols) $C_{60}(OH)_n$, where n=22-26, which are perfectly soluble in water but insoluble in any common organic solvent whereas the reverse is true for the employed matrices.

Following the findings of Räder, Müllen *et al.*,[1,2] regarding a new method of MALDI preparation for insoluble giant Polycyclic Aromatic Hydrocarbons (PAHs), we employed this new dry sample preparation in the investigations of derivatised fullerenes, which were either too fragile/reactive or insoluble in organic solvents. For fullerenes and their derivatives, it has recently been shown that the use of DCTB[3] as matrix produces the optimum results in both ion modes and exceeds the performance of 9-nitroanthracene, which is the current benchmark standard matrix employed for such compounds. Our attempts are focused on dry MALDI preparation of fragile hydrogenated fullerenes, such as $C_{60}H_{36}$, on fluorinated samples $C_{60}F_n$ where n=18, 36, 46-48, and on the organic solvent-insoluble fullerols.

The preparation method involves crushing known pre-weighed amounts of analyte and matrix into a fine powder at the selected pre-calculated molar ratios using a small pestle and mortar. Once the dry solid mixture has been finely divided and homogenised, it is spread on a strip of double-sided tape (DST) positioned along the sample holder covering the targets using a microspatula. In order to avoid contamination of the source of the mass spectrometer from any solid that still remained loosely bound on the tape, nitrogen was blown over it.

Using this dry method of preparation and MALDI-ToF MS, the above mentioned samples were analysed under direct LDI and also under MALDI conditions at M/A ratios of 100:1, 1000:1 and 4000:1. The results obtained were very encouraging showing the intact molecular/quasi-molecular ions in all cases without any interfering signals from the DST.

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References

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