A multi-vendor applicable target system for (MA)LDI instruments with distinct performance characteristics for the analysis of small WIEN organic molecules related to carbonaceous chondrites

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Introduction

Being able to efficiently compare the data obtained with different (MA)LDI MS instruments with distinct performance characteristics, not only the sample preparation needs to be the same but also the target surface onto which the samples are deposited/presented should be the same. For that reason we developed a target system, which enables the use of only one target on different MS devices.

As we are interested in the analysis of carbonaceous chondrites we tested our target system using small organic molecules related to the group of molecules already detected in the carbonaceous chondrites^[1]. Furthermore the second point for choosing these compounds was their different desorption/ionization behavior (proton or cation attachment, radical cation formation).

Carbonaceous chondrites
Stony meteorite
Primitive
Undifferentiated
Contain organic compounds

Materials and methods

The developed target system (4) consists of modified Bruker target adapter (1), an Au target plate (2) and a standard stainless steel Waters target plate (3).



The selected organic substances (i.e. tryptophan, 2-deoxy-D-ribose and triphenylene) were prepared using UHQ water and MTBE (methyl *tert*-butyl ether) and were spotted (volume 0.5 µL) onto the target plate (stainless steel or gold).



Compound	Solvent	mg/ml	Additive
L-tryptophan (α-amino acid)	UHQ H ₂ O	2	NaCl
2-deoxy-D-ribose (deoxy sugar)	UHQ H ₂ O	2	NaCl
triphenylene (polycyclic aromatic hydrocarbon)	MTBE	2	None

The measurements were performed on three (MA)LDI instruments namely an Axima TOF², an ultrafleXtreme and a Synapt G2 using laser desorption ionisation (LDI) mode. The samples were also analyzed on a TOF-SIMS 5 mass spectrometer equipped with Bicluster ion gun with a gridless RTOF using only the Au target plate.

Instrument	m/z range	Acquisition mode	Laser fluence a.u.	
Axima TOF ²	20-500	RP (+)/LN (-)	130-145 (max. 180)	
UltrafleXtreme	20-500	RP (+)/RN (-)	85 (max. 100)	
Synapt G2	20-500	RP (+)/RN (-)	350 (max. 500)	



Results and discussion

2-deoxy-D-riobose and triphenylene were analyzed only in positive ion mode while tryptophan was analyzed in positive and negative ion mode. All shown mass spectra were obtained using a solid Au target. Except for the target related background ions there was no difference between the spectra obtained from gold and the steel target.

Tryptophan, LDI (+), (-)

Tryptophan was analyzed in (+) and (-) ion mode on all instruments and was detected as [M+Na]⁺ at m/z 227.1 and [M+2Na-H]⁺ at m/z 249.1 (spectrum A1-A3), and as [M-H]⁻ at m/z 203.1 (spectrum B1-B3). Some *in*source generated fragment ions (m/z 130.1, m/z 159.1 and m/z 188.1)^[2], sodium related cluster ions and the gold cluster are also visible. Other fragment ions probably arise from the background or are the result of the photochemical reactions.

2-deoxy-D-ribose, LDI (+)

2-deoxy-D-ribose is present as sodium adduct ion at m/z 157.0 (spectrum C1-C3). No fragment ions or deprotonated molecular ions are generated. Gold cluster and sodium related cluster ions are visible on all spectra.

LDI (+) [(NaCI)Na]⁺



Conclusion

- The target system for multiple (MA)LDI instruments from different vendors was successfully developed.
- 337/355 nm LDI of small organic molecules is feasible.
- three selected compounds, The related to those found in meteoritic samples, were successfully analyzed on all devices including a SIMS-MS





Triphenylene, LDI (+)

Triphenylene did not exhibit any protonated, adduct or deprotonated molecular ion. Only an abundant radical cation is visible at m/z 228 obtained by all instruments (spectrum D1-D3). The Au₁ cluster ion is also visible.



ultrafleXtreme

- using a solid Au target.
- A serious comparison of data obtained different MS devices was with possible.
- Desorption/ionization behavior of the compounds was similar on all devices.
- With the Synapt G2 we were able to obtain for m/z values of interest (various molecular ions) with a mass accuracy of below 2.3 ppm (elemental composition).

Outlook

- Breaking down provided meteorite grains^[4] into small pieces - splinters.
- LDI-MS of the splinter extract as well as of the whole meteoritic splinters using the Au target.
- Accurate molecular mass determination - elemental composition with the use of the Synapt G2 instrument.
- MS/MS (HE-CID) for structural elucidation.
- Comparison of the meteoritic data to the already obtained mass spectra of our three selected compounds.



D-ribose (B) and triphenylene (C).

(A)	(B)	(C)
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tryptophan	[M+Na]+	227.0796	227.1 (89.8)	227.1 (89.8)	227.0791 (-2.2)
	[M- H+2Na]⁺	249.0616	249.1 (154.2)	249.1 (154.2)	249.0611 (2)
	[M-H]⁻	203.0820	203.1 (88.6)	203.1 (88.6)	203.0818 (1)
2-deoxy-D-ribose	[M+Na]⁺	157.0477	157.0 (-303.7)	157.1 (333)	157.0476 (0.6)
triphenylene	[M]+•	228.0939	228.1 (26.7)	228.1 (26.7)	228.0935 (1.8)

SIMS results

Because classical SIMS is used in the analysis of carbonaceous chondrites and cometary dust^[3], we investigated the behavior of our test compounds when spotted onto the gold target (usually used in SIMS analysis). As seen on the following mass spectra, except for some fragment ions and [M+H]⁺ of tryptophan all other molecular species correspond to those obtained by 337/355 nm UV LDI MS.

values



References:

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Synapt G2

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