

Novel Derivatization Strategies for Biomarker Analysis using APLI MS



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Introduction

For a couple of years we have developed the hyphenation of HPLC, GC, and CEC with APLI and high resolution TOF MS for the analysis of essentially non-polar poly aromatic hydro-carbons¹⁻³. For these compounds APLI is outstandingly sensitive.

However, only aromatic compounds are amenable to APLI. This selectivity has both advantages (selectivity in a complex matrix) and disadvantages (severe restriction of the analytical compound range).

To overcome these limitations, we have already reported on a derivatization strategy that facilitates ionization of polar non-aromatic compounds in complex matrices without hyphenated techniques or stable-isotope labeled standards⁴. In this contribution, the derivatization approach is considerably broadened and particularly extended toward various biomarkers.

Methods

Experimental Setup

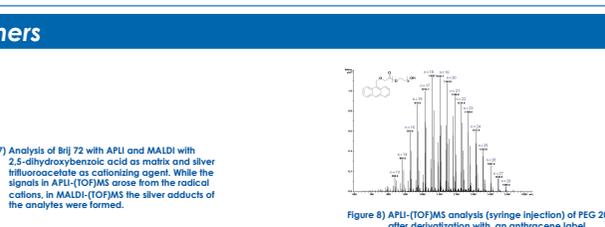
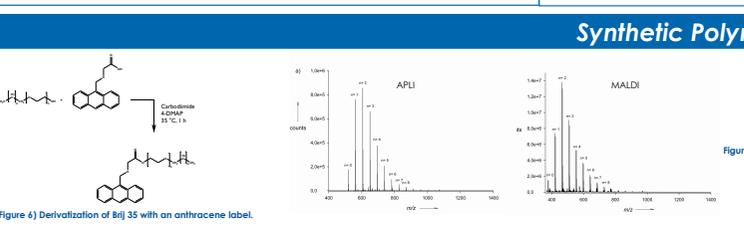
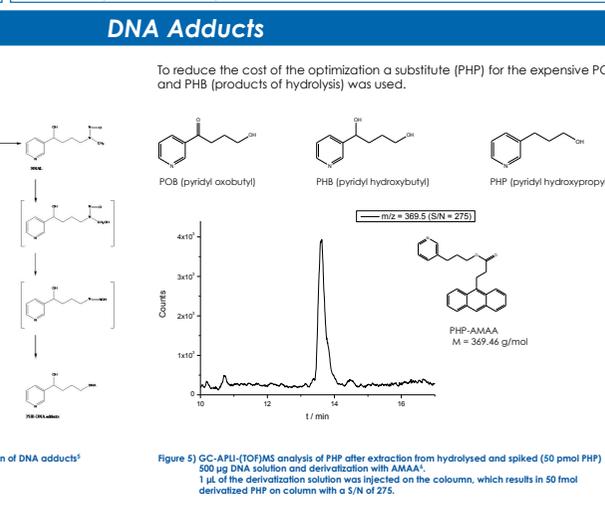
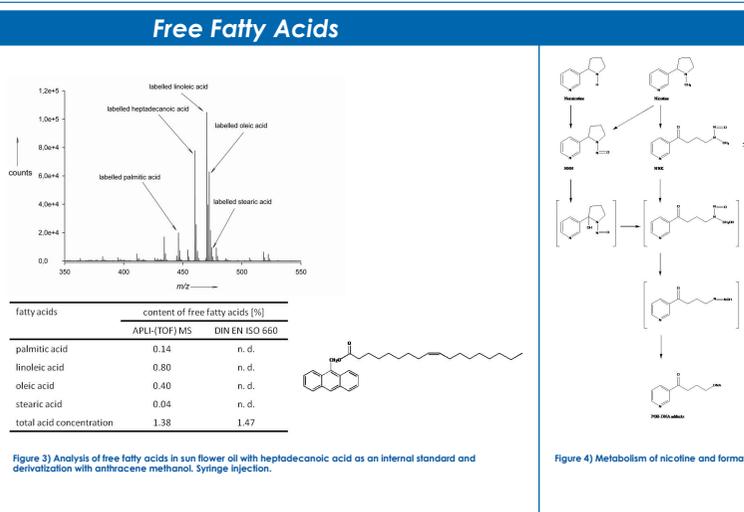
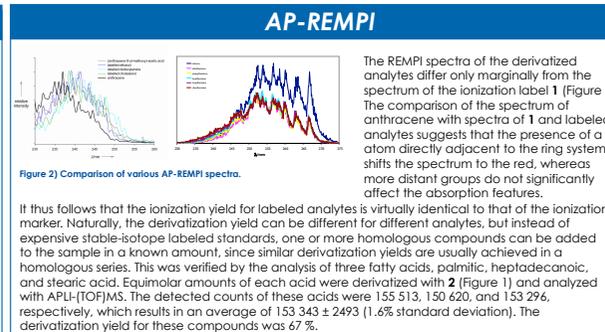
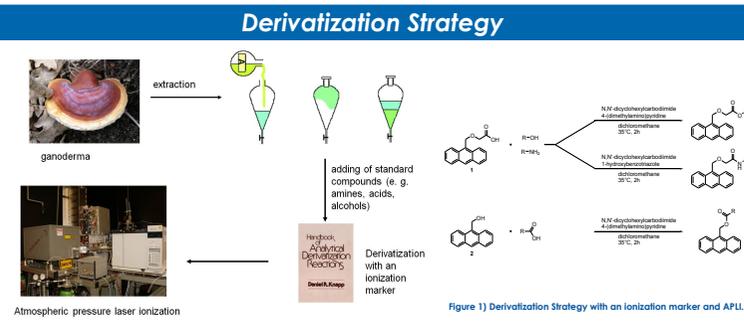
MS1: oaTOF MS (micrOTOF, Bruker Daltonics, Bremen, Germany)

Ion Source: home built temperature-controlled multipurpose ion source (IC-MPIS)

Laser System: excimer-laser (KrF, 248 nm) (ATLEX 300 Si, ATL Laser-technik, Wermelskirchen, Germany)

MS2: MALDI-reflectron-TOF mass spectrometer (AXIMA Performance™, Shimadzu Biotech, Manchester, UK)

Separation Technique: HPLC or GC



Conclusions

In summary, we have demonstrated that derivatization strategies significantly broaden the analytical applicability of APLI-MS.

First, the range of ionizable analytes is not restricted by their spectroscopic features (and thus aromatic hydro-carbons) but solely by the presence of reactive anchor groups and the availability of suitable APLI labels. We are currently developing synthesis strategies for various APLI labels that specifically target reactive analyte sites.

Secondly, once tagged with a specific APLI active label, the complex exhibits spectroscopic features virtually identical to those of the label itself.

This leads to advantages for the quantitative analysis of compounds in complex matrices.

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