Atmospheric pressure chemical ionization – constructing IONIZATION EFFICIENCY SCALE and derivatization reagent suitability.

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Understanding factors affecting the APCI-MS analysis through ionization efficiency, matrix effects, LoQs etc

Online poster

Methods

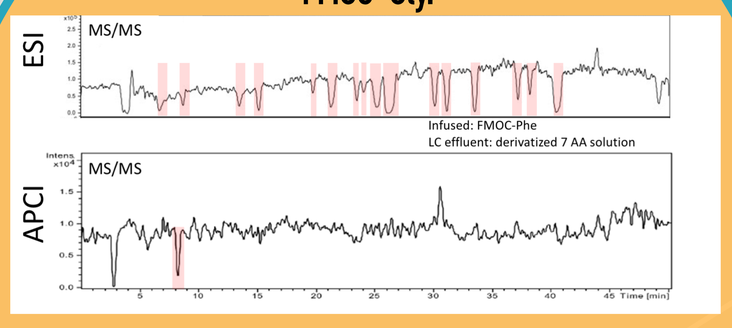
- MS responses recorded with flow injection for more than 40 compounds and logarithmic Ionization Efficiency parameter logIE calclulated.
- Method development for LC-APCI-MS analysis for derivatization reagents
- Matrix effects were evaluated with post-column infusion as well as sample dilution experiments for tea samples

logIE values for APCI

Tetrabutylammonium	4.32	Anthtracene	2.93
$[2,4,6\text{-}(MeO)_3C_6H_2]_3P$	4.30	Diphenylphthalate	2.92
Tetrahexylammonium	4.26	3-aminopyridine	2.82
$4\text{-}CF_3\text{-}PhP1(pyrr)$	4.22	Triethylamine	2.81
Centralite I	4.02	Aniline	2.75
Triphenylguanidine	3.96	2-methylpyridine	2.61
Triphenylamine	3.94	*DEEMM*	2.57
Dimethylphthalate	3.71	*DBEMM*	2.51
Diphenylamine	3.69	*PheDEEMM*	2.47
Tributylamine	3.68	Arginine	2.47
Triphenylphosphine	3.51	*GlyDEEMM*	2.42
Acridine	3.50	Pyridine	2.38
2.2'-bipyridine	3.48	Diethylamine	2.02
Pyrene	3.41	*EBEMM*	1.99
Tetraethylammonium	3.40	Phenylbenzoate	1.79
Sudan I	3.39	Azelaic acid	1.24
PheFmoc	3.28	Methylbenzoate	0.96
1-naphthylamine	3.27	Sulphanylamide	0.84
GlyFmoc	3.12	Benzoic acid	-0.47
Tetramethylguanidine	3.01	Myristic acid	-0.62

Spanning over 5 logIE units
-0.62 … 4.32

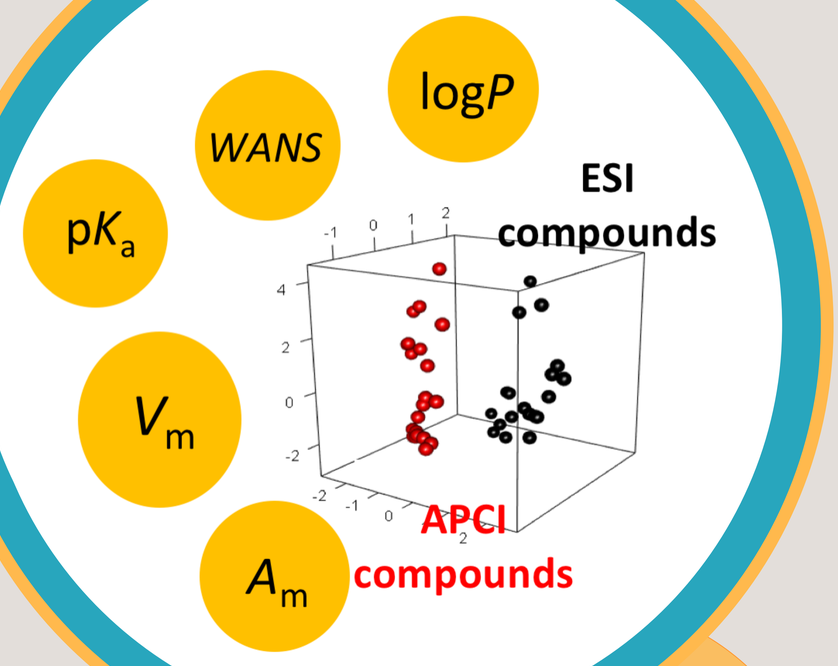
Extracted ion chromatograms of infused FMOC-Gly.



ESI: Strong signal suppression due to FMOC-derivatives of amino acids.

APCI: Only the signal suppression at the hold-up time and at the retention time of FMOC-His is present.

DEEMM
The signal suppression due to borate buffer was not present for APCI.



Ionization efficiency vs molecular structure trends in APCI are very similar to ESI

Acetonitrile proved to be more suitable for the analysis and sample dilution approach in green tea showed that APCI is, in general, less prone to matrix effect than ESI.

RESULTS DERIVATIZATION REAGENTS

FMOC-Cl had poor sensitivity and also high matrix effects (ME). DEEMM and DNS-derivatives were less influenced by the ME than DBEMM and FMOC- derivatives

Limit of Quantifications

in pmol on column.

	DEEMM	FMOC-Cl	DNS	DBEMM
Arg	[a]	9.4	[a]	5.9
Asp	25	43	[a]	5.2
Gly	0.8	73	0.2	3.9
β-Ala	0.9	38	8.2	2.0
Pro	[a]	15	0.7	5.4
Trp	1.6	2.4	1.6	2.7
Phe	0.9	28	0.4	7.7

[a] – stable signal was not obtained

Results IE

Best ionized compounds are not small volatile compounds.

Results imply that in APCI several ionization mechanisms operate in parallel and mechanism(s) not relying on evaporation of neutral molecules from droplets has significantly higher influence than commonly assumed.

References

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New publication for IE

Gornischeff A., Liigand J., Rebane R. systematic approach toward comparing electrospray ionization efficiencies of derivatized and non-derivatized amino acids and biogenic amines.
Journal of Mass Spectrometry (2018)
https://doi.org/10.1002/jms.4272

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