Hospital wastewater treatment by hydrothermal oxidation: Fate of pharmaceuticals

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Overview

- ✓ Development of GC-MS method, with N,O-Bis(trimethylsilyl) trifluoroacetamide (BSTFA) derivatization, for small carboxylic acids analysis in treated effluents.
- ✓ LODs = 28 and 72 ppb. Intra-day precisions = 9% and 23%. Linearity was tested up to1400 ppb for low volatility acids.

Introduction

- ❖ Hospital wastewater is a major source of pharmaceuticals in the environment.[1,2]
- ❖ After consumption, a part of the active ingredients is excreted, ends up in municipal water and is not treated adequately.
- ❖ Impacts of some pharmaceuticals on aquatic species are known but impacts of mixtures at concentrations < 1 µg/L (ppb) are not yet well understood.
- ❖ Pre-treatment of these effluents before releasing them into the sewers could greatly reduce contamination at the source.

Hydrothermal oxidation

- ❖ Advanced oxidation and chemical-free process with generation of radicals ($OH^{\bullet}$, $HO_2^{\bullet}$, $ROO^{\bullet}$).
- ❖ Rapid and effective elimination of organic compounds in a non-selective way.
- ❖ High removal (>90%) of pharmaceuticals under optimal conditions.
- ❖ **Oxidation pathways:**

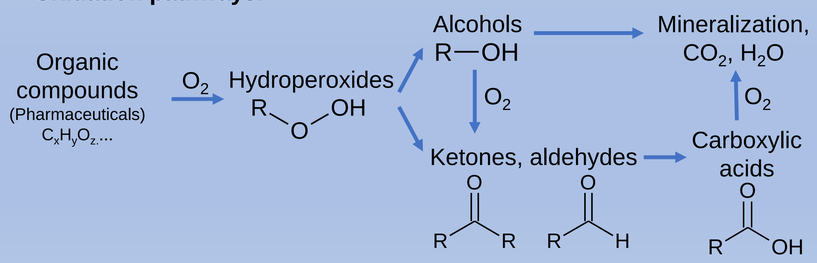
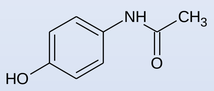


Figure 1: Simplified oxidation mechanism[3]

- ❖ According to the literature, small carboxylic acids are predominantly formed with hydrothermal oxidation of organic compounds.[4,5]
- ❖ **Objective:** To develop a reliable method for transformation products analysis after hospital wastewater treatment.

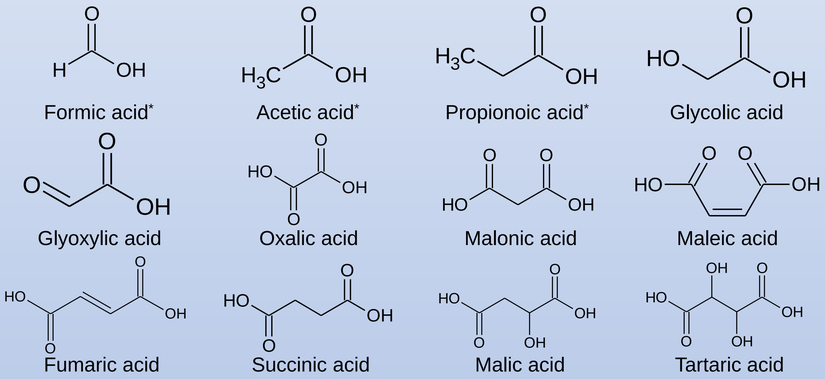
Target compounds



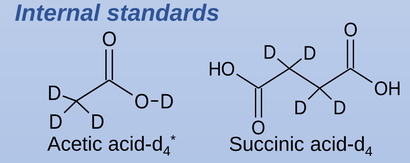
Acetaminophen

A widely used and known pharmaceutical as the first model compound in this study.

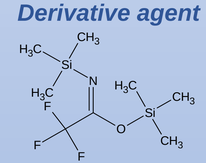
Transformation products



Internal standards



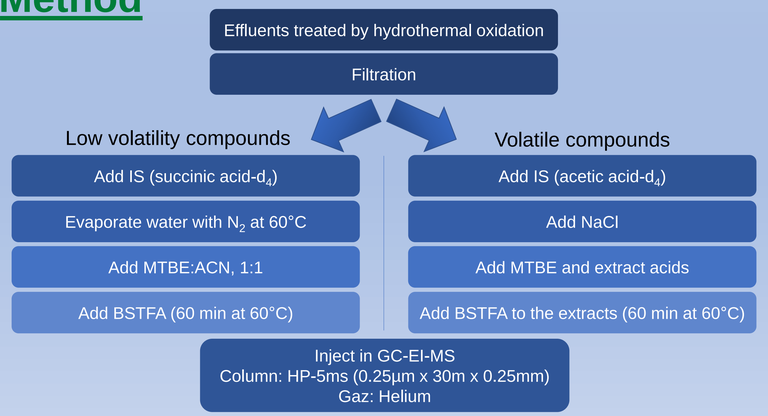
Derivative agent



BSTFA

* Volatile compounds

Method



Results

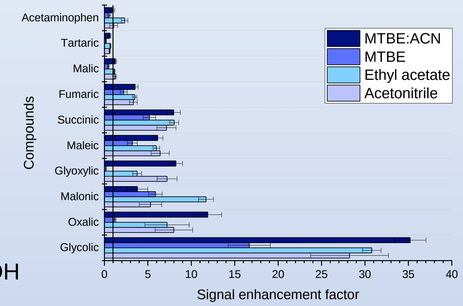


Figure 2: Signal enhancement factor by solvent used in derivatization compared to BSTFA only as reference.

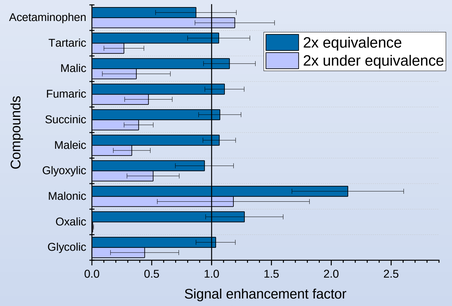


Figure 3: Signal enhancement factor compared to BSTFA molar equivalence.

Table 1: Method performance for low volatility acids

Acid	MDL (ppb)	R^2	Trueness (%)[a]	Intra-day precision (%)[a]	Inter-day precision (%)[a]
Glycolic	64	0.9845	-2	15	17
Oxalic	28	0.9953	-17	16	17
Malonic	29	0.9986	-7	12	8
Glyoxylic	72	0.9802	-25	23	25
Maleic	23	0.9992	-12	11	8
Succinic	40	0.9973	-4	12	12
Fumaric	35	0.9980	-4	9	23
Malic	37	0.9975	0.7	15	17
Tartaric	33	0.9980	8	18	17

[a] Trueness, intra-day and inter-day precision at 750 ppb; MDL: Method Detection Limit

Conclusions

- ✓ Best results for low volatility compounds are obtained with MTBE:ACN as solvent.
- ✓ Signals are optimal with 2x molar equivalence of BSTFA.
- ✓ Quantification of small carboxylic acids in pure water at ppb range is possible by GC-MS combined with BSTFA derivatization.
- ✓ Derivatization optimization for volatile acids is in development.

References

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