A simple approach for avoiding background contamination of quaternary ammonium compounds in LC-MS/MS analysis

E. Eichhorn, S. Schüler, S. Fieberg, E. Scherbaum, M. Anastassiades
E-Mail: Eric.Eichhorn@cvuas.bwl.de

Introduction

Quaternary Ammonium Compounds (QACs) are widely-used in biocidal products, cleansing agents and in personal-care products. According to Reg. (EC) No. 396/2005, maximum residue limits (MRLs) are set at 0.1 mg/kg for the sum of benzalkonium chlorides (BACs) (mixture of alkyl chain lengths of C_8, C_{10}, C_{12}, C_{14}, C_{16} and C_{18}) and the sum of didecyldimethyl-ammonium chlorides (DDACs) (mixture of alkyl chain lengths of C_8, C_{10} and C_{12}). Due to the broad range of QAC applications, background contamination of samples may occur in a multitude of different steps prior and during analysis, with the lab's responsibility being to minimize the latter as far as possible. The contamination of several components within the LC-system has been found to create significant contamination levels in routine analysis. Contamination levels as well as the concerned QACs may differ from day to day and from instrument to instrument. Localizing the source(s) of these contaminations in order to eliminate them, can be very laborious and not necessarily successful.

A simple and pragmatic approach to largely eliminate the background contaminations within the LC-system is presented here. The approach involves the use of a trap column and was inspired by the work of Zomer *et al*. (2020) [1].

Analytical principle and instrument setup

The setup of the LC system is schematically shown in Fig. 1.

In our case, we used two Phenomenex Aqua C_{18} (5 µm, 50x2.0 mm, 125 Å) columns, one as analytical column and one as trap column, but any C_{18}-based column would be suitable. A 1290 Infinity I system from Agilent coupled with a QTrap 6500+ from Sciex was used for validation experiments and routine analysis.

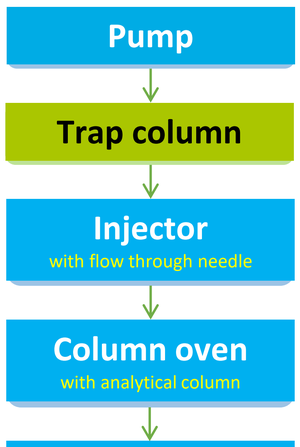

Figure 1: LC system set-up for using the trap column approach.

Observations

When no trap column is used, the QAC-contaminations eluting from the LC-system prior to or in-between injections accumulate on the entrance of the analytical column and fully co-elute with the analyte-QACs in the following run. By placing the trap column prior to the injector, the contaminant-QACs accumulate on the trap column and experience an extra retention during the analytical run, thus being effectively separated from the the analyte-QACs.

The retention times of the analyte-QAVs slightly increased by ca. 0.3 min due to the deferred gradient by the dead volume of the trap column (see Fig. 2).

Other methods running on the same instrument, that do not actually require the trap column set-up, were only marginally affected by this setup with only minor retention time shifts being observed.

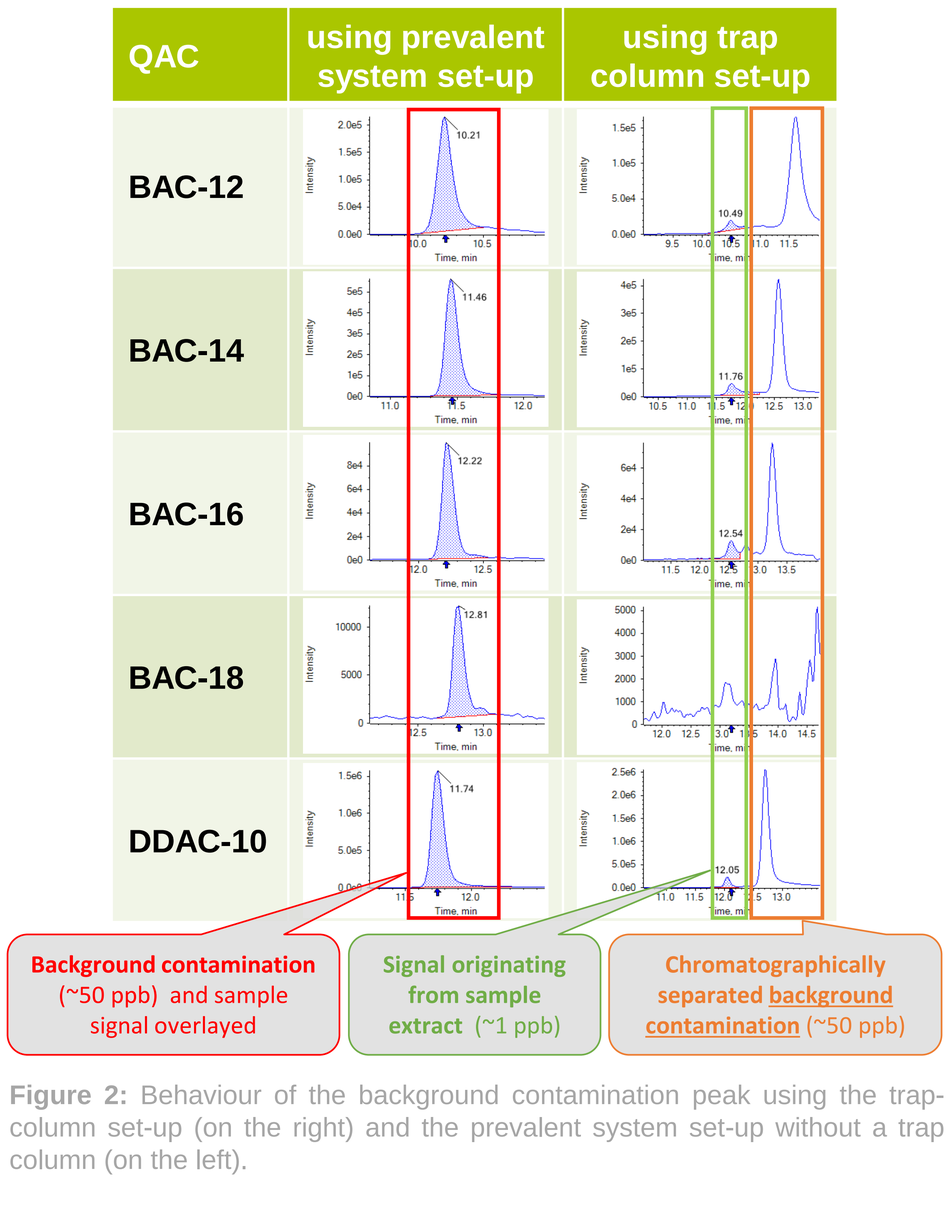

Figure 2: Behaviour of the background contamination peak using the trap-column set-up (on the right) and the prevalent system set-up without a trap column (on the left).

Using the above set-up, validation experiments using QuEChERS (EN 15662) and QuOil (CEN/TS 17062:2019) on various commodities of plant origin at spiking levels down to 0.005 mg/kg fullfilled the AQC criteria for all substances except for DDAC-10 in peanuts and grapes (which blanks contained DDAC-10 levels >30% of the spiking level). The validation data are shown in Table 1 (validation data at a spiking level of 0.01 mg/kg, all succesfull, are not shown).

Table 1: Mean recoveries (each n = 5) and variation coefficients (CV) from the validation experiments in different matrices at 0.005 mg/kg.

Substance	Detected mass trace	Cucumber		Grapes		Wheat flour		Peanuts	
		Rec. (%)	CV (±%)	Rec. (%)	CV (±%)	Rec. (%)	CV (±%)	Rec. (%)	CV (±%)
BAC-8	248 / 156	103	1.2	99	2.9	102	2.2	97	3.5
	248 / 91	102	1.4	100	1.2	101	2.4	98	2.9
BAC-10	279 / 184	100	2.2	100	2.7	99	2.8	98	0.6
	276 / 91	101	1.7	101	3.4	101	1.1	98	1.2
BAC-12	304 / 212	103	0.9	102	6.8	98	3.9	101	6.7
	304 / 91	101	1.5	99	4.4	98	3.2	103	10.4
BAC-14	332 / 240	97	1.3	100	3.3	87	3.0	96	5.5
	332 / 91	97	1.3	97	4.7	87	2.4	99	5.1
BAC-16	360 / 268	96	2.0	97	3.0	80	2.7	95	1.2
	360 / 91	95	1.9	103	1.7	77	3.0	97	4.7
BAC-18	388 / 296	92	2.4	102	2.6	71	3.8	91	5.1
	388 / 91	91	3.3	102	1.9	67	4.3	94	3.0
DDAC-8	270 / 158	101	1.4	104	4.6	101	1.9	100	2.4
	270 / 43	103	2.7	97	5.4	97	4.9	98	11.7
DDAC-10	326 / 186	107	4.7	**109**	**2.8**	105	11.1	**118**	**22.4**
	326 / 41	102	7.3	**106**	**10.0**	108	12.2	**117**	**21.5**
DDAC-12	382 / 214	91	2.9	98	4.7	74	3.7	98	3.1
	382 / 58	94	3.9	106	3.5	75	3.4	101	8.9

References

[1] P.Zomer, R. Boerrigter-Eenling, H. Mol, Wageningen University & Research, Improvement of LC-MS/MS analysis of quaternary ammonium compounds by using a trap column, Poster presented at the 13th EPRW (online), 2020

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