

Quaternary ammonium compounds (QUAT) in house dust

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SUMMARY

Like other surfactants quaternary ammonium compounds (QUAT) are enriched in adipose cell membranes of living organisms and can consequently impair the normal functions of cell membranes. Indoors surfactants are absorbed in house dust and are unlikely to be biologically degraded there, meaning that long-lasting contaminations are to be expected. To date only a few studies relating to the distribution of surfactants indoors and in house dust in particular have been carried out.

The first part of the study was to determine the limits of determination, the linearity and the reproducibility of the measurements of the concentration van QUATs.

In the 50 samples of house dust, taken from German Environmental Survey for Children 2003/06, the average concentration of the sum of the QUATs was 35.2 mg/kg with a 95-percentile of 105.7 mg/kg.

KEYWORDS

Quaternary ammonium compounds, House dust, Exposure

INTRODUCTION

Quaternary ammonium compounds (QUAT) are a class of industrial chemicals of commercial importance and belong to the surfactants group. They are therefore surface-active substances, which unite a hydrophobic (water-repellent) alkyl chain and a hydrophilic (water soluble) group in their molecule. Main characteristic of the compounds is a quaternary nitrogen atom, where the four hydrogen atoms of the ammonium group have been replaced by organic residue, mostly longer or shorter alkyl chains.

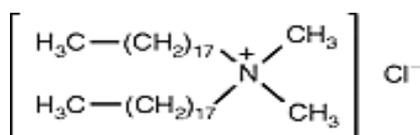
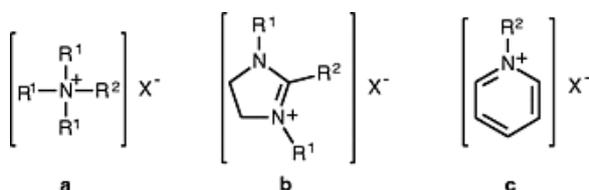


Abb.1: Structure of a QUAT using distearyldimethylammonium chloride as an example (Römpp, 2007).



- a) Linear alkyl ammonium compounds
b) Imidazolium compounds
c) Pyridinium compounds

Abb. 2: Various QUATS (Römpp, 2007).

QUATS belong to the cationic surfactants group. Surfactants are enriched in adipose cell membranes of living organisms and can consequently impair the normal functions of cell membranes. It is this property in particular which enable cationic surfactants to act as a biocide and to be used as pesticides and disinfectants in human and veterinary medicinal products, as additives for technical applications (asphalt, additives in paint, varnish, fluids) and also in cosmetic beauty products (Uhl, 2005).

Products containing benzalkonium chloride and dialkyldimethylammonium chloride are for example sold in supermarkets, chemists and home improvement stores as anti-mould agents in various applications and quantities. It is estimated that for the most part however they are used in fabric softeners, toiletries, textile auxiliaries and only a low percentage in cleaning products, disinfectants and industrial preservatives (Uhl, 2005).

The toxicity level of QUAT is determined by length and branching among other things of the alkyl chains. A mixture of cationic and anionic surfactants is up to 100 times less toxic than comparable single substances (Uhl, 2005).

Quaternary ammonium compounds are only considered acutely toxic in few cases. However it should be remembered that they increase the permeability of membranes compared to other organic substances, since they damage the protective water lipid membranes of the outer skin and consequently have a drastic effect on the absorption level of toxic substances.

This property is also used to improve the spectrum of activity through synergism in combination with other disinfectants and for example to achieve higher and longer-lasting levels of efficacy together with alcohols and aldehydes (Bode-Chemie, 2007).

There is currently a new evaluation process of active agents unfolding under the Biocide product directive framework, there having been no information relating to this until now.

Indoors surfactants are absorbed in house dust and in contrast to aquatic media they are unlikely to be biologically degraded there, meaning that long-lasting contaminations are to be expected, which are likely to exist years after use. To date only a few studies relating to the distribution of surfactants indoors and in house dust in particular have been carried out. For example Butte et al. (Butte, 2004) present the results of exploratory measurements of cationic, anionic and non-ionic surfactants in house-dust. However, owing to the photometric cumulative measurements applied in this study, no assumptions about individual substances can be made. Below studies into selected single substances from representative dusts are presented, in order to provide for a better evaluation of results. The following substances were selected for analysis:

- BAC-10 (Benzalkonium chloride with $R=C_{10}$)
- BAC-12 (Benzalkonium chloride with $R=C_{12}$)
- BAC-14 (Benzalkonium chloride with $R=C_{14}$)
- BAC-16 (Benzalkonium chloride with $R=C_{16}$)
- DDAC (Didecyldimethylammonium chloride)

METHODS

Collecting

The samples come from the widest possible representative selection from the pool of house dust samples taken for the German Environmental Survey for Children 2003/06 and by

courtesy of the German Federal Environment Agency (Umweltbundesamt) for the analysis of quaternary ammonium compounds (QUAT). The research collection consists of 50 filtered vacuum cleaner bag samples of < 63 µm fraction. Both the drawing and selection is made from a pool of dust particles, which originate from the sampling period in the first year of research (2003/2004) and which were already analyzed as part of the German Environmental Survey for Children 2003/06 on organic chloride compounds, flame retardants and plasticizers (Phthalate) (Becker, 2008). A sample was selected randomly from each point (47), which contained at least 5 g of dust. For the 3 samples which were missing further dust particles were taken randomly from 3 points.

Analysis

Brief description of the process (validated in-house method with LC-MSMS):

1 g fine dust (<63 µm fraction) is weighed out into a 50 ml centrifugal receptacle and mixed with one internal standard, 1 ml water containing cooking salt and 20 ml acetonitrile. After a 10 minute ultrasound treatment the extract is centrifuged at 4,500 U/min, an aliquot is taken from the excess and 1+9 diluted with acetonitrile.

Apparatus

Liquid chromatograph: Agilent 1200
 Eluent: Water (0.1 % formic acid); acetonitrile (0.1 % formic acid)
 Analytical columns: Phenomenex Aqua, 150mm x 2.0mm, 3µm
 Detector: Varian Kodiak 1200 MS
 Mode: MRM-Mode; ESI+

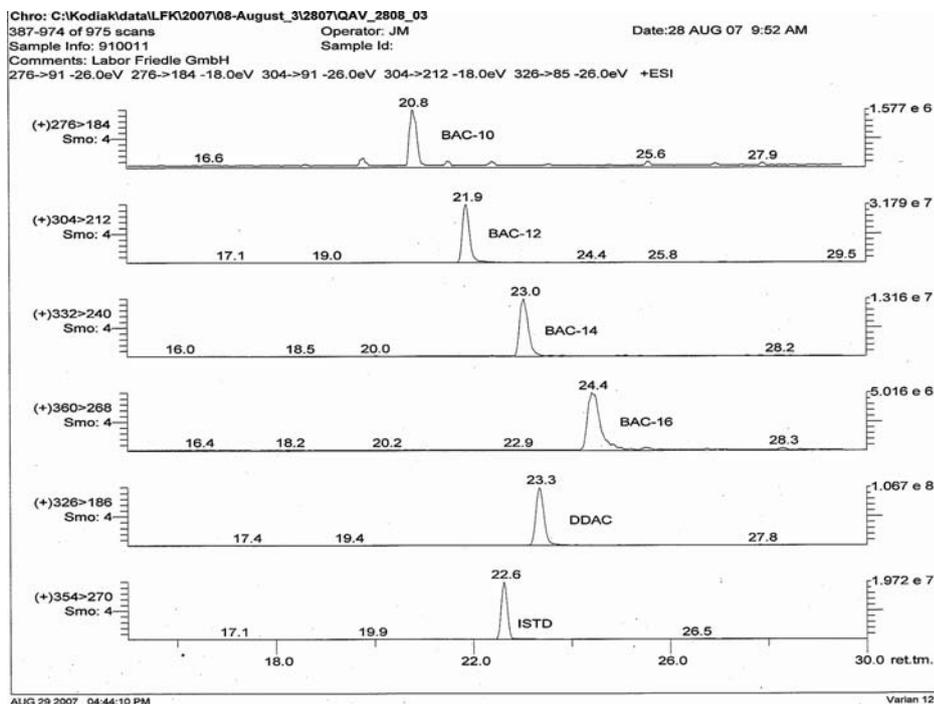


Figure 3. Mass fragmentographs of an exemplary dust sample with concentration level between 0.7 mg/kg (BAC-10) and 46.8 mg/kg (DDAC).

Linearity

For each QUAT the linearity was tested with 6 samples with different concentrations. The linearity proved to be well between the limits.

Table 1. The raw data of the calibration series with example BAC-12.

| Concentration of Standards [mg/kg] | Total area | Response factor |
|------------------------------------|------------|-----------------|
| 0 | 5558 | 2.00 |
| 10 | 46760 | 16.36 |
| 30 | 107200 | 37.21 |
| 50 | 176100 | 55.03 |
| 70 | 248800 | 78.54 |
| 90 | 302300 | 93.77 |

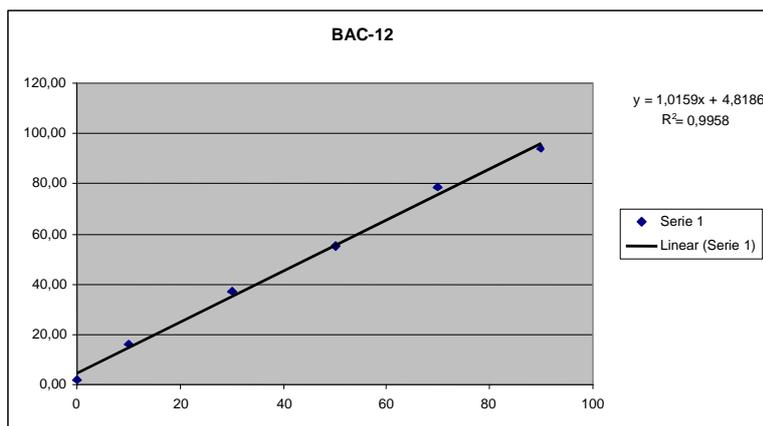


Figure 4. Linearity of the process with example BAC-12.

Limits of determination

The analytical limits of determination are clearly below 0.1 mg/kg for each substance. Decided was to set the limits of determination at 0.1 mg/kg owing to the fluctuating and sometimes increasing blind value in this concentration range.

Repeatability

To determine the repeatability of the entire analysis process a selected dust sample was processed 5 times and measured. The standard deviation was 6.23%. This was better than expected.

Table 2. Raw data of repeatability with example BAC-12.

| Measurement No. | Total surface | Response factor | Calculated concentration in the sample [mg/kg] |
|--|---------------|-----------------|--|
| 1 | 28790 | 1.0628 | 6.12 |
| 2 | 24640 | 1.0525 | 6.06 |
| 3 | 27620 | 1.0264 | 5.91 |
| 4 | 27690 | 1.2003 | 6.91 |
| 5 | 25070 | 1.0820 | 6.23 |
| Average value | | | 6.24 |
| Standard deviation | | | 0.389 |
| <i>relative standard deviation [%]</i> | | | 6.23 |

Recovery

To determine the recovery rate 10 mg/kg and 50 mg/kg of QUAT were added to two selected samples. The samples were processed and injected in the LC-MS/MS. Except for BAC-16 the

recovery rate for the low concentration was about 15% lower than for the concentration of 50 mg/kg.

Table 3. Data of the recovery trial:

| Substance | Recovery [%] with 10 mg/kg | Recovery [%] with 50 mg/kg |
|-----------|-------------------------------|-------------------------------|
| BAC-10 | 79.2 | 93.5 |
| BAC-12 | 78.5 | 94.0 |
| BAC-14 | 80.5 | 98.7 |
| BAC-16 | 89.0 | 91.5 |
| DDAC | 69.6 | 85.7 |

RESULTS

The following tables illustrate the statistics of the individual QUAT internal standard and adjusted blind value. All examined substances in all dust samples up to BAC-10 can be detected above the limits of determination.

Table 4. Statistics for QUAT in dust [mg/kg].

| Percentile | BAC-10 | BAC-12 | BAC-14 | BAC-16 | Σ BAC | DDAC | Σ QAV |
|----------------------|--------|--------|--------|--------|-------|------|-------|
| 2 | <0.1 | 1.8 | 1.0 | 0.1 | 4.0 | 0.6 | 5.0 |
| 10 | <0.1 | 3.7 | 1.3 | 0.5 | 5.7 | 0.9 | 6.9 |
| 20 | <0.1 | 4.3 | 2.0 | 0.6 | 7.8 | 1.3 | 9.2 |
| 30 | <0.1 | 5.9 | 2.6 | 0.7 | 9.4 | 1.6 | 13.8 |
| 40 | 0.1 | 6.8 | 2.9 | 0.8 | 11.5 | 2.2 | 14.8 |
| 50 | 0.1 | 8.4 | 3.4 | 1.0 | 13.3 | 2.8 | 17.6 |
| 60 | 0.1 | 9.4 | 3.9 | 1.1 | 14.9 | 4.1 | 20.0 |
| 70 | 0.1 | 11.1 | 4.8 | 1.2 | 18.0 | 5.1 | 22.7 |
| 80 | 0.2 | 14.4 | 5.7 | 1.8 | 22.1 | 6.7 | 28.7 |
| 90 | 0.7 | 24.3 | 8.3 | 3.2 | 29.5 | 10.0 | 44.3 |
| 94 | 0.8 | 29.0 | 13.5 | 5.7 | 45.4 | 11.6 | 66.6 |
| 95* | 0.9 | 53.3 | 26.4 | 7.2 | 88.7 | 12.2 | 105.7 |
| 96 | 0.9 | 77.5 | 39.3 | 8.7 | 131.9 | 12.8 | 144.7 |
| 98 | 2.6 | 190.8 | 63.6 | 14.4 | 263.8 | 16.6 | 269.5 |
| 100 | 3.0 | 285.2 | 119.5 | 19.1 | 426.9 | 46.8 | 431.8 |
| Average value | 0.3 | 19.9 | 8.1 | 2.0 | 30.2 | 5.0 | 35.2 |

* Average value of 94. and 96. percentile

The following graph shows the frequency distribution of QUAT levels.

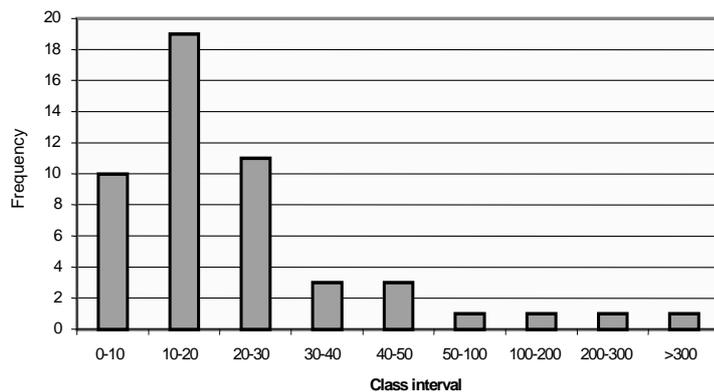


Figure 5. Frequency distribution of QUAT levels [mg/kg].

DISCUSSION

Relationship of the BAC to each other

If for example BAC 12 and BAC 14 are correlated with one another it first appears that a good correlation is created with a R^2 of 0.9767. However if the three highest values are eliminated, then the remaining correlation with a R^2 of 0.5258 is still only moderately good. This suggests various substance combinations as a cause for established house dust content.

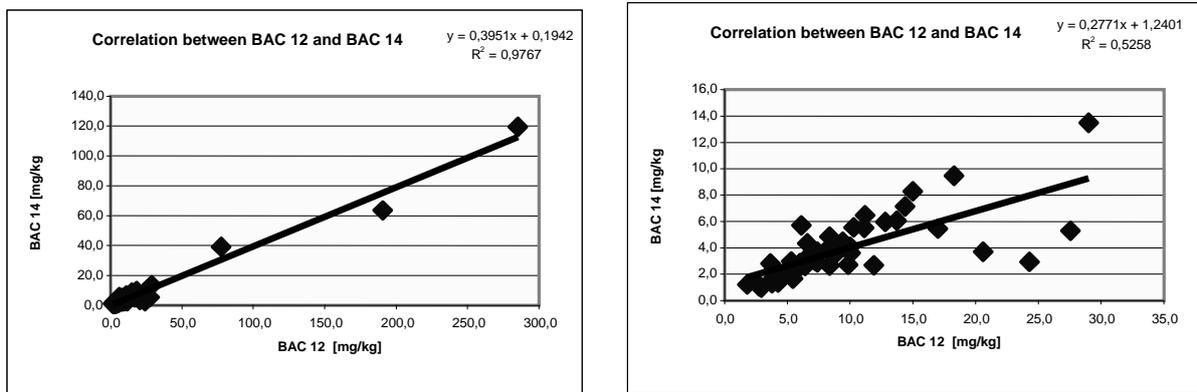


Figure 6. Correlation between BAC 12 and BAC 14 (right graph after eliminating three highest values).

If the total concentration of BAC is correlated with the concentration of DDAC, then a R^2 of 0.0046 determines that both substance groups are practically used independent of each other indoors.

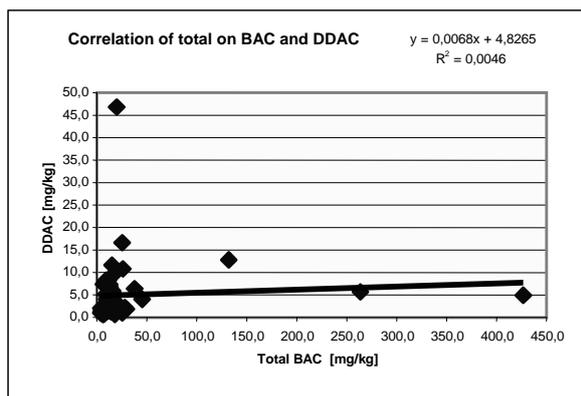


Figure 7. Correlation of BAC and DDAC levels.

Comparison with studies to date

A comparison with the concentration levels of cationic surfactants recorded photo metrically by Butte et al. (Butte, 2004) is interesting.

Table 5. Comparison of concentration levels [mg/kg].

| | Median | Min | Average value | 95-Percentile | Max |
|-----------------------|--------|-----|---------------|---------------|-------|
| Cationic (Butte 2004) | 18.0 | 6.8 | 20.6 | 34.4 | 47.1 |
| QUAT level | 17.6 | 5 | 35.2 | 105.7 | 431.8 |

While minimum and median values tally surprisingly well with one another, the deviation with increasing concentration levels at higher percentiles is significantly greater. If the QUAT level recorded with the HPLC-MS is correlated with the cationic surfactant level recorded photo metrically there is a good correlation between the data groups with a R^2 of 0.9882. This suggests that the differences relating to the high percentiles are more likely to be seen in the exceedance of the linear range with the photometric procedure than in the too small sample sizes.

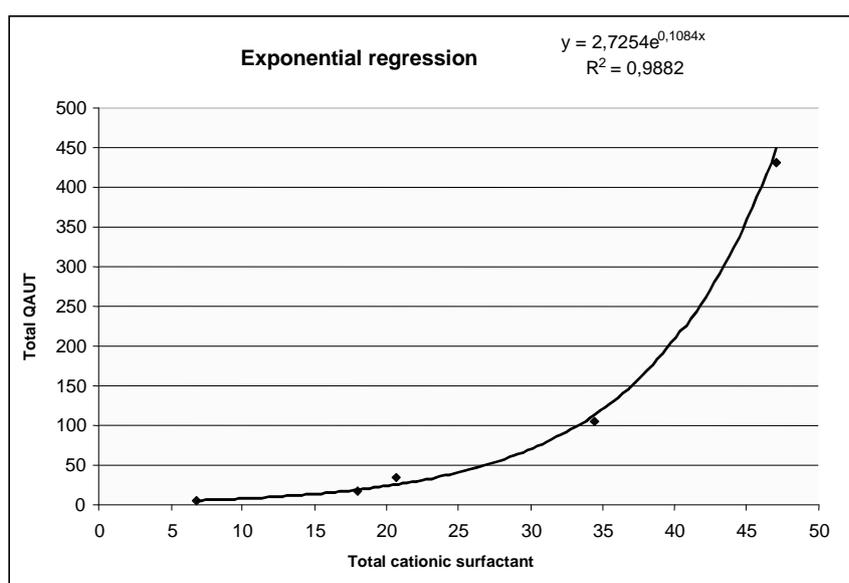


Figure 7. Correlation of the cationic surfactant level to the QUAT level.

CONCLUSIONS

For the first time the results give an impression about the distribution of specific quaternary ammonium compounds (QUATs) in German house dust and the related toxicological data allows the exposure situation to be assessed.

Correlation with certain structural or social household characteristics from which the samples originate is possible when the results are related with other data from the German Environmental Survey for Children 2003/06 (Becker 2008).

ACKNOWLEDGEMENT

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