

## Quantitative prediction of K values

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## Problem 6

Develop one (or better) various models (i.e. equations), that facilitate the prediction of equilibrium partition constants of organic chemicals between air and Tenax at 100°C. As a basis you can use experimental partition coefficients for the following compounds: h-heptane, n-octane, n-decane, ethylbenzene, propylbenzene, butylbenzene, 2-butanone, 2-hexanone, 2-heptanone und 2-nonanone, ethyl acetate und di-ethylether (see [Tenax.xls](#), reference: Schneider, M. and K.-U. Goss *Anal. Chem.* **2009**, *81*, 3017–3021. [Journal link](#) [Download pdf](#) ).

Which physico-chemical properties of these chemicals do you need for setting up a model?

Which general form (equation) should the model have?

How do you proceed in order to get the concrete prediction model?

What can you say about the applicability range of your model?

Some of the calibration compounds listed above have boiling points below, others above 100°C. Does that matter for the calibration and applicability of the model? What about compounds that are solid at 100°C?

If you could measure 3 or for more experimental values for the partitioning to Tenax, which compounds would you choose and what improvement would this bring to your model?

### Answer:

The simplest possibility is the development of compound class specific models for each of the compound classes for which several experimental data are available (alkanes, alkylbenzenes and ketones). The compounds within such classes differ from each other mainly through their size, that is through one property. Hence, it should be possible to describe the differences in log K within these compound classes through a correlation with any single variable that is proportional to their molecular size (e.g. molecular weight, C-number, saturation vapor pressure  $\diamond$ ). You can see this in [Tenax\\_results.xls](#), [sheet 1](#). For 3 compound classes (data for alcohols are added here) one can see the expected good correlations. With these equations one can expect to get reliable predictions for sorption of additional alcohols, alkanes and ketones. In contrast, the regression for the alkylbenzenes cannot be regarded as a good model. One can see this in the rather small  $r^2$  and more importantly in the slope, which differs significantly from the others. This should not be, because in all compound classes the slope is simply reflecting the contribution of a  $\text{CH}_2$  unit to the log K value. The problem likely stems from an inaccurate experimental value. Can you name the suspect?

The different offsets of the various equations indicate that Tenax cannot be a completely apolar sorbent.: the ketones and alcohols sorb stronger than the alkylbenzenes and alkanes. And this is the reason why additional values for the characterization of the Tenax were desirable. H-donor compounds had been missing in the original compound set. In order to cover all compounds by a single model one would have to revert to a pp-LFER model.

