Measurement of multicomponent adsorption isotherms based on a temperature-step approach and mass spectrometry

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Equilibrium single-component measurements are routinely performed using volumetric or gravimetric techniques. However, because industrial processes deal with mixtures and different molecules compete for the same adsorption sites, single-component isotherms are of **limited use in designing a separation process**. Researchers have long tried to predict mixture adsorption based on single-component isotherms (*e.g.*, ideal adsorbed solution theory), but non-ideal behavior remains challenging to forecast without actual mixture adsorption experiments. Unfortunately, **measuring multicomponent adsorption is complex and time-consuming**. A range of methods has been developed, yet none combines ease of operation, straightforward data analysis, and fast measurements. Breakthrough methods, by far the most common approach, illustrate this trade-off. While it provides robust multicomponent adsorption data, each data point requires a few hours to one day due to the relatively large adsorbent mass (> 100 mg) and the reactivation of the adsorbent between each measurement, making this approach time-consuming for the collection of full multicomponent isotherms.

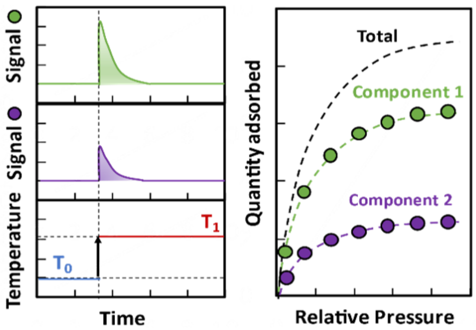

Figure 1: Multicomponent isotherm measurement approach*. A heat pulse is applied to desorb all guest molecules, which are quantified using MS. Each desorption pulse yields one point on the multicomponent isotherm, i.e., one uptake value for each component for a given mixture composition.*

In this presentation, we will present a new methodology for the rapid measurement of reliable multicomponent adsorption isotherms. Instead of a concentration change in the atmosphere surrounding the adsorbent, a **<u>sudden temperature change of the adsorbent is used</u>** to induce full desorption after equilibration at every partial pressure. The desorbed fraction is quantified downstream using a mass spectrometer, by integration of the signal in excess of its baseline. Because of the use of downstream MS analysis, the method can be readily extended to multicomponent measurements (Figure 1).

Compared to breakthrough measurements the temperature-step approach is **much faster**. The temperature-step approach uses much smaller adsorbent quantities (< 100 µg), which considerably decreases the equilibration time. Moreover, since at each step all guest molecules are thermally desorbed, no separate re-activation step of the adsorbent is necessary in between measurements. Our results show **a data acquisition time of < 10 min per point** on a multicomponent isotherm and **straightforward data analysis** (*i.e.*, integration of the MS signal).

The methodology has first been validated for the measurement of single-component isotherms. The high sensitivity of a triple-quadrupole MS allows for the quantification of small amounts of pre-adsorbed species (*e.g.*, 1 nmol or 60 ng for 1-propanol). A full isotherm of 1-propanol on ZIF-8 (using a 57µg sample) was compared to results obtained by Quartz Crystal Microbalance and volumetry measurements, showing a good agreement between the different methods. Results of multicomponent adsorption measurements on industrially relevant adsorbents and their interpretation will be further detailed in the presentation.