Quantification of Adsorbates by X-ray Absorption Spectroscopy: Getting TGA-like Information for Free

Supporting information

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1. Derivation of the expression (3) of the main text

Combining the expressions (45) and (50) from the work of Henke et al.[1], one gets:

$$\mu_m = \frac{N_A}{M} 2r_e \lambda \sum_j N_j f_j'', \quad (1)$$

where μ_m is mass-absorption coefficient of the sample, N_A – Avogadro number, M – molar mass of the molecule constituting the sample, r_e – electron radius, λ – X-ray wavelength, N_j – number of j-type atoms in the molecule and f_j'' - imaginary part of their atomic scattering factor.

By definition, mass-absorption coefficient is related to the linear absorption coefficient by the following expression

$$\mu_m = \frac{\mu_L}{\rho}, \quad (2)$$

where ρ is the density of the sample. Total absorption is obtained from linear absorption coefficient by multiplying it by the length of beam path through the sample d:

$$\mu_T = \mu_L d \quad (3)$$

Combining the expressions (1-3) and substituting $M = \frac{m}{\nu}$, yields

$$\mu_T = \rho d \nu \frac{N_A}{m} 2 r_e \lambda \sum_j N_j f_j'', \tag{4}$$

where m is the mass of the sample exposed to the beam and ν is its amount of substance in moles.

Taking into account that $\rho = \frac{m}{V}$, where V is the volume of the sample exposed to the beam, one gets

$$\mu_T = \frac{d \nu N_A}{V} 2 r_e \lambda \sum_j N_j f_j'', \tag{5}$$

For a flat sample (such as pellet), oriented at an angle θ to the beam (Figure S1),

$$V = S d \sin\theta. \tag{6}$$

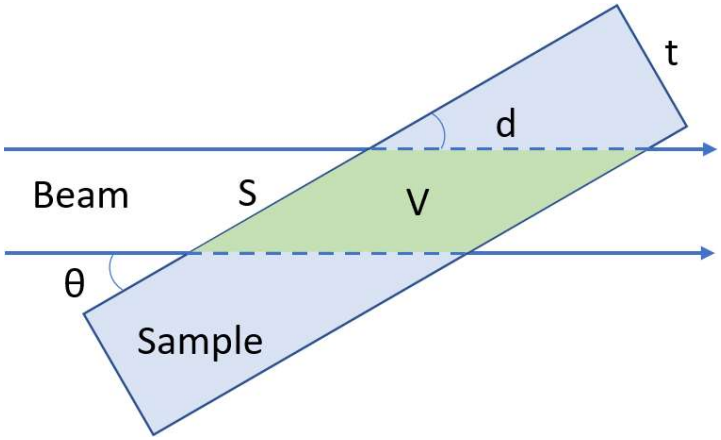

Figure S1 Cut of the sample interacting with the X-ray beam. S is the area of the sample surface interacting with the beam, V is the interaction volume, d is the path of the beam through the sample, t – sample thickness, θ – X-ray incidence angle.

Therefore, (5) becomes:

$$\mu_T = \frac{\nu N_A}{S \sin\theta} 2 r_e \lambda \sum_j N_j f_j'', \tag{7}$$

Provided that $\frac{\nu}{S} = \Theta$ is the molar surface density of the sample (surface being defined as the face of the sample exposed to the beam), one obtains the final expression:

$$\mu_T = \Theta \frac{2 r_e \lambda N_A}{\sin\theta} \sum_j N_j f_j''. \tag{8}$$

The change of the total absorption of the sample $\Delta\mu_{sam}$ upon adsorption/desorption of guest species is thus expressed by:

$$\Delta\mu_{sam} = \Theta_{ads}\frac{2r_e\lambda N_A}{\sin\theta}\sum_j N_j f_j'', \tag{9}$$

where Θ_{ads} is the molar surface density of adsorbed or desorbed species.

In most XAQ cases $\sin\theta = 1$, since for the XAS in transmission mode θ is usually equal to 90°. In such cases (9) becomes the expression (3) of the main text. The exception is the case when the XAS measurements are carried out in fluorescence mode, but the sample is transparent enough to allow recording the transmitted I_1 signal. In such cases XAQ is still possible (if the amount of adsorbates is sufficient to give a decent signal), but the orientation of the sample (usually $\theta = 45°$) has to be taken into account.

2. Accounting for absorption of the gas inside the experimental cell.

In order to get the formula for absorption of gas inside the cell, we start from the formula (5). Taking into account that

$$V = \frac{\nu RT}{P} = \frac{\nu N_A kT}{P}, \tag{10}$$

where R is a gas constant, k is Boltzmann constant, P is the gas pressure and T is the temperature of the gas, it transforms into

$$\mu_{gas} = \frac{2dr_e\lambda}{kT}P\sum_j N_j f_j'' \tag{11}$$

For gas mixture consisting of several components with non-negligible absorption at the energy of interest, a sum over all components has to be done:

$$\mu_{gas} = \frac{2dr_e\lambda}{kT}\sum_i P_i\sum_j N_{ij} f_{ij}'', \tag{12}$$

where P_i is a partial pressure of i-th component of the gas mixture.

The change of μ_{gas} due to the variation of temperature or partial pressure of gas components can be expressed thus by the final expression:

$$\Delta\mu_{gas} = \Delta\left(\frac{2dr_e\lambda}{kT}\sum_i P_i\sum_j N_{ij} f_{ij}''\right), \tag{13}$$

3. Quantification of adsorbates for the cases reported in Figures 1 and 2 of the main text.

For both samples, the pellets of 13 mm diameter were prepared, so the surface area of the samples was known. The mass of the pellets was optimized for the best signal-to-noise ratio in the XAS data, so it was known as well. Knowing the composition of the sample, the amount of Cu (for Cu-CHA) and Co (for Co_2Cl_4BTDD) in the pellets was calculated, and their molar surface density was obtained. Then the ratio between the molar surface density of adsorbates (calculated from XAQ) and metals was calculated, which yields the molar ratio between the adsorbates and metals, as reported in Figures 1 and 2 of the main text. The details of the calculations are presented below in the Table S1.

Table S1. Details of calculation of adsorbate/metal ratio reported in Figures 1 and 2 of the main text

Experiment	Pellet diameter, cm	Pellet surface area, cm^2	Pellet mass, mg	Metal content in the pellet, mmol	Metal molar surface density, $mmol/cm^2$	$\Delta\mu_{sam}$ from the XAQ signal	Adsorbate type	Adsorbate molar surface density, $mmol/cm^2$	Adsorbate per metal, mol/mol
Cu-CHA, desorption	1.3	1.33	126	0.0140	0.0105	-0.0735	H_2O	0.557	53
Co_2Cl_4BTDD, desorption	1.3	1.33	30	0.1145	0.086	-0.2606	Cl	0.061	0.71

References

1. B. L. Henke, E. M. Gullikson, J. C. Davis, X-ray interactions - photoabsorption, scattering, transmission, and reflection at E=50-30,000 eV, Z=1-92, *Atom. Data Nucl. Data Tables* **1993**, *54*, 181-342.