

Supplementary Information

Insight into the mechanisms controlling the chemical vapor generation of cadmium

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Experimental Design

The geometry of the central composite design, 3^2 factorial + 4 center points, for a total of 13 points, was the same to study both S/S_0 vs THB and HCl, and (Figure S1) and S/S_0 vs THB and NaOH (Figure S2).

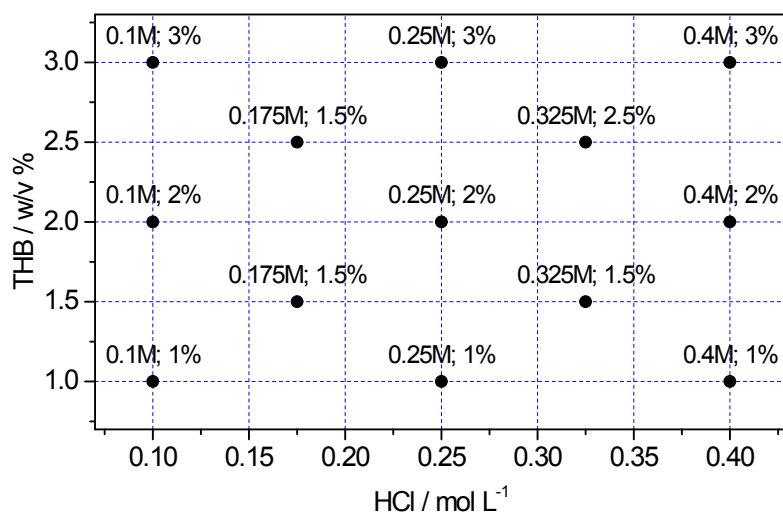


Figure S1- Experimental points selected for experimental design to study the effect of THB concentration (w/v %) in NaOH 0.1 mol L⁻¹ solution, and HCl sample acidity (mol L⁻¹).

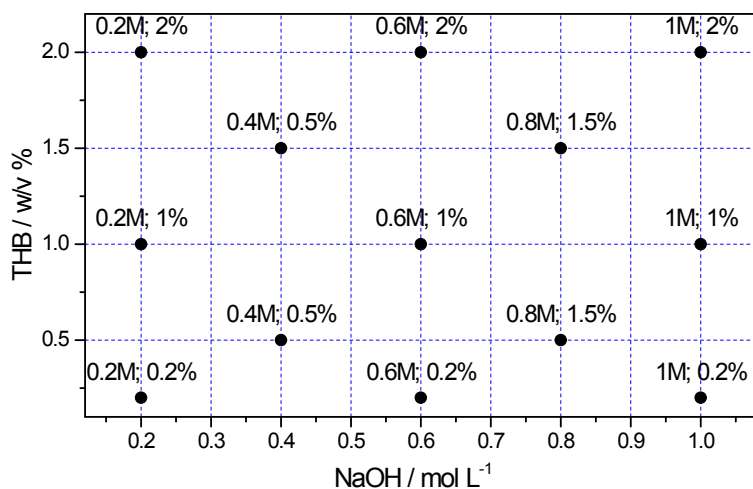


Figure S2 - Experimental points selected for experimental design to study the effect of THB concentration (w/v %) and NaOH concentration (mol L^{-1}) in THB solution.

Estimation of the fraction of THB hydrolyzed at different pH and reaction time

In the reaction coil BH_4^- starts to hydrolyze at a pH value that is reached after the neutralization reaction between the sample HCl and the NaOH of THB solution (reaction 6). At constant acidity the fraction of BH_4^- which is hydrolyzed at a given reaction time can be estimated by the pseudo-first order approximation of equation 8:

$$\alpha = 1 - \exp(-k_1 [H^+] t) \quad (\text{E1})$$

In this case, the pH increase during hydrolysis due to reaction of BH_4^- with H_3O^+ or H_2O and the first order approximation cannot be applied.

However, considering the limited reaction times involved in the continuous flow CVG system (< 0.5 s for a $50 \mu\text{L}$ loop) the use of equation E1 could be useful for the estimation of approximated α . This can be verified with the aid of Table S1, where the value of α (equation E1) are reported at different acidity. Assuming that the acidity reported in Table S1 are those achieved after pH equilibration, the acidity will decrease during hydrolysis due to reaction 7, slowing the rate of hydrolysis of BH_4^- , and the corresponding value of α reported in Table S1 will be overestimated. This allows, at least, to conclude that when the hydrolysis of BH_4^- starts at $\text{pH} > 7$, after the neutralization step, the fraction of hydrolyzed BH_4^- is negligible for the reaction times involved in a CVG apparatus.

Table S1- Fraction of BH_4^- hydrolyzed at different acidities and reaction times.

| Time/s | Hydrolyzed Fraction, α (%) ^a | | | | | | | |
|--------|--|------|------|------|-------|-------|-----------------------|----------------------|
| | pH=4 | pH=5 | pH=6 | pH=7 | pH=8 | pH=9 | pH=10 | pH=11 |
| 0.02 | 86 | 18 | 2.0 | 0.20 | 0.020 | 0.002 | 2.0×10^{-4} | 2.0×10^{-5} |
| 0.05 | 99 | 39 | 4.9 | 0.50 | 0.050 | 0.005 | 52.0×10^{-4} | 5.0×10^{-5} |
| 0.1 | 100 | 63 | 9.5 | 1.00 | 0.10 | 0.010 | 1.0×10^{-3} | 1.0×10^{-4} |
| 0.2 | 100 | 86 | 18 | 2.0 | 0.20 | 0.020 | 0.0020 | 2.0×10^{-4} |
| 0.5 | 100 | 99 | 39 | 4.9 | 0.50 | 0.050 | 0.0050 | 5.0×10^{-4} |

a-Calculated from equation E1, $k_1=10^{-6} \text{ L}^{-1} \text{ mol}^{-1} \text{ s}^{-1}$.

MDF atomizer: fitting of the linear portion of calibration graphs

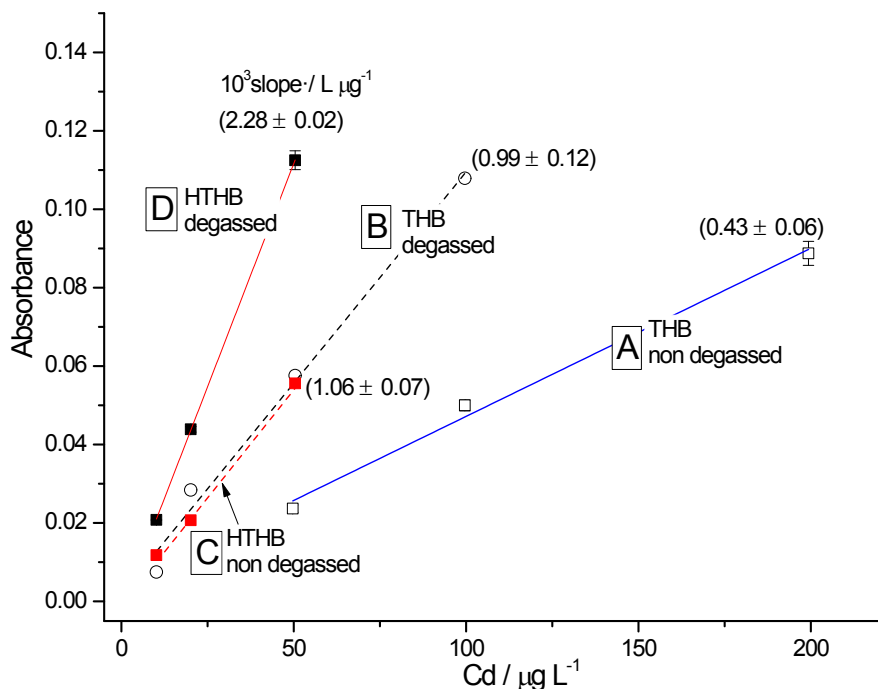


Figure S3 – Slope of the linear portions of calibration graphs reported in Figure 8a, obtained by CVG of cadmium using miniature diffusion flame atomizer and different reaction conditions.