Electronic supplementary material

Supporting information

**Sensitive method for determination of molybdenum in natural groundwater
at sub-ppb levels using DLLME coupled to ETAAS**

Florencia Tissot[1], Julia Torres[2], Moisés Knochen[1] (*)

Universidad de la República (UdelaR), Facultad de Química, Departamento Estrella Campos

*(1) Área de Química Analítica. (2) Área de Química Inorgánica*

Av. Gral. Flores 2124 – 11800 Montevideo, Uruguay

Species distribution diagram of molybdenum.

These diagrams were obtained by means of Hyperquad Simulation and Speciation software (HySS).

Figure S1a shows the species distribution diagram of Mo(VI) in the presence of medium concentrations of calcium and magnesium for groundwater scenarios. Results show that the most abundant alkaline earth metal ions exert a major influence on Mo(VI) speciation above pH 4. However, the acidity of the extraction solution precludes the interaction with these metal ions under the conditions of this study. As it is depicted in Figure S1b, at pH 2.5, molybdenum is present mostly as H_2MoO_4, with a low percentage of $HMoO_4^-$. Thus interaction, even with the most abundant cations is not possible under these conditions. On the other hand, the less abundant cations do not generally influence the formed species because they are present in much lower concentrations in the natural waters. Figure S1b shows the species distribution diagram of molybdenum in the presence of naturally occurring Cd concentrations. Again, for the pH value of the molybdenum determination, no association between the two metals is expected. Even though a high excess of Pb or Cd was used in this study, no detectable interference was observed.
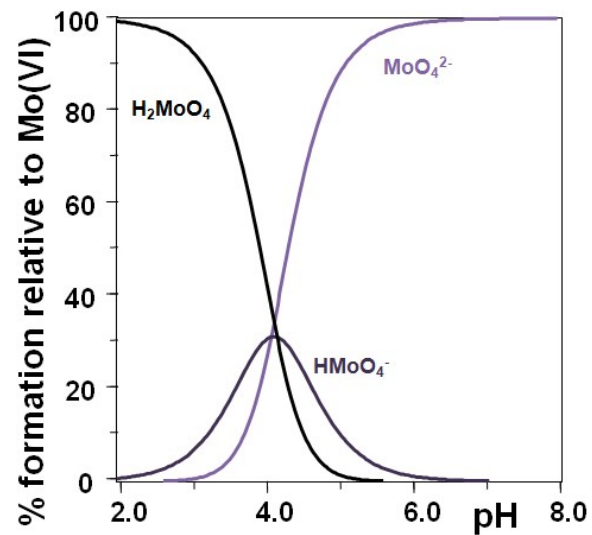
a)
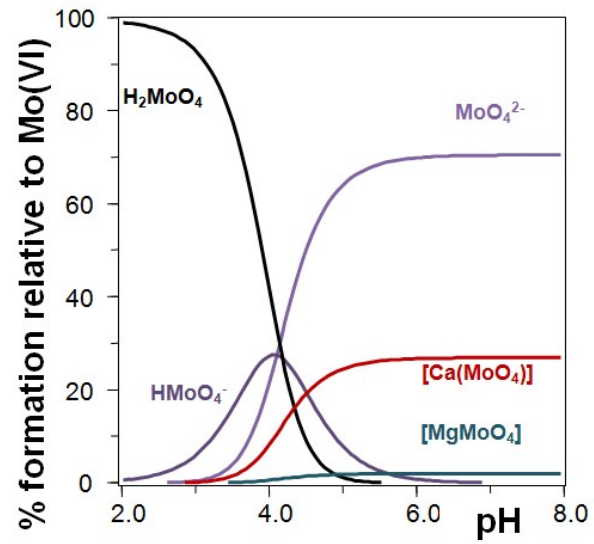
b)

Figure S1: Species distribution diagrams calculated from data in Torres et al.[9] Mo(VI) total concentration = 1 x 10^{-7} mol L^{-1}.

  a) Ca(II) total concentration = 13.6 mmol L^{-1}, Mg(II) total concentration = 0.092 mmol L^{-1}.
  b) Cd(II) total concentration = 9 x 10^{-7} mmol L^{-1}.

Hypothesis test of the joint confidence region for slope and intercept

This hypothesis test was applied to compare the results obtained by the reference method and the one developed in this work, according to   J. Mandel, F. J. Linnig, Study of Accuracy in Chemical Analysis Using Linear Calibration Curves, *Anal. Chem.*, 1957, 29, 743-749. If the results are equivalent the regression line should have slope (b) equal to 1 and intercept (a) equal to 0.

In general the experimental results will not fit exactly to a line of slope 1 and intercept 0. It is necessary to carry out tests of the significance of the estimated experimental values of a and b with respect to the "theoretical" values of 0 and 1 respectively. For this, we used the hypothesis test of the slope and the intercept for the regression line. They are evaluated together, involving a "region of joint trust", taking into account the interaction between these parameters.

The hypothesis H_0: a = 0; b = 1; H_A: not H_0, was tested, the statistic being:

$$F = \frac{n(a'-a)^2 + 2(a'-a)(b'-b)\sum x + (b'-b)^2 \sum x^2}{2\sigma^2}$$

(1)

where

$$\sigma^2 = \frac{1}{n-2}\left\{\left[\sum y^2 - \frac{(\sum y)^2}{n}\right] - \frac{(\sum xy - \frac{\sum x \sum y}{n})^2}{\sum x^2 - (\sum x)^2}\right\},$$

(2)

x and *y* are the respective concentrations found for the two methods and a' and b' are the estimated regression parameters.

H_0 can be accepted if the experimental value of the statistic, $F_{exp} \leq F_{(1-\alpha,2,n-2)}$ where n is the number of concentration samples.