TRACE METAL DETECTION IN NATURAL WATER

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Abstract. Fluorescencemeasurements of metal ions in drinking water employing complex forming organic agents result in signals depending linearly on the metal ion concentration in the low concentration range. In this paper we present and analyze measurements with and without additives with potential influence on the complexation. We found that sulfite addition to neocuproine does not sensitize the fluorescence. Moreover we found that neocuproine can be used as an efficient masking agent for spurious copper in the analysis of nickel with Newport Green®.

Key words: Fluorescence, Ni - Cu - detection, model comparison, odds-Ratio

Human drinking water supplies have to be checked routinely for possible contaminants. In particular heavy metal contaminants are of interest since they are health hazardous. Among the various analytical methods for detection of contaminants in water, laser induced fluorescencehas the best prospects for continuous real time analysis [1]. In this technique the metal ion is first bound to an organic molecule as complexing agent. The complexing agent is excited by e.g. nitrogen laser ultraviolet radiation. The excited state then decays by emission of visible radiation. Upon formation of the metal-ligand complex the intensity of the fluorescenceis changed. It may be either amplified as in the case of Newport Green® which is employed for nickel detection or the fluorescencemay be attenuated as in the case of neocuproine which is used for copper detection (see Fig. 1). Complex formation of a specific metal ion with the complexing agent is an equilibrium reaction. This means, that it depends on various parameters among which the oxidation state of the metal ion and concentrations of competing metal ions are of special importance in the context of this paper. Consider the influence of the oxidation

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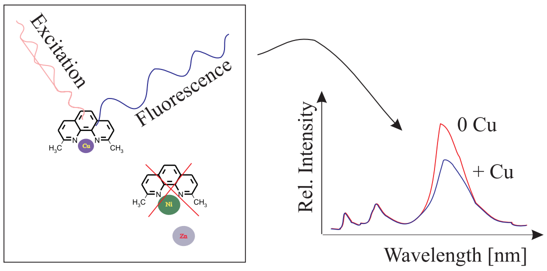

Figure 1. Schematic diagram of the reaction neocuproine + copper: Complexation of copper ions leads to a quenching of the neocproine-fluorescence. Nickel does not exhibit an effect on the neocuproine-fluorescence. In contrast thereto the Newport Green$^{\circledR}$fluorescenceis strongly enhanced by nickel complexation and copper ions interfere by quenching this fluorescence.

Figure 2. a) Influence of the copper concentration on the fluorescence intensity of neocuproine with (■) and without (▲) reducing SO_3^{2-} ions b) Distribution of the Ni^{2+}-Newport Green$^{\circledR}$fluorescenceintensity with varying Cu^{2+} concentration. (■) 5.6 μM Ni^{2+}, 3.5 μM Newport Green$^{\circledR}$, 9.35 μM neocproine. (△) 1 μM Ni^{2+}, 3.5 μM Newport Green$^{\circledR}$, 1.6 μM neocuproine. The dotted line indicates the range of 3% error.

state first. Literature results [2] suggest that the complex formation reaction constant for reactions of copper with neocuproine increases, when Cu^{2+} is reduced to Cu^{+}. This raises the question whether copper ion detection in water by complex formation with neocuproine can be sensitized upon addition of a reducing agent. Experimental results on the (inverse) attenuation I_0/I of the neocuproine fluorescenceas a function of copper concentration with and without addition of reducing SO_3^{2-} ions are shown in Fig. 2a. If the two measurements differ at all, then the difference is very small. This is not necessarily at variance with the observation that reduction of Cu^{2+} to Cu^{+} speeds up the metal organic compound formation. It may well be that the equilibrium of the reaction is strongly in favor of the metal organic compound, such that further increase of the reaction constant does not lead to a measurable modification of the equilibrium concentration of the product. However, let us return to the question whether the two measurements in Fig. 2a should be described by the same or by different linear relationships. This is a problem of Bayesian model comparison[3]. We denote by H_1 the hypothesis that a common model applies and by H_2 the complementary hypothesis that the distinction is justified. Our interest is then in the odds ratio [3].

$$O = \frac{p(H_1|\boldsymbol{d}_1, \boldsymbol{d}_2, \boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, I)}{p(H_2|\boldsymbol{d}_1, \boldsymbol{d}_2, \boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, I)} = \frac{p(H_1|I)}{p(H_2|I)} \frac{p(\boldsymbol{d}_1, \boldsymbol{d}_2|\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, H_1, I)}{p(\boldsymbol{d}_1, \boldsymbol{d}_2|\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, H_2, I)} . \tag{1}$$

$\boldsymbol{d}_1, \boldsymbol{d}_2$ denote the two sets of fluorescencesignals with known true errors $\boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2$ measured at copper ion concentrations $\boldsymbol{x}_1, \boldsymbol{x}_2$. Since we have no prior information which favors H_1 over H_2 we put the prior odds equal to one which leaves us with the calculation of the Bayes factor[3]. The two measurements are of course uncorrelated. The total likelihood function $p(\boldsymbol{d}_1, \boldsymbol{d}_2|\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, b_1, b_2, s_1, s_2, I)$ factors therefore into $p(\boldsymbol{d}_1|\boldsymbol{x}_1, \boldsymbol{\sigma}_1, b_1, s_1, I) \times p(\boldsymbol{d}_2|\boldsymbol{x}_2, \boldsymbol{\sigma}_2, b_2, s_2, I)$ where b_i and s_i are intercept and slope of the linear model function.

$$p(\boldsymbol{d}|\boldsymbol{x}, \boldsymbol{\sigma}, b, s, I) = Z_L^{-1} \exp\{-\frac{1}{2} \sum_i (d_i - b - s x_i)^2 / \sigma_i^2\} . \tag{2}$$

We introduce the definitions $\omega^{-2} = \sum_i \sigma_i^{-2}$, $\overline{y} = \omega^2 \sum_i \sigma_i^{-2} y_i$ and marginalize over b assuming a flat prior to obtain

$$p(\boldsymbol{d}|\boldsymbol{x}, \boldsymbol{\sigma}, s, I) = Z_L^{-1} \omega \sqrt{2\pi} \exp\{-\frac{1}{2\omega^2} \left[\overline{\Delta x^2}(s - s^*)^2 + \overline{\Delta d^2} - s^{*2}\overline{\Delta x^2}\right]\} \tag{3}$$

where $s^* = \overline{\Delta d \Delta x}/\overline{\Delta x^2}$ is the maximum likelihoodvalue of the slopes. (3) may now be used to calculate the marginal likelihoods entering the Bayes factor. The numerator of (1) is then simply the product of two factors obtained by marginalizing (3) over s with a suitable prior. The denominator on the other hand is the marginal over a common s of two factors of the form (3) for datasets 1 and 2, respectively. Unlike the previous marginalization over b, where an improper prior was used without complication since it entered twice in the numerator and the denominator of the Bayes factorand therefore a proper limit existed, marginalization over s has to employ a proper prior since it enters twice in the numerator but only once in the denominator. If we assume a flat prior distribution of angles between the linear function and the x-axis, this transforms into

$$p(s|I) = (\pi(1 + s^2))^{-1} . \tag{4}$$

The integrations over s in either case (H_1, H_2) are not possible analytically. We employ the peak approximation, that is we assume that the curvature of the prior in the region where the likelihood differs appreciably from zero can be neglected. The prior can then be taken out of the integral with s replaced by s^*, the maximum of the likelihood function. This procedure yields for the odds ratio O

$$O = \sqrt{\frac{2}{\pi}} \sqrt{\frac{\mu_1 \mu_2}{\mu_1 + \mu_2}} \frac{1}{1 + s^{*2}} \exp\{\frac{\mu_1 \mu_2}{2(\mu_1 + \mu_2)} (s_1^* - s_2^*)^2\} , \tag{5}$$

with $\mu_\alpha = \overline{\Delta x_\alpha^2}/\omega_\alpha^2$ and the additional assumption $s_1^* \approx s_2^* \approx s^*$ which is mild because otherwise the data would already present clear evidence for H_2. For the data displayed in Fig. 2a we obtain an odds ratio $O \approx 19$ which clearly favors a description of all data by a common linear relationship. Sulfite addition to neocuproine does not sensitize the fluorescence. The second experiment which we want to present and interpret here is concerned with the competition of metal ions in the reaction with a complexing agent. We consider fluorescencedetection of nickel reacted with Newport Green®(see Fig. 1). This fluorescenceis normally quenched in the presence of copper ions. Copper on the other hand is quite selectively bound by neocuproine which in turn raises the question whether the Ni^{2+}-Newport Green®fluorescencecan be made independent of competing copper traces when neocuproine is added to the solution as a masking agent. Data relating to two different Ni ion concentrations (5.6 μM Ni^{2+} + 9.35 μM Neocuproine and 1 μM Ni^{2+} + 1.5 μM Neocuproine) but with the same ratio Ni^{2+}/Neocuproine are shown in Fig. 2 b. Since it is not immediately obvious whether Cu^{2+} can be masked completely, we employ Bayesian model comparison to decide whether the Ni^{2+}-Newport Green®fluorescencechanges linearly with or is independent of the copper concentration. The likelihood function for the constant model (H_1) is simply

$$p(\boldsymbol{d}|\boldsymbol{x}, \boldsymbol{\sigma}, b, I) = Z_L^{-1} \exp\{-\frac{1}{2}\sum_i (d_i - b)^2 / \sigma_i^2\} \tag{6}$$

and the likelihood function for the linear model (H_2) is the same as in (2). Proceeding with the marginalizations as before we obtain the odds ratio for H_1

$$O = \sqrt{\pi\overline{\Delta x^2}/(2\omega^2)}\,\left(1 + c^2\overline{\Delta d^2}/\overline{\Delta x^2}\right)\exp\left\{-c^2\overline{\Delta d^2}/(2\omega^2)\right\} \tag{7}$$

where we introduced the correlation coefficient$c = \overline{\Delta x \Delta d}/(\overline{\Delta x^2}\,\overline{\Delta d^2})^{\frac{1}{2}}$. For the optimal case for the constant model, i.e. zero correlation, we obtain an odds ratio of $\sqrt{\pi\overline{\Delta x^2}/(2\omega^2)}$ in favor of the constant model. For increasing c the increase in the prior factor is overcompensated by the decreasing exponential and the odds ratio decreases monotonically with c. For approximately constant errors $\sigma_i = \sigma$ we have $\omega^2 = \sigma^2/N$ and see the strong dependence of the odds ratio on the number of measurements given the signal to noise ratio $(\overline{\Delta d^2}/\sigma^2)^{\frac{1}{2}}$. For the data in Fig. 2b we obtain $O = 143$. The analysis therefore clearly favors constant nickel-Newport Green®fluorescenceand we conclude that neocuproine is a perfect masking agent for the fluorimetric detection of nickel by complexation with Newport Green®.

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