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ProMCC: An all-in-one tool for trace metal complexation studies

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ABSTRACT

A new windows-based, user friendly program (ProMCC) for (i) the determination of metal complexation parameters (ligand concentration (L) and conditional stability constants (K')) and for (ii) theoretical simulation of metal complexometric titration, assuming discrete ligand model, is developed. Although primarily intended for treatment of experimental data obtained either by anodic stripping voltammetry (ASV) or competitive ligand exchange adsorptive cathodic stripping voltammetry (CLE-AdCSV), it could manage titration-type data of other techniques (e.g. ISE, sorption isotherm). Currently, the program is capable to process (fit and/or simulate) titration data up to three discrete ligand classes. Procedure for adjustment of "true" analytical sensitivity incorporated in ProMCC was found to provide reasonably good estimates of sensitivity either for one-ligand or two-ligand system. The particular feature of ProMCC is that it incorporates two complementary fitting methodologies: (1) a non-linear fitting of conventional linearized transformations (e.g. Ružić/Van Den Berg, Langmuir/Gerringa) and (2) a "complete complexation model" — a matrix based optimization of mass balance equations. Comparison test of different non-linear fitting modes and titration types revealed that a slight underestimation of ligand concentration and overestimation of conditional stability constant may occur if titration is performed in logarithmic mode, mainly due to unfavorable noise distribution. An advantage of implemented "complete complexation model" fitting mode is that it allows simultaneous analysis of titrations obtained at multiple detection windows as unified dataset (multi-detection window approach), providing complexation parameters for up to three ligand classes. A new alternative "RAL-approach" in analyzing complexometric titrations obtained at multiple detection windows for copper–salicylaldoxime (Cu–SA) system is suggested. It assumes that the analytical sensitivity is changing along the titration curve respecting the true speciation of Cu–SA in sample. An adapted empirical equation for calculation of relative intensity (RAL) is proposed. Flexibility in adjusting parameters, immediate graphical feedback and visualizations make ProMCC handy for treatment of large set of experimental data, and a tool for research in refinement of the methods of metal complexing capacity determination which is continuously improving.

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1. Introduction

It is well recognized that the speciation of trace elements in natural waters is a key factor in understanding their reactivity, transport, bioavailability and/or toxicity for micro-organisms (Bruland et al., 1991; Gledhill and Buck, 2012; Hirose, 2007). In oceanographic community, a research focus is directed toward elements (mainly metals) having known biological function (e.g. Fe, Cu, Zn, Co) (Baars and Croot, 2011; Bruland et al., 2000; Buck et al., 2012; Ellwood and Van Den Berg, 2001; Gledhill and Buck, 2012; Ibisanmi et al., 2011; Thuroczy et al., 2010; Town and Filella, 2000; Van Den Berg and Dharmvanij, 1984). While the inorganic speciation of elements is known and predictable, still the challenging task is understanding of metal vs. natural organic matter (NOM) interactions (either of mainly terrestrial origin (coastal regions) or autochthon one produced in water column). The great efforts are particularly directed toward understanding of Fe speciation, due to its role in primary production in oceans (Gledhill and Buck, 2012). In spite of low solubility in marine waters (~0.01 nM) (Liu and Millero, 2002), dissolved Fe concentration could exceed this limit mainly because of Fe complexation with organic ligands, producing complexes with high stability constants (Boyd and Ellwood, 2010; Boye et al., 2010; Cullen et al., 2006; Hunter and Boyd, 2007). While in open ocean conditions, biologically derived ligands (e.g. siderophores, exopolysaccharides) are found to largely control Fe speciation (Barbeau et al., 2003; Hassler et al., 2011; Hirose, 2007; Hunter and Boyd, 2007; Velasquez et al., 2011), complexation with humic material may dominate in coastal regions (Batchelli et al., 2010; Laglera et al., 2007; Laglera and Van Den Berg, 2009). From the other side, Cu is a micronutrient at its low concentration levels, while it can be toxic for some micro-organisms at higher concentrations (Duran and Beiras, 2013; Sunda et al., 1987). The range of the "optimal" Cu concentrations is relatively narrow. For both elements (Fe, Cu) it is reported that in oceans they exist predominantly in a form of strong organic complexes

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(>99%) (Gledhill and Van Den Berg, 1994; Rue and Bruland, 1995). Understanding the speciation of trace elements at their ambient concentration in the ocean and predicting their speciation in relation to increased concentrations (e.g. due to anthropogenic pollution) or change of physico-chemical conditions (e.g. ocean acidification/climate change) are the main interests of complexation studies (Hirose, 2006; Millero et al., 2009). The main purpose of metal speciation analysis, i.e. the determination of complexation parameters, is to estimate (I) the metal speciation at actual concentration of the natural sample and (II) the ability of the "sample" to complex metals at their increased concentration (to predict the metal speciation).

Although different methods and protocols of direct characterization of metal–organic complex are reported in literature (Wiramanaden et al., 2008), due to very low concentration of metals in seawater and experimental limitations of separation, extraction and measurement of different metal complexes, an alternate indirect approach in characterization of metal–organic ligand interactions is usually practiced by marine chemists (Bruland et al., 2000; Buck et al., 2012; Campos and Van Den Berg, 1994; Capodaglio et al., 1995; Gerringa et al., 1995; Louis et al., 2009a; Monticelli et al., 2010; Omanović et al., 1996; Plavšić et al., 2009; Ružić, 1982; Van Den Berg, 1982). It is based on the titration of the sample by the target metal at natural pH. Upon addition, metal is redistributed between different species, among them one (or group) of them is used as an "active" component for measurement, whereas the rest is considered to represent undetectable organic complexes. The most utilized technique for quantification of "active" components is electrochemical techniques due to their good sensitivity and selectivity. Basically two methods/protocols exist: anodic stripping voltammetry (ASV) and competitive ligand exchange adsorptive cathodic stripping voltammetry (CLE-AdCSV).

There are two distinct concepts in ASV methodology. The first assumes that after the addition, metal is redistributed between the strong inert organic complexes (which will not be reduced at selected accumulation potential) and other labile electroactive species having comparable diffusion coefficients (inorganic and some weak organic complexes) (Bruland et al., 2000; Croot et al., 1999; Garnier et al., 2004b; Lorenzo et al., 2007; Plavšić et al., 2009). The second concept assumes that all chemical species are electroactive at selected accumulation potential, but having different diffusion coefficients and that the curvature shape of titration curve is a product of average diffusion coefficients which is changing along the titration curve (Chakraborty et al., 2007; Town and Filella, 2000). The first approach is widely accepted, however it is certain that neither of the models by itself is "correct", and an effort should be made in order to resolve how the mutual behavior is translated to the titration curve and calculation of complexation parameters. A crucial step for both concepts is selection of adequate deposition accumulation/redox potential. A pseudopolarograhic (PP) "fingerprint" of the sample, displaying one or more distinct PP waves, provides not only the basis for selection of adequate accumulation potential, but additional quantitative and qualitative information of the metal complexation (Croot et al., 1999; Cullen et al., 2006; Gibbon-Walsh et al., 2012; Louis et al., 2008, 2009a; Omanovic and Branica, 2003, 2004; Omanović et al., 1996; Town and Filella, 2000; Town and van Leeuwen, 2006). The potential 100–200 mV more negative than the redox potential of labile (inorganic) metal is usually sufficient. As an alternative to ASV, a potentiometric stripping analysis (PSA) (known also as stripping chronopotentiometry, SCP) could be applied (Waeles et al., 2008).

In CLE-AdCSV method a known concentration of competing ligand (CL), forming metal complex(es) with known stability constants, is added to titrated sample (Campos and Van Den Berg, 1994; Donat and Van Den Berg, 1992; Ellwood and Van Den Berg, 2001; Laglera et al., 2007; Monticelli et al., 2010; Rue and Bruland, 1995; Van Den Berg and Huang, 1984). An equilibrium redistribution between added ligand (AL) and the natural ligand (L) is established at each titration point of added metal. The extent of formed metal complex(es) with AL is measured by their reduction. The high sensitivity of AdCSV method is based on the ability of the formed metal–AL complex to adsorb and accumulate on the surface of electrochemical sensor (usually mercury drop). In most cases, an accumulation potential more positive than the reduction of metal–AL complexes is selected. However to increase the sensitivity, a potential more negative than the reduction of metal–AL complexes is used as well (Campos and Van Den Berg, 1994). The concentrations of added competing ligand determine the so-called "detection window" (DW) of the CLE-AdCSV method (Bruland et al., 2000; Donat and Van Den Berg, 1992; Gledhill and Buck, 2012; Hirose, 2006; Sander et al., 2011; Van Den Berg and Huang, 1984). Although the shape of the titration curve depends on the chosen DW, calculated complexation parameters should not depend on it. However, due to experimental uncertainties no consistent data could be obtained for the same sample (Campos and Van Den Berg, 1994; Hudson et al., 2003; Sander et al., 2011). To overcome problems associated with the single DW and to provide more reliable complexation parameters, titrations at multiple DW or multiple analytical window (MAW) (Bundy et al., 2014; Hudson et al., 2003; Sander et al., 2011; Wells et al., 2013) were suggested.

Although the range of metal binding sites of different strength exists (heterogeneity of NOM) (Dzombak et al., 1986), a discrete model, representing sites of "similar characteristics", is usually exploited in complexation studies in seawater. In practice one, two or even three ligand classes, forming 1:1 metal–ligand complexes, are considered to reliably represent the titration curve, i.e. to describe the scenario of the metal complexation with organic ligands. With increasing metal additions, a free organic ligand is progressively saturated, producing linear range at the high-end of titration curve, representing non-complexing behavior. Although in theory the "linear range" is only asymptotically approaching a non-complexing relationship, it is often used to represent the sensitivity of the method (called "internal calibration"), and it is used to transform signal intensities to measured concentrations (needed for further calculations). The problem of "internal calibration" approach comes to the fore when an additional (e.g. third) weak organic ligand is present in solution and is progressively saturated in the linear range of the titration curve (Hudson et al., 2003; Kogut and Voelker, 2001; Laglera et al., 2013; Turoczy and Sherwood, 1997; Voelker and Kogut, 2001; Wu and Jin, 2009).

Once the titration curve is acquired, the next step is calculation of complexation parameters (total ligand concentrations and conditional stability constants) by fitting experimental data on appropriate model/relationship. Either direct fitting of titration curve or fitting of Langmuir/Gerringa (Gerringa et al., 1995), linearized Ružić/Van Den Berg (Ružić, 1982; Van Den Berg, 1982) or Scatchard (Scatchard, 1949) transformations is performed. In case of one ligand model (1L-model), Ružić/Van Den Berg and Scatchard transformations linearize the data and fitting is easily performed. However, for direct fitting of "1L" titration curve or fitting of "1L" Langmuir/Gerringa transformation, as well as for two (or more) ligand models (2L, 3L) a non-linear fitting is favored. Calculation of complexation parameters in such cases is performed by fitting data on chosen "analytical solution" and/or by numerical "complete complexation model" fitting (Duran and Nieto, 2011; Garnier et al., 2004c; Gerringa et al., 1995; Hudson et al., 2003; Laglera et al., 2013; Lorenzo et al., 2007; Sander et al., 2011; Wells et al., 2013). The satisfactory accuracy and precision of measured data are essential in obtaining reliable final parameters. Deviations from the predicted fitting model may lead to non-convergent or unreliable results.

Apart from using equilibrium principles in estimation of the complexation parameters by above described approaches, an alternative kinetic approach has been shown to provide comparable results, which also provide results of association/dissociation kinetics of the studies chemical system (Louis et al., 2009a). An additional point which could be raised in the overall protocol, which is largely overlooked in the literature, is the treatment of the primary voltammetric curves, i.e. determination of peak heights (Cobelo-Garcia et al., 2014; Pižeta et al., 1999). It

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