Advanced Workshop on

# Solution Chemistry of TCEs

Białystok / 22-23 January 2019

# Book of Abstracts

## COST Action TD1407

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EUROPEAN COOPERATION
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# Preface

Thermodynamic parameters describing chemical equilibria are needed in many fields to predict the behaviour of chemical elements in environmental, biological or industrial systems. However, serious discrepancies between published thermodynamic parameters exist and the field is often considered as 'old-fashioned' and receives scarce funding. How to tackle some of the uncertainties that currently restrict the chemical modelling of aqueous, multicomponent mixtures was discussed in the Advanced Workshop on Solution Chemistry of TCEs that took place in Białystok, Poland on 22-23 January 2019.

Forty-three participants from 13 countries (Australia, France, Germany, Israel, Hungary, Italy, Macedonia, the Netherlands, Poland, Spain, Sweden, Switzerland, United Kingdom) attended the workshop. It followed a mixed model with Master Classes in the morning followed by oral communications the rest of the day. Two different aspects were discussed. Aspects concerning equilibria of TCEs with low molecular mass ligands were discussed the first day while issues involved in the election of the parameters needed to describe trace element binding by natural organic matter, a key factor when evaluating element behaviour and ecotoxicity in environmental systems, was the object of the second half of the workshop.

Montserrat Filella & Beata Godlewska-Żyłkiewiczx

Białystok, January 2019

# COST Action TD1407

There are a number of trace elements that were considered just as laboratory curiosities but now are key components for the development of new technologies. For most of these elements, the present understanding of their concentrations, transformation and transport in the different environmental compartments is scarce and/or contradictory. These elements, here defined as technology-critical elements (TCEs) include Ga, Ge, In, Nb, Ta, Te, Tl, the platinum group elements (Ir, Os, Pd, Pt, Rh and Ru), and most of the rare earth elements (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Y, Yb). They are undergoing a significant change in their cycle at the Earth's surface due to their increase use in a variety of technological applications. Their impact on their biogeochemical cycles and potential biological and human health threats needs to be further explored.

The aim of COST Action 1407 (*Network on Technology-Critical Elements: From Environmental Processes to Human Health Threats*) is to create a network of scientists working and interested on TCEs with the objective of defining the current state of knowledge and gaps, proposing priority research lines/activities and acting as a platform for new collaborations and joint research projects.

COST Action TD1407 covers:

- Analytical challenges for quantitative and screening purposes.
- Environmental processes including biogeochemical cycles of the TCEs.
- Exposure of humans to these elements and their compounds through air, water, and food, and potential ecological and human health threats (eco-toxicology).

# Funders





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# Sponsors

# Organisers

Montserrat Filella

Beata Godlewska-Żyłkiewicz

University of Geneva, Switzerland

University of Białystok, Poland

# Participants

| | | | |
|---|---|---|---|
| Maciel Baradyn | University of Białystok | Poland | m.baradyn@uwb.edu.pl; |
| Silvia Berto | University of Torino | Italy | silvia.berto@unito.it |
| Rosita Cappai | University of Cagliari | Italy | cappai@unica.it |
| Charlotte Catrouillet | University of Lausanne | Switzerland | charlotte.catrouillet@unil.ch |
| Antonio Cobelo-García | IIM-CSIC | Spain | acobelo@iim.csic.es |
| Krzysztof Drwal | University of Białystok | Poland | kdrwal@chem.uw.edu.pl; |
| Montserrat Filella | University of Geneva | Switzerland | montserrat.filella@unige.ch |
| Mauro Formica | University of Urbino | Italy | mauro.formica@uniurb.it |
| Sofia Gama | University of Jena | Germany | sofia.gama@uni-jena.de |
| Teba Gil-Díaz | University of Bordeaux | France | tebagil90@gmail.com |
| Beata Godlewska-Żyłkiewicz | University of Białystok | Poland | bgodlew@uwb.edu.pl |
| Jan Groenenberg | University of Wageningen | Netherlands | bertjan.groenenberg@wur.nl |
| Jakub Gruszka | University of Białystok | Poland | jakubgruszka@onet.pl; |
| Wolfgang Hummel | Paul Scherrer Institut | Switzerland | wolfgang.hummel@psi.ch |
| Guillaume Jiranek | University of Geneva | Switzerland | guillaume.jiranek@etu.unige.ch |
| Katarzyna Kinska | University of Warsaw | Poland | kkinska@chem.uw.edu.pl |
| Anatol Kojło | University of Białystok | Poland | kojlo@uwb.edu.pl |
| Yasmine Kouhail | Weizmann Institute of Science | Israel | yasmine.kouhail@weizmann.ac.il |
| Zofia Kowalewska | Warsaw University of Technology | Poland | zofia.kowalewska@pw.edu.pl |
| Nicholas Lachaux | University of Lorraine | France | nicolas.lachaux@univ-lorraine.fr |
| Barbara Leśniewska | University of Białystok | Poland | blesniew@uwb.edu.pl |
| Johannes Lutzenkirchen | Karlsruhe Institute of Technology | Germany | johannes.luetzenkirchen@kit.edu |
| Julita Malekko | University of Białystok | Poland | j.malejko@uwb.edu.pl |
| Michel Meyer | University of Bourgogne | France | michel.meyer@u-bourgogne.fr |
| Demetrio Milea | University of Messina | Italy | dmilea@unime.it |
| Edyta Nalewajko-Sieliwoniuk | University of Białystok | Poland | nedyta@uwb.edu.pl |
| Ewa Oleńska | University of Białystok | Poland | chwelat@uwb.edu.pl |
| Alba Otero-Fariña | University of Lorraine | France | alba.otero-farina@univ-lorraine.fr |
| Ewelina Palak | University of Białystok | Poland | ewelinapalak92@gmail.com |

| Zoran Pandilov | Ss.Cyril and Methodius University | Republic of Macedonia | zoran.pandilov@mf.edu.mk |
| Anna Potysz | University of Wroclaw | Poland | anna.potysz@uwr.edu.pl |
| Ana Romero | IIM-CSIC | Spain | anaromero@iim.csic.es |
| Darren Rowland | University of Western Australia | Australia | darren.rowland@uwa.edu.au |
| Monika Sadowska | University of Warsaw | Poland | msadowska@chem.uw.edu.pl |
| Matteo Savastano | University of Florence | Italy | matteo.savastano@unifi.it |
| Vladimir Sladkov | Institute of Nuclear Physics | France | sladkov@ipno.in2p3.fr |
| Ed Tipping | Centre of Ecology and Hydrology | UK | et@ceh.ac.uk |
| David Turner | University of Gothenburg | Sweden | david.turner@marine.gu.se |
| Katalyn Varnagy | University of Debrecen | Hungary | varnagy.katalin@science.unideb.hu |
| Izabela Wigda | University of Białystok | Poland | izaw@wp.pl |
| Elżbieta Wołyniec | University of Białystok | Poland | elaw@uwb.edu.pl |
| Irena Wysocka | Polish Geological Institute | Poland | iwys@pgi.gov.pl |
| Elżbieta Zambrzycka | University of Białystok | Poland | elazamb@uwb.edu.pl |

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# Oral communications

# Master class

## The choice of equilibrium constants

Darren Rowland[1,2] and Peter May[2]

[1] Fluid Science & Resources Division, University of Western Australia, Crawley, WA 6009
[2] Chemistry, Murdoch University, Murdoch, WA 6150

e-mail: darren.rowland@uwa.edu.au

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Our ability to design processes for extracting, purifying, recycling and/or disposing of critical elements depends heavily on our understanding of their interactions in aqueous media. In order to obtain reliable estimates of species distributions, predominance or solubility from speciation models, large numbers of accurate equilibrium constants are required.

This talk will discuss some of the major obstacles that currently hinder chemical speciation modelling and its application. Topics include the persistence of differences in model results even when the same equilibrium constants are used, the size of realistic measurement uncertainty and its relation to reported uncertainties, the continuing loss of expertise in the solution chemistry community, and decline in financial and other support from authoritative organisations that jeopardise the necessary works of critical assessment and persistent data storage.

The sensitivity of stability constants and speciation calculations to uncertainty in quantities such as activity coefficients, enthalpy, heat capacity are also discussed. Issues surrounding achieving and preserving thermodynamic consistency are discussed in relation to recent work on the Joint Expert Speciation System (JESS) developed at Murdoch University (http://jess.murdoch.edu.au).

# OC 1

## Mission impossible: Building the all-purpose chemical thermodynamic database

Wolfgang Hummel

Laboratory for Waste Management, Paul Scherrer Institut, 5232 Villigen, Switzerland

e-mail: wolfgang.hummel@psi.ch

All major existing thermodynamic databases have been built with some applications in mind. If we use these databases outside their original focus we may calculate slightly, sometimes grossly wrong results, depending on how strongly we "misuse" them. However, merging all these databases to "the all-purpose thermodynamic database" will not work either.

The basic problem behind this "mission impossible" is that we do not have a proper fundamental theory of aqueous electrolyte solutions. Thermodynamic parameters have to be derived from experimental data by model assumptions (simplifications) about ionic interactions.

For modelling surface and subsurface aqueous systems (rivers and freshwater lakes, groundwater, sea water, brines and salt lakes) different model approaches have been used, i.e. variants of the extended Debye-Hückel equation, the specific ion interaction theory (SIT), and the Pitzer formalism. These different model approaches lead to different thermodynamic databases which cannot be merged to a single consistent database without re-fitting the basic experimental data.

The simplest approach in the realm of hydrothermal systems (high temperatures and pressures, i.e. T > 300 °C and P > 500 bar) assumed solid phase equilibria with $H_2O$ and $CO_2$ as the only components in the fluid phase. A more elaborate approach (SUPCRT) considered ionic species in the fluid phase with salt effects restricted to NaCl solutions.

In the first group of databases, developed for modelling surface and subsurface aqueous systems, temperature and pressure effects are either ignored, or limited to T < 150 °C and saturated vapour pressure. By contrast, in databases developed for modelling hydrothermal systems temperature and pressure effects are the main focus, and 25 °C and 1 bar are mere "reference conditions" far outside their field of application. Attempts to merge databases from these "two worlds" lead to impressive looking data collections which revealed their deficiencies and needed additional data evaluation work whenever they were used in whatever field of application.

# OC 2

## The thermodynamics of speciation in natural waters: uncertainties, modelling, and software development

David R. Turner[1], Simon Clegg[2], Sylvia Sander[3]

[1]Department of Marine Sciences, University of Gothenburg, Sweden
[2]School of Environmental Sciences, University of East Anglia, United Kingdom
[3]IAEA Environment Laboratories, Principality of Monaco

e-mail: david.turner@marine.gu.se

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A major international project, building on a SCOR working group and focusing on seawater and related natural waters, is developing chemical speciation modelling software that will be freely available. Our guiding best practice principles are thermodynamics and uncertainty assessment. While thermodynamics underlies all speciation modelling, we mean here the use of activities of all components in calculating the equilibrium state. All interactions are described by thermodynamic equilibrium constants, and Pitzer equations are used to calculate the activity coefficients of all species present. The lack of uncertainties in current speciation models can lead to over-interpretation of results, and thus risk incorrect conclusions. Both equilibrium constants and Pitzer coefficients are derived from laboratory measurements: we are developing methods to assess the resulting uncertainties in individual parameters and in the speciation calculations. While our ambition is to cover all components present in seawater, the first phase of the project focuses on the seawater electrolyte and pH. Here our work is linked to an international effort to define a seawater pH scale that is traceable to the SI base units. We expect to release the first version of the calculation program by the end of the year 2020.

# OC 3

## Solution equilibrium studies of lanthanides and actinides with hydroxamic siderophores

Michel Meyer[1], Stéphane Brandes[1], Tamas Fodor[1], Alejandra Sornosa-Ten[1], Christine Stern[1], Shanthilal Amarasinghe[1], Pawel Jewula[1], Jean-Claude Chambron[2], Vladimir Sladkov[3], Frédéric Coppin[4], Lauréline Fevrier[4]

[1]Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), UMR 6302 CNRS, Université de Bourgogne–Franche-Comté, 9 avenue A. Savary, 21078 Dijon, France
[2]Institut de Chimie de Strasbourg (ICS), UMR 7177 CNRS, Université de Strasbourg, 1 rue B. Pascal, 67008 Strasbourg, France
[3]Institut de Physique Nucléaire d'Orsay (IPNO), UMR 8608 CNRS, Université Paris Sud, 15 rue G. Clemenceau, 91406 Orsay, France
[4]Institut de Radioprotection et de Sûreté Nucléaire (IRSN/PRP-ENV/SERIS/L2BT), Centre d'Etudes de Cadarache, 13115 St Paul lez Durance, France

email: michel.meyer@u-bourgogne.fr

Siderophores are ubiquitous microbial high-affinity iron(III) chelators excreted under iron-stress conditions. Their primary biological role is to supply microorganisms with iron, an essential nutrient and growth factor, according to an energy-driven mechanism involving specific outer-membrane receptors. Hydroxamates are common bidentate chelating groups found in many siderophores, such as the emblematic desferrioxamine B.
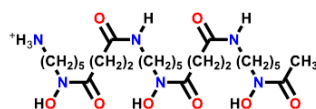


Desferrioxamine B

As their concentration in soils is typically in the □g/kg range, these compounds might significantly increase the solubility, migration rate, and bioavailability of highly toxic metals in case of environmental contamination. In relation to the management and remediation of contaminated fields or the disposal of nuclear wastes in geological repositories, it is of outmost importance to gain a deeper understanding of the coordination chemistry of lanthanides and actinides by siderophores. The speciation of desferrioxamine B and model compounds with 4f and 5f elements will be discussed on light of potentiometric, capillary zone electrophoretic, and spectroscopic data (UV-vis, luminescence, IR, Raman, X-ray absorption, mass, $^{17}O$ NMR).

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## Acknowledgements

# OC 4

# Physicochemical parameters affecting the equilibrium between Tl(I) and Tl(III) in water solutions

Monika Sadowska, Ewa Biaduń, Krzysztof Drwal, Beata Krasnodębska-Ostręga

Faculty of Chemistry, University of Warsaw, Poland

e-mail: msadowska@chem.uw.edu.pl, bekras@chem.uw.edu.pl

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Thallium has two stable oxidation states. Tl(I) is thermodynamically stable, while Tl(III) is more reactive and hydrolyzes in alkaline and neutral solutions. Hydroxyl species of Tl(III) are formed even at low pH (~2), similar to iron hydroxyl species. In contrast to Tl(III), hydrolysis is rather insignificant for Tl(I). Also its complexes with such ligands as carbonates, sulphates and phosphates, are relatively weak (log K = 1.0-3.4). The reduction potential of Tl(III) to Tl(I) is +1.26 V. The reduction rate is affected by pH and the presence of complexing agents. Chlorides lower the reduction potential (+0.77 V), because of forming a complex of $TlCl_4^-$ (log K = 18), also the presence of oxalate ions prevents fast reduction. Even more stable complexes are formed by Tl(III) with large organic ligands such as EDTA (log K = 37) or DTPA (log K = 46), but the strongest inter-complex is formed with DDTC, as precipitation of Tl(III)DDTC from Tl(III)DTPA solution is observed. The reduction of Tl(III) (log k = 40) is much faster than the complexation of Tl(III) (log k = 3-9). Therefore, partial reduction is inevitable, and the equilibria taking place in aqueous solutions containing Tl ions are complex and often difficult to predict, especially in environmental systems.

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# OC 5

## Fluorescent systems for metal cations and anions

Mauro Formica, Gianluca Ambrosi, Vieri Fusi, Daniele Paderni, Luca Giorgi

Department of Pure and Applied Sciences, University of Urbino "Carlo Bo", Urbino (PU), Italy

e-mail: mauro.formica@uniurb.it

The development of chemical sensors able to signal the presence of a species has always been of great interest for biological and environmental applications. In the last few years, the interest about chemical sensors based on the fluorescent response found a rapid growth because they are versatile and easy to use; moreover, they allow the use of low cost instrumentation with respect to classical analytical one also permitting a real time analysis of the sample.

A fluorescent chemosensor is able to interact with a target species as a metal cation or an anion, revealing such interaction modifying his emission properties.

Chemosensors for metal ions generally contains one or more fluorophores linked to a coordinating active moiety through a spacer. The coordinating active part shows functions able to coordinate a metal ion, as amines or other binding functions, and can be open-chain structure or closed macrocyclic structure. The choice of the donor-functions and of the molecular framework is determined by the metal ion that has to be detected.

In the last years, we are interested in fluorescent chemosensors able to signal metal cations and anions in solution, designing and achieving several fluorescent molecular frameworks. These systems were able to interact with the target ion in solution signalling the presence by a fluorescent photochemical response, as well as the emission wavelength, and emission intensity, or by the appearance of a new fluorescence band different from those of the free sensor.

In this contribution, the correlation of spectroscopic data with the stability constants for some of these systems will be reported.

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## OC 6

# Capillary electrophoresis in studying the complex equilibria of metal ions with inorganic and organic ligands in aqueous solutions

Vladimir Sladkov

Institut de Physique Nucléaire, UMR-CNRS 8608, 15 rue Georges Clemenceau, Orsay, France

e-mail: sladkov@ipno.in2p3.fr

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This presentation will be devoted to the investigation of chemical equilibria between metal ions and inorganic (organic) ligands in aqueous solutions by affinity capillary electrophoresis (ACE). Several systems will be examined. The influence of the pH, the ionic strength and the temperature will be discussed. The cases of the systems with different kinetics (rapid, intermediate and slow) will be also treated. Special attention is paid to methodological development of ACE for the determination of:

- number of species involved in equilibrium;

- species constituents (number of ligands, protonated, deprotonated);

- stability constant values of complex formed;

- $\Delta G$, $\Delta H$, $\Delta S$ (influence of temperature).

# OC 7

## The use of multi-technique approaches for the accurate assessment of the chemical speciation of complex systems

Sofia Gama[1], Demetrio Milea[2], Winfried Plass[1]

[1]Institute for Inorganic and Analytical Chemistry, Friedrich-Schiller-Universität Jena, Jena, Germany
[2]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, Messina, Italy

e-mail: sofia.gama@uni-jena.de

Potentiometry and UV/Vis spectrophotometry, followed by computer data analysis, are the most widely used techniques in chemical speciation studies, and they still remain among the most adequate and accurate for the determination of the stability constants in solution. Nevertheless, the investigation of more and more complex systems (e.g., ligands with several and different binding sites, very strong chelants, unconventional conditions, multicomponent solutions, etc.) opened up new challenges and questions for solution chemists. As such, other techniques and/or approaches are becoming ever more necessary to get further information, for example, on the nature of species effectively formed, on their structure, and on their reactivity.

In this communication, some examples will be reported to evidence how these techniques and approaches have been exploited to complement potentiometric and/or spectrophotometric results to solve some issues related to the assessment of the chemical speciation of exceptionally complex systems. In particular, results relative to the binding ability of some multi-hetero-dentate ligands (namely natural and synthetic metallophores) towards molybdate or other metal cations of relevance will be discussed.
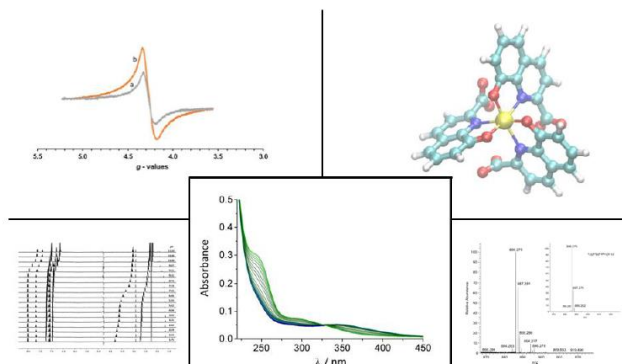


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**Acknowledgements**

# OC 8

## Thermodynamic and chemometric modelling of metal cations chemistry in aqueous solution

Silvia Berto[1], Eugenio Alladio[1], Enzo Laurenti[1], Joanna Lachowicz[2], Valeria M. Nurchi[2]

[1]Università di Torino, Dipartimento di Chimica, Via Pietro Giuria 7, 10125 Torino, Italy
[2]Università di Cagliari, Dipartimento di Scienze Chimiche e Geologiche, Cittadella Universitaria, I-09042 Cagliari, Italy

e-mail: silvia.berto@unito.it

By using potentiometric and spectroscopic techniques, such as UV-vis, fluorescence, EPR (Electronic Paramagnetic Resonance) and NMR (Nuclear Magnetic Resonance) spectroscopy, it is possible to characterize the chemistry of metal cations in aqueous solution. The thermodynamic parameters that control the chemical equilibria can be defined by the elaboration of experimental data; then, the speciation distribution diagrams can be plotted. The combination of different techniques allows fortifying the model reliability and to get structural information about the species formed also. The thermodynamic parameters are usually obtained through potentiometric or spectroscopic data elaboration applying a stoichiometric approach based on mass/charge balances and physic-chemical equations [1].

In recent works, chemometry have also been applied to the study of different types of chemical systems, in particular to process spectroscopic data [2-3]. The investigation on two different chemical systems, concerning the complexation capability of kojic acid derivatives towards oxovanadium(IV) and the protonation and complexation capability of tannic acid [4], are reported as examples. The aim was to evaluate the usability of these methods for speciation studies.

The interaction of oxovanadium(IV) with four newly synthetized compounds [5] derived from kojic acid were studied. The ligands are composed of kojate groups linked to each other by an ethylenediamine, a propylenediamine, a butylenediamine or a tris(2-aminoethyl)amine. Potentiometric titrations, UV-vis absorption and EPR spectra were recorded as a function of pH on the systems examined. The experimental data demonstrated the formation of rather stable complexes, and that the coordination of the metal takes place mainly through the intervention of the kojate units. The data were processed with software dedicated to speciation studies [6-7] and with Matlab for chemometric elaboration. Principal Component Analysis - PCA and Multivariate Curve Resolution - Alternating Least Squares - MCR-ALS were applied. MCR-ALS resulted to be rather suitable to interpret the experimental data, in particular to achieve speciation information from EPR data.

As about tannic acid, it is a natural polymers derived from the vegetable kingdom and belonging to the polyphenol family. The protogenic and spectroscopic properties of commercial tannic acid were studied and the role of gallic acid impurities on the acidity and spectroscopic properties of tannic acid solutions was elucidated. The latter task was carried out by the application of MCR-ALS on fluorescence data collected on tannic acid and gallic acid solutions. The same approach was used to investigate the coordination capability of tannic acid towards iron(III). Both MCR-ALS and PARAFAC (Parallel Factor Analysis) were used for the elaboration of spectroscopic data and chemical models were proposed.

The MCR-ALS and PARAFAC techniques turned out to be useful in the interpretation of the spectroscopic data and this chemometric approach could support the study of those real systems that show a not well defined stoichiometry, such as humic acids or natural polymers, but that present peculiar functions able to interact with metal cations.

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# OC 9

# Survey on the criteria adopted for the quantification of the sequestering ability of ligands towards metal cations

Francesco Crea[1], Concetta De Stefano[1], Sofia Gama[2], Gabriele Lando[1], <u>Demetrio Milea</u>[1], Alberto Pettignano[3], Silvio Sammartano[1]

[1]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, Messina, Italy
[2]Institute for Inorganic and Analytical Chemistry, Friedrich-Schiller-Universität Jena, Jena, Germany
[3]Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, 90128 Palermo, Italy

e-mail: dmilea@unime.it

Chemical speciation calculations based on numerical equilibrium data are of outmost importance in several technologically, environmentally and biologically relevant processes. One of the most interesting applications of these studies is related to the evaluation and the quantification of the sequestering ability of one (or more) ligand(s) towards selected metal cations in real (aqueous) systems, in which other components are simultaneously present and may interfere with the "target" sequestration process. This means that the selectivity and the whole sequestering ability of a ligand toward one or more cations, as well as the comparison between that of two or more ligands, cannot be easily assessed by the simple analysis of single sets of stability constants its/their complexes in real conditions, especially if more than one single species is formed. In this light, several methods have been proposed during the years to evaluate the efficiency (intended as both selectivity and binding ability) of a ligand in a given sequestration process. In this contribution, some of the most common approaches (e.g., pM, $pL_{0.5}$, $BC_{50}$, etc.) are reviewed and critically analysed, with the aim of evidencing their pros and cons, by different examples.
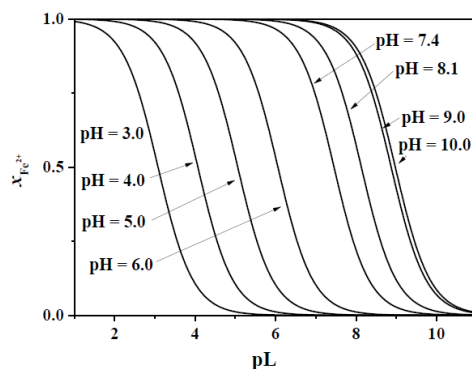


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## Acknowledgements

## OC 10

# Presumption of innocence and solution chemistry

Matteo Savastano,[1] Carla Bazzicalupi,[1] Celeste García-Gallarín,[2] Maria Dolores López de la Torre,[2] Antonio Bianchi,[1] Manuel Melguizo[2]

[1]Department of Chemistry "Ugo Schiff", University of Florence, Italy
[2]Department of Inorganic and Organic Chemistry, University of Jaén, Spain

e-mail: matteo.savastano@unifi.it

When faced with the challenging task of determining thermodynamic parameters for a given system, we oftentimes make meaningful decisions without even realizing it.

One of such decisions is the choice of the working ionic medium. In this context, the use of the so-called innocent anions - among which weakly coordinating nitrate and perchlorate are still among the most common - is widespread. Yet, how do we know for sure that such species are truly innocent? The only meaningful answer is that most of the times we do not, we simply decide to assume so and not to bother any further.

An even more critical parameter is the choice of the solvent: when studying solution equilibria, we generally focus on solute-solute interactions (e.g. binding phenomena), but this does not mean that the implicit presence of solute-solvent interactions is not affecting the position of the equilibrium itself.

Despite this being true for all chemical species, including TCEs, transition metals cations and their gigantic binding constants generally prevent appreciation of these comparatively small effects. On the other hand, anion coordination chemistry, cation's neglected twin, offers unique insights on these across-the-board topics.

Our group recently developed novel s-tetrazine-based ligands which allowed to explore subtle ion-specific effects and thermodynamics of anion complexes formation in aqueous solution [1]. Despite these studies having been proven relevant for core inorganic chemistry (e.g. discriminating between halide anions according to their periodic properties [2]), organic chemistry (e.g. shedding light on the interplay of different supramolecular forces [3]) and the make-up of novel supramolecular materials [4], the amount of accumulated evidence is just a humble memorandum that different ions behave differently in solution, demanding that anyone dealing with solution chemistry is aware of this and remains vigilant concerning his own experimental set-up.

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# Master class

## The case of natural organic matter

Ed Tipping

Centre of Ecology and Hydrology, UK

e-mail: et@ceh.ac.uk

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Subjcts treated:

- Natural organic matter, NOM
- Weak acid chemistry
- Cation binding by NOM
- WHAM
- Testing WHAM with field data
- TCEs

# OC 11

## Metal-humic binding models: Make them as simple as possible, but not simpler

Wolfgang Hummel

Laboratory for Waste Management, Paul Scherrer Institut, 5232 Villigen, Switzerland

e-mail: wolfgang.hummel@psi.ch

Humic substances, or natural organic matter in general, cannot be characterised by well-defined molecular structures, as small organic ligands are. We cannot define a "mole" of humic substance.

Defining conditional equilibrium constants for metal binding by small organic ligands is not always straightforward, as ambiguities can arise when different stoichiometries equally well describe experimental data. However, we always can start modelling with quantities like [mol / litre] or [mol / $kg_{H2O}$]. This is impossible in the case of humics and the problems already start with the question how to normalise experimental data concerning metal – humic binding with respect to a common basis [1].

Any model trying to describe metal – humic binding has to cope with this ambiguity by making assumptions about the structure of humics. These assumptions determine how simple or complicated the model and its parametrisation are, and ultimately limit the field of application of the humic binding model.

Two very simple metal – humic binding models with limited fields of applications, the 'conservative roof' model [2], and the 'local charge neutralisation' model [3], will be shortly discussed and set into perspective with more sophisticated models like 'Model VII' [4] and the 'NICA-Donnan' model [5].

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**OC 12**

# A comparison between aqueous solution and surface complexation models

Johannes Lützenkirchen

Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Germany

e-mail: johannes.luetzenkirchen@kit.edu

A comparison between complexation models in aqueous solutions and on mineral surfaces is given. Various aspects are addressed including the treatment of activity coefficients and multi-dentate complexes, the role of ion-pairs, or the relation between hydrolysis of cations in solution and at interfaces.

The surface potential vs. pH relationships at a given salt level are the most important property related to non-ideality in modelling surface complexation equilibria. They are discussed in numerous disciplines in terms of model results and more recently also in terms of experimental results as related to more easily accessible measurements of zeta-potential [1]. The precise dependence on salt level is under debate. In solutions the variation of the activity coefficient is typically strongly affected when the electrolyte concentration is varied up to saturated salt solutions, while the pH-dependence is negligible.

This and the intervening role of ion-pairs [2] is discussed in some detail based on published parameter sets with focus on the differences between solution and surface reactions.

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# OC 13

# Revisiting the NICA-Donnan model and its parameterisation for metal binding to humic substances

Jan E. Groenenberg[1,2]

[1]Soil Chemistry and Chemical Soil Quality, Wageningen University and Research, The Netherlands
[2]LIEC: Laboratoire Interdisciplinaire des Environnements Continentaux, UMR 7360 CNRS-Université de Lorraine, France

e-mail: bertjan.groenenberg@wur.nl

The bio-availability and fate of metals in the environment is largely determined by their binding to particulate and dissolved organic matter. The humic fraction therein is considered the most important fraction with respect to metal binding. The binding of various metals to humic substances (HS) has been successfully modelled with WHAM Models VI and VII [1] and the NICA-Donnan (N-D) model [2]. Since the publication of the generic N-D model parameters for proton and metal binding by Milne in 2001-2003 [3] various new experimental data on metal binding to humic substances have become available which may be used to derive more reliable model parameters for those metals already included. Furthermore the upcoming interest in the environmental behaviour trace metals of emerging concern including the technological critical elements (TCEs) demand for an update of the N-D model parameters.

Together with the update it is timely to critically review the model and the way it is parameterised. A closer look at the parameters derived by Milne et al. shows weaker model fits for some metals, especially some trivalent metals compared to the divalent metals. There is criticism on the non-uniqueness of the model parameters derived for the N-D model which is partly due to the problem inherent to any electrostatic model that it is impossible to find a unique mathematical solution to vary the local electrostatic potential at the binding sites [4]. Furthermore the electrostatic Donnan model and its present parameterisation results in physically unrealistic Donnan volumes particularly for the fulvic acid [4].

The alternative optimisation procedure as proposed by Lenoir et al. [5] may help to overcome the criticized points to some extent. Furthermore the use of structural relations between model parameters as used by Tipping et al. [1] may help to come to a more coherent set of model parameters for metal binding. Here we will derive an extended set of model parameters for metal binding and evaluate the consequences in terms of model fit and robustness using an alternative procedure as a first step to come to a revised parameterisation of the NICA-Donnan model.

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**OC 14**

# Rare Earth Elements binding to humic substances: NICA-Donnan modelling

Alba Otero-Fariña[1], Noémie Janot[1], J. E. Groenenberg[2]

[1]LIEC: Laboratoire Interdisciplinaire des Environnements Continentaux, UMR 7360 CNRS-Université de Lorraine 15, Avenue du Charmois, F-54500 Vandoeuvre-lès-Nancy – France
[2]Department of Soil Quality Wageningen University, Wageningen University and Research, P.O. box 47, 6700 AA Wageningen, the Netherlands

e-mail: alba.otero-farina@univ-lorraine.fr

The biogeochemical cycle of Rare Earth Elements (REEs) is being affected by their increased use in new technologies. Thus, enrichment of certain REEs has been detected in natural waters. There are no regulatory thresholds for REE as present knowledge on their environmental behaviour and effects is limited.

REEs fate and behaviour is mostly determined by their binding to reactive components such as organic matter, metal oxides and clays. Thus, the use of thermodynamic models which could predict the partitioning and speciation of trace metals in terrestrial and aquatic systems is of key importance. Humic substances (HS, humic and fulvic acids) are the most reactive fractions of natural organic matter, having a high affinity for metal ions. The NICA-Donnan model (NDM) is one of the advanced models for ion binding to HS however, at present there are no NDM parameters for REEs binding to HS except Eu.

Here we obtain generic ND parameters for all the 14 stable lanthanides based on experimental or published data on their binding to HS. The new model parameters were evaluated with published data and were used to predict the solid solution partitioning in soils using a multi-surface model and compared with previously obtained experimental data.

**OC 15**

# Formation of mixed Eu(III)-carbonate-fulvic acid complex: spectroscopic evidence and NICA-Donnan parameters estimation

Yasmine Kouhail[1,2, †], Marc Benedetti[1], Pascal Reiller[2]

[1]Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Université Paris Diderot, UMR 7154 CNRS, F-75005 Paris, France

[2]Den – Service d'Etudes Analytiques et de Réactivité des Surfaces (SEARS), CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France

[†]Present address: Department of Earth and Planetary Sciences, Weizmann Institute of Science, 761001, Rehovot, Israel

e-mail: yasmine.kouhail@weizmann.ac.il

Humic substances are one of the main components of organic matter in aquatic and soil systems and are known to play an important role in the transport and binding of trace metal elements such as rare earth elements (REEs). The formation of mixed complexes between REEs, carbonates, and humic substances is still a matter of debate and further studies are needed. Europium speciation was studied in presence of Suwannee river fulvic acid (SRFA), used as a proxy for natural organic matter reactivity. Time-resolved luminescence spectroscopy (TRLS) was used to evidence the presence of Eu(III)-carbonates-SRFA ternary complexes in media representative of environmental conditions. The evolutions of the Eu(III) luminescence spectra obtained by TRLS from the $^5D0 \rightarrow ^7F0$ to the $^5D0 \rightarrow ^7F2$ transitions are showing modifications of the asymmetry ratio — area ratio of the $^5D0 \rightarrow ^7F2$ over the $^5D0 \rightarrow ^7F1$ transition — that indicates the presence of several species in addition of the $EuCO_3^+$ and Eu-SRFA complexes. The analyses of the indirect excitation of the $Eu-CO_3$-SRFA system are used to build complexation isotherms varying both SRFA or total carbonate concentrations in the framework of the NICA-Donnan modelling of the Eu(III)-SRFA system. We have implemented in the model a $\log_{10}\tilde{K}Eu^{3+},CO_3^{2-},1 = 5.6$ and $nEu^{3+},CO_3^{2-},1 = 1$ for a $Eu-CO_3$-SRFA ternary complex on low affinity for proton sites that helps better describing the system. These ternary complexes represent a significant proportion of the Eu(III) complexes in solution and should be consider in future studies.

**OC 16**

# REE as efficient tracer of active colloidal organic matter composition

Charlotte Catrouillet[1,2], Hélène Guénet[1], Mélanie Davrance[1], Anne-Catherine Pierson-Wickmann[1], Aline Dia[1], Sarah Deville[1], Quentin Lenne[1], Yasushi Suko[1]

[1]Géosciences Rennes UMR 6118, Université Rennes 1, CNRS, 35042 Rennes cedex, France
[2]Institute of Earth Surface Dynamics, University of Lausanne, Lausanne CH-1015, Switzerland

e-mail: charlotte.catrouillet@unil.ch

Rare earth elements (REE) are a group of fourteen elements, whose patterns are able to provide a signature of the functional groups activated on mineral and organic surfaces. REE patterns are controlled by both the heterogeneity and density of the sites available in the humic molecules, which depend on the organic molecules' composition and origin. This work is dedicated to the evaluation of the potential of REE patterns to fingerprint the composition of natural humic substances (HS) active in metal binding. REE complexation experiments with Leonardite (LHA) and Aldrich (AHA) humic acids, Pony Lake fulvic acid (PLFA) were performed at pH 4. Suspensions were filtrated at 0.2 µm and 10 kDa to obtain three fractions studied for REE pattern and HS composition. Results showed that the C amount depends on the HS occurring in the fraction > 0.2µm, whereas the 10kDa < fraction < 0.2µm was the most C- and REE-enriched. Both fractions exhibited quite flat REE patterns, whichever the HS was. On the contrary, REE patterns were different for LHA/AHA and PLFA in the fraction < 10kDa. From fluorescence index analyses, PLFA origin was evidenced as microbial, whereas LHA and AHA origins were assessed as terrestrial. These results showed that REE patterns could record microbial vs. terrestrial origins of organic substances.

# OC 17

# (Bio)weathering of metallurgical at slag-vegetation cover interface

Anna Potysz[1], Artur Pędziwiatr[2], Sebastian Hedwig[3], Markus Lenz[3,4]

[1]University of Wroclaw, Institute of Geological Sciences, Cybulskiego 30, 50-205 Wrocław, Poland
[2]Warsaw University of Life Sciences (SGGW), Faculty of Agriculture and Biology, Department of Soil Environment Sciences, Nowoursynowska Str. 159, 02-776 Warsaw, Poland
[3]Institute for Ecopreneurship, School of Life Sciences, University of Applied Sciences and Arts Northwestern Switzerland, Switzerland
[4]Sub-Department of Environmental Technology, Wageningen University, 6700 AA Wageningen, The Netherlands

e-mail: f.bok@hzdr.de

**Research problem statement**; Metals are routinely used in production of various consumer goods (Radetzki, 2009). Pyrometallurgical production is responsible for large part of worldwide metal supply (Themelis, 1994). However, next to the production profits gained, this industrial chain also generated large amount of wastes such as residues, ashes and slags (Ettler et al., 2001; Piatak et al., 2015; Potysz et al., 2015). The latter are important in terms of production volume. It is important to note that pyrometallurgical activity goes back many centuries when environmental safe waste management concept has not been yet developed. That resulted in inappropriate slag management manner that disposed the slags at poorly protected dumping sites where vegetation cover (involving soil, plants and microorganisms) developed over time (Potysz et al., 2017). Interactions ongoing at slag/vegetation cover interface caused weathering of slag surfaces. This process is undesirable, because toxic elements (e.g. As, Cd, Pb) initially incorporated in slag structure may be released to the environment (Parsons et al., 2001). Metal transfer to the environment may affect bacterial and plant functions (Sobariu et al., 2017) as well as it may lead to accumulation in living organisms and reach the highest level of food chain - humans. Therefore, despite former smelting activities have long ceased, historical mining sites may continue to represent a risk for the environment and human health. It is hypothesized that various weathering pathways result in various slags behavior and therefore various plant responses to the presence of slags may be observed.

Materials and methods; Metallurgical slags selected for this study represent smelting activity that took place in the Middle ages. Detailed sample characterization may be found in Kierczak et al. This study was undertaken to assess environmental risk posed by old copper metallurgical slags upon contact with various organic solutions that included: i) litter extracts (*Fagus sylvatica* leaves, *Picea abies* needles), ii) natural soil solutions and iii) stream water. Further, the potential of direct slag phase (bio)weathering was investigated using: iv) biostimulated soil solution (mineral salt medium addition) and v) water extractable soil medium. Batch leaching experiments were performed with above mentioned solutions over 42 days. In addition, slags weathering simulation under extremely acidic conditions was done in a dynamic experimental system with bacterial culture (*Aciditiobacillus thiooxidans*) renewal every 7 days during 42 days. The risk for metal mobilization was assessed by means of both (bio)chemical leaching experiments (by qqq-ICP-MS) as well as phytotoxicity (*Zea mays* germination; direct contact and soil pot experiments). Potential metal donor slag phases were identified by microscopy (SEM-EDX).

Results; Weathering of slags may result in important metal discharge. The amount of metal released depends on susceptibility of phase being metal-carrier to dissolution. Batch incubations of slags resulted in release of up to 52.6% of total Pb incorporated in slag structure (slags exposed to sterile soil solution). The same slag exposure time (42 days) to bacteria *A.thiooxidans* resulted in release of up to 86% of Pb. In addition, the slags accompanied by bacteria *A.thiooxidans* revealed weathering signals on major phases such as glass and fayalite. In contrast, glass dissolution was promoted in the presence of organic plant derived extracts as proven by solution chemistry and direct Scannning Electron Microscope observations.

Concluding remarks; Results of our study demonstrated that: a) metallurgical slags disposed on the surface ground where litter-derived organic matter comes into contact with slag surface, may be

indeed a serious source of local metallic contamination, b) under all studied conditions (excepting slags exposure to bacteria *A.thiooxidans*) the most liberated element was Pb, c) activity of acidophilic bacteria significantly affected slags stability in a way that volumetrically major and minor phases underwent important dissolution, d) beech leaves and spruce needles extracts affected stability of glass, enhancing leaching (e.g. potassium).

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**Acknowledgements**

# Poster communications

## P 1

# Chemical speciation and geochemical behaviour of platinum in natural waters – A critical review

Antonio Cobelo-García[1], Charlotte Catrouillet[2]

[1]Instituto de Investigacións Mariñas (IIM-CSIC), Vigo (Galicia), Spain
[2]Faculté des géosciences et de l'environment, Université de Lausanne, Switzerland

e-mail: acobelo@iim.csic.es

Platinum (Pt) is amongst the least abundant elements in the Earth's crust, with average concentrations around or below the nanogram per gram level. However, its distribution in several environmental compartments is undergoing a significant transformation due to the considerable increase in its anthropogenic emissions over the last three decades mainly due to its use in automotive catalytic converters. During abrasion and aging of washcoat layer of the catalyst, metallic and oxide forms of Pt are emitted as particles (normally 10-30 μm) at rates up to several hundred nanogram per kilogram per vehicle [1] and then are subject to mobilization through interaction/complexation with naturally occurring ligands [2]. Accordingly, Pt concentrations well above background values have been reported in areas subject to vehicular traffic and also evidence for a long range transport and contamination has been given from the study of Greenland and Antarctic ice cores [3,4].

In this context, rivers, estuaries and coastal areas are subject to increasing Pt anthropogenic inputs. Their solution speciation and geochemistry is, therefore, much required in order to study and predict its biogeochemical behaviour (reactivity, transport, fate, toxicity). To this end, thermodynamic and kinetic models that accurately describe its interactions in the environmental compartments are needed. The solution speciation of Pt in natural waters has been, however, poorly characterised, and the available speciation calculations given in the literature are not fully consistent. The main characteristics of the information available on the geochemistry and speciation of Pt are the following: (i) stability constants with some inorganic ligands are still unknown; (ii) thermodynamic data has been derived from experiments using Pt concentrations well above ambient values. The extremely low concentrations of these elements hamper the study of their complexation at their natural concentrations; (iii) several constants with inorganic ligands are from 'old' papers and/or from the grey literature, and therefore the accuracy of the calculations is under debate; (iv) a significant fraction of the work on the inorganic complexation of Pt was made to calculate their speciation in systems with a different composition than natural waters (e.g. industrial recovery of platinum group elements from acidic solutions). Therefore, some of the reported stability constants with inorganic ligands are given at ionic strengths or temperatures different to those in natural waters; (v) an important fraction of trace elements in natural waters is known to be complexed with natural organic matter (NOM). Although several papers report the interaction of Pt with NOM [5,6], the stability constants of its complexes have not been calculated yet and only constants with few model and synthetic ligands (e.g.desferrioxamine-B, etc.) are available [2].

The present paper, therefore, constitutes a critical review of the literature dealing with the speciation and geochemistry of Pt (II and IV) in natural waters. Calculations of the 'best' estimation of their speciation will be given as well as the implications for their geochemical behaviour. Needs for future research will be outlined.

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## P 2

# Equilibrium constants for the low-molecular-weight species of LSTCE: update

Montserrat Filella

Department F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, CH-1205 Geneva, Switzerland

e-mail: montserrat.filella@unige.ch

This communication will focus on the following group of technology-critical elements (TCE): Nb, Ta, Ga, In, Ge and Te. Their main common characteristic is that they have not been much studied, probably because they are much less used than other TCE (e.g., platinum-group or rare-earth elements) and their applications are more recent. They are sometimes grouped under the term 'Less-studied technology critical elements' or LSTCE [1]. Relatively little data are available in the literature regarding the speciation and solubility of these elements in aqueous solutions. Available thermodynamic data are now being critically evaluated. The current situation will be summarised.

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**Acknowledgements**

# P 3

# Tellurium radionuclide dispersion scenarios in aquatic systems: coupling of adsorption kinetics, radionuclide decay and estuarine hydrodynamics

Teba Gil-Diaz[1], Jörg Schäfer[1], Lionel Dutruch[1], Frédérique Eyrolle-Boyer[2]

[1]Université de Bordeaux, UMR CNRS 5805 EPOC, NB18, Allée Geoffroy Saint-Hilaire, 33615 Pessac, France
[2]Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PRP-ENV, SESURE/LERCM, SERIS/LM2E, L2BT, STEME/LMRE, BP 3, 13115, Saint Paul Lez Durance, France

e-mail: teba.gil-diaz@u-bordeaux.fr

Tellurium (Te) is a Technology Critical Element (TCE), an emerging contaminant and a relevant radionuclide produced in nuclear power plants (NPPs), potentially released into the environment after major NPP accidents [1]. Little is known about the environmental behaviour and fate of both, stable and radioactive Te, particularly in complex aquatic environments such as continent-ocean transition systems [2], such as the Gironde Estuary, France. Information on solid/liquid partitioning is necessary for developing dispersion scenarios to simulate dissolved Te radionuclide discharges into dynamic coastal environments featuring strong salinity and turbidity gradients and seasonal variations in hydrodynamics.

This study presents experimental adsorption kinetics of dissolved Te exposed to a wide range of suspended particulate matter (SPM) concentrations in both, freshwater and seawater. Tellurium solid/liquid distribution kinetics in simulated estuarine salinity and turbidity gradients are compared to Te radionuclide decay timescales (i.e., several min to months) and to estuarine dynamics controlling water and SPM residence times as well as the seasonal position of the Maximum Turbidity Zone (MTZ) in the Gironde Estuary. Solid/liquid partitioning (equilibrium: log Kd~5.3) was achieved within ~5 h in highly turbid conditions (1000 mg $L^{-1}$) and after more than 2 days for average SPM concentrations (100 mg $L^{-1}$; log Kd~4.9), independent from salinity.

Radionuclide releases into low-turbidity conditions would imply that, within the first days, part of Te radionuclides decay into other elements (I, Cs, Xe) and/or are transported to the ocean in the dissolved phase. Further dilution in the coastal ocean would be expected, although radionuclide transfer to marine organisms (e.g. oysters) cannot be excluded. Contrastingly, Te radionuclide release into turbid conditions, i.e. when the MTZ is located near to /downstream from the NPP, would result in rapid, nearly total adsorption onto SPM within the first tide. Given the long estuarine residence times of SPM (1-2 years [3]) and the seasonal upstream migration of the MTZ, this scenario potentially implies the risk of upstream transport of radionuclides with relevant half-lives ($^{127m}$Te, $^{129m}$Te) into the fluvial estuary (Bordeaux agglomeration) during the following dry season.

The aqueous solution properties treated within the Pitzer approach that pertains to a nuclear waste repository in salt is divided into different categories: (i) "Oceanic" for the main components of high ionic-strength brine including interactions of main components with carbonate, (ii) "Radionuclide/actinide" for the key radionuclides (and their analogs) and their interactions with main inorganic and organic ligands that need to be addressed to support the safety case, and (iii) "Others" including selected non-radioactive elements of high relevance like iron or lead. The vast majority of the available literature deals with the brine chemistry associated with "oceanic" systems (~1000 species-specific) and this remains a very active area of research for a number of reasons outside of the nuclear repository application. For the radionuclide/actinide data set, there are new data reported for all the key oxidation states of the actinides but there are significantly less literature publications (~65) on this key topic. There is especially a significant lack of temperature-variable data for the radionuclide/actinide data set as well as ternary species and a number of gaps exist in current database applications. A critical assessment of these key data gaps will be provided.

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## P 4

# Building a consistent thermodynamic database for gadolinium inorganic complexes in aqueous solution

Guillaume Jiranek, Montserrat Filella

Department F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, CH-1205 Geneva, Switzerland

e-mail: guillaume.jiranek@etu.unige.ch

Among the so-called Technology-Critical Elements (TCEs), gadolinium occupies à special place because it is the TCE whose concentration is increasing more in continental surface waters. The main reason seems to be it uses as contrast agent in Magnetic Resonance Imaging (MRI) due to it paramagnetic properties [1]. Due to gadolinium toxicity as free ion, it is administered in a chelated form by a strong complexing molecule. Use of gadolinium in medicine seems to increase water contamination, as those chelates pass water treatments plants without problems. However they are sensitive to UV radiations and anaerobic treatments [2].

It behaviour in both biological fluid and natural compartments is thus important to know. To do so, thermodynamic modelling is quite an useful tool, but require an extensive knowledge of the solution chemistry of the studied element [3].

With this objective, we have performed a comprehensive compilation of existing equilibrium constant values for gadolinium inorganic complexes. Once all published values collected, they have been uploaded in JESS (http://jess.murdoch.edu.au/jess_home.htm) and the 'best' set of equilibrium constants calculated following the embedded approach. Less original data than initially thought exist, with a lot of 'reuse' of old equilibrium constant values even in recent studies.

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## P 5

# Studies of palladium uptake by plants – important aspects of experiment design

Katarzyna Kińska, Joanna Kowalska, Beata Krasnodębska-Ostręga

Faculty of Chemistry, University of Warsaw, Poland

e-mail: kkinska@chem.uw.edu.pl

An important part of environmental studies is related to the bioavailability of metals, with special attention to the transformation of their nanoparticles. In the environment ionic and metallic forms can often coexist. As part of the conducted studies, we investigated the response of white mustard to the presence of palladium, introduced to the nutrient solution in the form of nanoparticles and salts. One of the tested was $Pd(NO_3)_2*2H_2O$, highly soluble in water and already applied in some toxicological studies. To control the process of the conversion of one form into another, we applied three different methods – transmission electron microscopy (TEM), single particles ICP MS and adsorptive stripping voltammetry. Based on the obtained results, it was shown that in the aqueous solution palladium ions concentration decreased just after standard preparation. Analyzes completed by TEM have shown, that nanoparticles with a diameter below 5 nm are formed. These nanoparticles, as well as those around 50 nm, can be taken up by plant. Nanoparticles embedded in plant tissues can subsequently undergo some processes that cause their dissolution. As in the natural environment, metal ions can form complexes with different ligands, such conditions should be simulated in studies concerning metals uptake and its detoxication in plants.

# P 6

# Ecotoxicology of Rare Earth Elements (REE) in freshwater systems: behaviour and biological effects

Nicolas Lachaux, Sandrine Pain-Devin, Laure Giamberini

LIEC UMR 7360 CNRS, Université de Lorraine, Rue du Général Delestraint, Metz 57070, France

e-mail: nicolas.lachaux@univ-lorraine.fr

Rare Earth Elements (REE) are essential to produce efficient permanent magnet used in high-technology. Their increasing production and use have led to the release of anthropogenic REE in the environment including aquatic systems. However, little is known about the ecotoxicology of REE, particularly in complex systems. To understand better the behaviour and biological effects of REE, we conducted two ecotoxicological assays which aim to study the capacity of REE to inhibit the mobility of the crustacean *Daphnia magna* (ISO 6341, 2012) and the growth of the green microalga *Raphidocelis subcapitata* (ISO 8692, 2012). We test three REE: neodymium (Nd), gadolinium (Gd) and ytterbium (Yb) alone and in mixture. The assays were performed in absence and presence of dissolved organic matter (DOM: 8 mg/L of dissolved organic carbon including 6.8 mg/L fulvic acid). First results on *D. magna* show similar effective concentration (ECx) of mobility inhibition for Nd, Gd and Yb, which suggests a similar toxicity pattern among all REE. The presence of DOM tends to decrease the toxicity of REE. This result was probably caused by the complexation of REE (trivalent metals).

## P 7

# A short overview of the use of PGEs (Platinum Group Elements) in modern industrial applications

Zoran Pandilov

Ss.Cyril and Methodius University in Skopje, Faculty of Mechanical Engineering, Karpos II b.b, P.O.Box 464, Republic of Macedonia

e-mail: zoran.pandilov@mf.edu.mk

The platinum-group elements (PGEs) have similar physical and chemical properties and occur together in nature [1]. The properties of PGEs, such as high melting points, corrosion resistance, and catalytic qualities, make them indispensable to many industrial applications [2,3,4]. PGE are strategic and critical materials for many nations because they are essential for important industrial applications but are mined in a limited number of places and have no adequate substitutes [5,6].

This paper gives a short overview of the use of all PGEs (Platinum Group Elements) in modern industrial applications.

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# P 8

## Assessment of Pt (IV) kinetics in an ecotoxicological aquatic test with *Dunaliella salina*

Ana Romero-Freire, Antonio Cobelo-García

Marine Biogeochemistry Research Group, Instituto de Investigacións Mariñas (CSIC), Vigo, Spain

e-mail: anaromero@iim.csic.es

A metal spike added to natural waters may take times ranging from hours to months to equilibrate with the natural pool of both organic and inorganic ligands [1], implying that its accumulation and toxicity in spiked solutions will not necessary mimic real speciation conditions. This situation is especially critical for elements like Pt, which is well-known to display extremely slow reaction kinetics [2]. The aim of this work is, therefore, to discuss if Pt speciation spiked to model solutions reflects the natural speciation after few days of equilibration and according to this, how different equilibration periods may affect the observed platinum toxicity. To this aim, toxicity test using the marine green microalgae Dunaliella salina was selected. To detect potential variation of the spiked Pt speciation with time, media was measured by UV–vis spectroscopy to detect speciation changes and total dissolved platinum was determined by ICP-MS. Toxicity was studied from Pt spiked aged solutions and from freshly spiked. Preliminary results show that kinetic of Pt had differences between freshly and aged Pt, and results will be discussed in terms of how equilibration of the spiked Pt may influence toxic assessments.

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**P 9**

# The role of side chains in the fine tuning of metal binding ability of peptides

Katalin Várnagy, Enikő Székely, Gizella Csire

Department of Inorganic and Analytical Chemistry, University of Debrecen, Egyetem tér 1, 4032 Debrecen, Hungary

e-mail: varnagy.katalin@science.unideb.hu

Peptides have high metal binding affinity, but both the thermodynamic stability and the coordination geometry of peptide complexes are very much influenced by the amino acid sequence of the ligands. One field of our present research work is the synthesis and investigation of polypeptides containing various side chain donor groups, in which the coordination of side chain donor atoms comes to the front and their sequences serve as the models of different metalloproteins. The histidine imidazole nitrogens are frequent side chain donor groups in these metallopoteins and imidazole nitrogen is one ot the most important binding sites of transition metal ions. Such metal ion – protein interaction plays role for example in the function of Cu,Zn superoxide-dismutase enzyme or neurodegenerative diseases.

We synthesized such series of multihistidine peptides in which the systematic change of the amino acid sequence is carried out and the equilibrium, structural and electrochemical parameters of their complexes are determined. These molecules include oligopeptides built up from 4 to 12 amino acid residues containing histidines in different positions and amino acid environments. To understand the specific effects of these side chains lysine, aspartic acid or phenylalanine were systematically inserted into the sequence of the multihistidine peptides: $Ac-HDAH-NH_2$, $Ac-HADH-NH_2$, $Ac-HXHZH-NH_2$ (X, Z = Ala, Phe, Asp, Lys) and $Ac-HXHAHXH-NH_2$ (X = Asp or Phe). We performed the equilibrium, structural and electrochemical studies of copper(II), nickel(II) and zinc(II) complexes of these multihistidine peptides. The stoichiometry, stability and structure of complexes were studied using pH-potentiometric, UV-vis, CD spectroscopy and ESI-MS techniques. The electrochemical parameters of copper(II) complexes were determined on the basis of CV measurements and these data were completed by SOD activity measurements in some cases.

The results clearly show that the stability of the metal complexes significantly depend on the metal ion and the number and position of histidines in the peptide. The metal binding ability of the peptide is, however, affected by the amino acids which are present in the neighbourhood of the histidine amino acids, also. These conclusions strongly suggest that the thermodynamic and structural properties of the peptide complexes could be finely tuned by the change of quality and sequence of amino acids around the side chain donor atoms of coordinating the metal ions. This means, that the systematic planning of the sequence of peptides could increase the metal binding selectivity of peptides as well.

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