New reagents and concepts for complexometric titrations

Complexometric titration is an important titrimetric method that is a mature analytical technique for quantitative determination of metal ions. Chelators and indicators are the two important parts. The chelator is a usually a compound that can form a complex with the target ion while the indicator serves to show the titration end point. The indicator can be as simple as a colored compound such as Eriochrome Black T, but it also includes more sophisticated ones such as ion-selective electrodes. Recently, we highlighted the most recent developments on the complexometric titration reagents and methods, and we provide here a summary of this review.

Good chelators should fulfil three criteria: (i) the complexation reaction must be rapid; (ii) it must proceed stoichiometrically (for instance, either 1:1 or 2:1, etc.); (iii) the decrease in free energy must be sufficiently large (as this is the ultimate driving force). The most widely used chelators include ethylenediamine tetraacetic acid (EDTA), its derivatives and EDTA-functionalized materials, able to bind the metal ions with 1:1 ratio (stoichiometry). However, metal-EDTA complexes are pH dependent and exhibit a rigid selectivity sequence that are often insufficient for real samples analysis. New designs and concepts of chelators are therefore constantly being pursued. One recent strategy introduced by the group of Bakker is to move the titration process from one phase to two phases, which now renders a number of lipophilic compounds excellent chelator candidates. Other groups also reported that lipophilic extractants such as diglycoamides and their derivatives can be dissolved into organic solvents or ionic liquids together with an ion exchanger to extract metal ions based on the ion exchange principle. Also, based on the same principle, highly selective ionophores can be doped into emulsified nanospheres to work as chelators that have been successfully applied in real samples. The high selectivity, sensitivity and pH independence of these nanospheres make them a new generation of the chelators. In addition, titrants can also be quantitatively released from ion selective electrodes based on Faraday’s law, requiring no longer the standardized solution.

If a dye molecule is to act as an indicator, it also needs to be selective to the analyte and sensitive enough to exhibit a drastic color change at the end point. Special designs are needed rather than a simply modified fluorophore/chromophore with the chelating group. For example, some dyes show a metal-triggered optical signal change, such as squaraine derivatives that can be switched off in colorimetric and fluorescence ways when reacted with the thiols. The reaction between target ions and thiols then releases the indicator. Another good example is quinacridone derivatives symmetrically functionalized with ethylenediamine groups (binding site) via a linker. The long linker can avoid the influence of protonation/deprotonation of the binding site and result in pH independence. Besides the design of new compounds as indicator, ion selective optical nanospheres doped with ion exchanger, ionophore and solvatochromic dye was also demonstrated as indicator with high selective, sensitive and pH independence properties. By simply changing the ionophore, the nanospheres can be extended to indicate other ions. Instrumental methods have been used to identify the end point as well, typically electrochemical methods such as potentiometry, amperometry and coulometry. In addition, thermometric titration was found to be a promising universal method by measuring the change of temperature during the titration. Compared with other methods, the heat released or produced, does not suffer from the light scattering, absorption induced surface blocking, color change or overlay.

In summary, we have described in the review recent attractive new designs and concepts of chelators and indicators for complexometric titrations. Every chelator and indicator seems to have its own pros and cons, and appropriate chelator and indicators should be carefully selected depending on what analyte will be determined.

Jingying Zhai *and* ***Eric Bakker***
Department of Inorganic and Analytical Chemistry, University of Geneva,
Quai Ernest-Ansermet 30, CH-1211 Geneva, Switzerland

Publication

Complexometric titrations: new reagents and concepts to overcome old limitations.
Zhai J, Bakker E
Analyst. 2016 Jul 21