Mixed Ligand Ion Buffers for Calibrating Ion-Selective Electrodes at Trace Levels

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The calibration of cation-selective electrodes has been facilitated by the use of ion buffers. Hitherto, calibration was made using solutions containing the metal ion and an appropriate complexing ligand, such as EDTA in an appropriate concentration ratio, or by changing the pH value of a solution with fixed metal–ligand concentration. To cover a wide calibration range, say from 10^{-7} to 10^{-3} M [Ca^{2+}], standard solutions involving at least two different ligands had to be prepared. These approaches were both cumbersome and lacked precision in the unbuffered region near the equivalence point of titration of ligand with metal ions.

A more effective approach has been demonstrated for the calibration of free calcium ions (Otto & Thomas 1984; Otto *et al.* 1985). This involves the use of a mixture of ligands rather than a single complexing agent. An example, for calcium, being *N*-(2-hydroxyethyl)ethylenediamine-triacetic acid (HEDTA), nitrilotriacetic acetic acid (NTA), and ethyleneglycol bis(β-aminoethylester)-*N,N,N′N′*-tetraacetic acid (EGTA). Such a calibration system ensures that the metal ion is highly buffered at any calibration point.

In passing from one calibration point to another, the EMF of a cell containing the appropriate ion-selective electrode changes gradually with the free metal ion level, because the individual equivalence points for the ligands in the titration with metal ions are obscured by competing equilibria among the different metal–ligand complexes.

For $-\log_{10}[Ca^{2+}]$ between 8 and 5, the best system is a combination of EGTA and HEDTA, while for $-\log_{10}[Ca^{2+}]$ between 8 and *ca.* 3, a mixture of three ligands, namely, EGTA, HEDTA and NTA is best. Better agreement between theoretical and experimental has been obtained in the presence of a background of 0.01 M Tris than for higher levels of the pH buffer.

It is reasoned that calibration standards for other cations can be similarly set up. For anions, such as fluoride, feasible systems might be based on soluble metal complexes with fluoride.

References

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