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METAL BUFFERS IN CHEMICAL ANALYSIS PART II: PRACTICAL CONSIDERATIONS

Prepared for publication by

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Metal buffers in chemical analysis—Part II: Practical considerations

Abstract - In Part I of this series (PAC 59 (1987) 1681) the theoretical considerations concerning the use of metal buffers in chemical analysis were given. In this part some practical aspects of the use of metal buffers are discussed, and examples are given where such have been found in the literature.

1. INTRODUCTION

Metal buffers find various applications in analytical chemistry and in other fields of science and life, but their main use in analytical chemistry has until now been connected with calibration of ion-sensitive electrodes in the low concentration range. Ion-sensitive electrodes in principle measure activity but analytical chemists are mainly interested in concentration and therefore use solutions of known concentration (at constant ionic strength) for the calibration.

The principal requirements of metal buffers are:

- Accurately known activities or concentrations of free (hydrated) ions of interest.
- Well established correlation between concentration and activity of free (hydrated) ions.
- Sufficient metal buffer capacity to eliminate the effect of dilution or changes of the concentration of the ion of interest, due to accidental losses or contamination.
- Sufficient pH buffer capacity.

The theory of metal buffers has been summarized in Part I (ref. 1) of this series. The aim of the present paper is to draw the attention to certain properties of the buffers that need to be kept in mind when using them.

A metal buffer solution can be defined as a solution for which the pM-value is only slightly affected by the addition of the metal ion (M) or the ligand (X) which complexes with the metal ion.

2. PREPARATION OF METAL BUFFERS

2.1. One phase metal buffers

The preparation of metal buffers is based on mixing solutions of metal salts and ligands in proper proportions. As shown in Part I, there are two types of metal buffer solutions which can be prepared in a one phase system:

A. A solution containing a metal ion and a complexing agent at a given ratio, and the pH-value of the solution is adjusted with a noncomplexing pH buffer. For mononuclear complexes, dilution of the solution does not affect the pM-value if c(X) > c(M).

For a given metal ion the ligand is chosen which best provides buffers of the required pM- and pH-values. This is usually done on the basis of the stability constants of the complexes, also taking into account possible side reactions both of the metal ion and of the ligand. For a given chemical system more exact pM- and pH-values may be obtained by varying the pH-value at a fixed metal/ligand ratio, by stepwise addition of the metal ion to a solution of the ligand at constant concentration (ligand titration with metal ion) or by varying the concentrations of both components to achieve their proper ratio (see ref. 1). Usually such pM buffers contain additional components to control a required pH-value and ionic strength. It must, however, be remembered that such additions may change the initial characteristics of the buffer. It is also important that those additional components should not enter into side reactions with the main constituents of the pM buffer. For pH-control the following substances are often added: acetates, maleates, borates, TRIS [tris(hydroxymethyl)-methylamine] or buffers used in biochemical experiments such as ACES [2-(2-amino-2-oxoethyl-amino)ethanesulfonic acid], PIPES [4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid)], MOPS [3-morpholinopropanesulfonic acid], PIPES [piperazine-1,4-bis(2-ethanesulfonic acid)], etc.

B. A solution containing two metal ions and one complexing agent (see ref. 1). The metal M and the complexing agent are mixed at a given ratio (c(X) > c(M)), the pH-value of the solution is adjusted with a noncomplexing pH buffer (if possible) and the concentration of the second metal ion (N) is varied. Note that (c(M) + c(N)) > c(X). Dilution of the solution affects the pM-value. If $\alpha_{X(N)} >> \alpha_{X(H)}$, it is not necessary to adjust the pH-value carefully (for the definition of α_X see Part I).

Perrin and Dempsey (ref. 2) have discussed both pH and pM buffers and describe their preparation including the purification of substances used in buffers. Different complexing agents which are useful for metal buffering have been discussed by Martell (ref. 3).

2.2. Two phase metal buffers

Most of what has been stated for the one phase systems applies also in this case. The main advantage of a two phase buffer system stems from the fact that the metal ion-bearing organic phase will act as a reservoir for the metal complex and for the ligand, thus permitting systems that are sparingly soluble in water to be used with a high buffer capacity. Also, the range of maximum buffer capacity is shifted from the value obtained in a one phase system, and can be adjusted by appropriate choice of the organic phase.

The principal disadvantages of this type of buffer system are that the pM-values in the aqueous phase may depend on the phase volume ratio, which should therefore be kept as constant as possible, and that the pM-value may - especially in metal buffers utilizing a complexing ion exchanger - depend strongly on the pH of the solution. It is therefore necessary to ensure good pH-buffering when using this kind of metal buffer.

3. USE OF METAL BUFFERS

The two principal applications for metal buffers are:

- A. When a known, constant, not necessarily low, concentration of free metal ions in a solution is desirable. An example of such cases is in the speciation of metals in natural waters.
- B. Calibration of, for example, ion-sensitive electrodes at low activities of the measured ion.

In practical applications of pM buffers, the following points must be carefully considered, since they are often sources of errors.

- 1) The accuracy of the calculated pM-value is never better than the accuracy of the stability constants used in the calculations. Care must be taken when the data of various authors given in the literature show a significant scatter.
- 2) At low or high pH-values protonated or deprotonated complexes may be formed. Their presence is not always mentioned in tables of constants, which is also the case with polynuclear complexes. Neglecting such species in calculations may introduce errors.
- 3) The temperature and ionic strength effects must be taken into account though the effects can be very difficult to predict. When necessary the appropriate corrections should be introduced (ref. 4).
- 4) The effects of other metal ions present in the solution can either be minimized by masking them or taken into account in calculations (this means that all stability constants should be known).

Several application areas will now be discussed and some advice given about critical properties of the buffers and possible experimental difficulties. The various fields of application are treated separately.

3.1. Potentiometry and ion-sensitive electrodes

Calibration of ion-sensitive electrodes in the range below 10^{-5} – 10^{-6} mol/l with solutions obtained from salts or by dilution of more concentrated standard solutions is undesirable. For the following reasons, it leads to serious errors or is even completely inadmissible:

- The preparation of very dilute solutions of accurately known concentration is neither simple nor accurate,
- Loss or contamination of dilute solutions may give rise to serious, positive or negative errors in electrode response,
- Various processes at the electrode-solution interface (such as adsorption, interaction with interstitial ions, redox processes, etc.) may affect the electrode response.

The use of metal buffers avoids these difficulties and may give many additional advantages. When metal buffers are used for the calibration of ion-sensitive electrodes (ref. 5,6), the following points should be remembered:

- The linearity of the electrode working curve may, especially in the low concentration range, be affected, e.g., by the membrane solubility.
- Some membrane materials may in certain ligand systems exert a specific interaction, which may lead to erroneous results. Such effects were found, for example, with metal sulphide membranes (Cu,Pb,Cd) interacting with EDTA or NTA (ref. 7-9). The origin of such effects is often connected with the occurrence of interfering redox reactions (ref. 10).

Table 1 summarises some literature pM-values for copper, cadmium, lead and calcium. The most commonly used metal buffers in analytical chemistry are those for the calibration of copper and calcium ion-sensitive electrodes. The extensive use of pCa buffers is connected with the importance of calcium for biochemical and medical studies; for example, in the study of calcium-sensitive enzymes such as ATP phosphohydrolase (ref. 4). Such systems show optimal activity in a rather narrow pH range hence the simultaneous choice and adjustment of pH and pCa is of special importance.

Table 1. Some metal-ligand systems used as metal buffers. The range of pM has been given according to the published values.

Metal ion	Ligand	pM range	Reference	Metal ion	Ligand	pM range Rei	ference
Сип	EDTA		11	PbII	EDTA	9.84-18.56	20
	NTA				NTA	5.78-11.91	
Сип	EDTA	10.72-18.31	12				
	NTA	6.91-13.05		CaII	NTA	3.6-7.3	4
Cu ^{II}	[12] ane N ₄ *	23-26	13		EGTA		
	[16] ane N ₄ *	20-22		Ca ^{II}	EDTA	5.0-7.7	21
CuⅡ	NH ₃	11	14		EGTA		
CuII	NH ₃	12	15		NTA		
CuII	Ethylenediamine	3-19	16	Ca ^{II}	NTA	4-8	22
	•			Сап	EDTA	7.3	23
Cd¤	Diethylenetriamine	3-11	17	Сап	EDTA	4.4-10.28	24
CqII	EDTA	8.4616.12	18		NTA	3.6-6.63	
	NTA	4.10-10.05		CaⅡ	EGTA+HEDTA+NTA	3.3-8.4	25
CdII	NH_3						
	CH ₃ COOH			*Macrocyclic polyamines			
	Glycine			EDDA	Ethylenediaminediacetic acid		
	IDA	4-11	19	EDTA	Ethylenediaminetetraacetic acid Oxybis(ethylenenitrilo)tetraacetic acid N-(2-Hydroxyethyl)ethylenediamine-N,N,N-triacetic acid		
	EDDA			EGTA			
	NTA			HEDTA			
	2,2'-bipyridine			IDA Iminodiacetic acid			
	1,10-phenanthroline			NTA	Nitrilotriacetic acid		

3.2. Precipitation reactions

Buffering can also be achieved by use of a sparingly soluble precipitate in equilibrium with a common ion. The systems based on a slightly soluble precipitate are not strictly buffers in the sense defined earlier. They should be treated as solutions having a known, often very small concentration of the ion in question. From the solubility product for a slightly soluble salt, MX, the following expression can be derived when c(X) > c(M).

$$pM = pK_s - \log \alpha_X + \log(c(X) - c(M))$$

where X is the counter ion and K_S the solubility product. From this expression it follows that the acidity of the solution affects the pM-value only when X is a weak base and that dilution causes a proportional change of pM.

The use of metal buffers in precipitation reactions will not be treated in more detail here.

3.3. Biological systems

Many biological systems are sensitive to low concentrations of metal ions. Such concentrations can be controlled with a metal buffer. It seems, however, that metal buffers have yet to find use in this application as no good examples have been found in the literature.

3.4. Other applications

The role of metal buffers may sometimes be reversed, and from the optimal buffer range the stability constants of the metal/ligand system can be evaluated. Constants determined in this way in systems expected to act as good metal buffers may then be used in calculations of buffer properties. The additional advantage of such a procedure is the possibility of checking the determined stability constants with literature data published earlier. Such investigations were, for example, performed in the case of cadmium complexes with ten ligands (ref. 19), copper complexes with seven ligands (ref. 9), copper and lead complexes with nine ligands (ref. 8), copper complexes with ethylenediamine (ref. 16) and copper complexes with macrocyclic polyamines (ref. 13).

If the solution containing metal ions (one or two) and ligand has the metal in excess, it can act as a ligand buffer based on a similar principle. Such systems also find analytical applications, for example, in determination of stability constants (ref. 26) or for masking of interfering species in analysis, as was reported for masking calcium in the photometric determination of magnesium (ref. 27).

The metal (and ligand) buffers have been used in many investigations and analytical procedures without mentioning the term explicitly. A buffer, however, always results when metal and ligand solutions are mixed in proper proportions. Some early examples are described in the papers by Reilley and coworkers (ref. 28–30). For example, Reilley and Schmid (ref.28) studied the use of a mercury droplet electrode as a pM-electrode for numerous metal ions. In the presence of mercury-EDTA and metal-EDTA complexes in proper concentrations, the electrode potential was shown to be dependent on the pM-value of the solution. Reilley, Schmid and Lawson (ref.29) used the mercury electrode for end-point detection in the titration of alkaline earth, rare earth, and a number of transition and heavy metals in water solution with EDTA. The electrode potential was dependent on the logarithm of the ratio between the concentrations of the metal ion and the metal-EDTA complex as long as the mercury-EDTA concentration was not changed through interaction with the metal ion in the solution.

4. REFERENCES

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1. E.V. Wänninen and F.Ingman, Pure Appl. Chem., 59, 1681 (1987).
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- 2. D.D.Perrin and B.Dempsey, Buffers for pH and Metal Ion Control, Chapman and Hall, London, 1979.
- 3. A.E.Martell, Pure Appl. Chem., 50, 813 (1978).
- 4. O.Scharff, Anal. Chim. Acta, 109, 291 (1979).
- 5. G.I.Moody and J.D.R.Thomas, Ion-Selective Electrode Rev., 1, 3 (1979)
- Panel discussion Proc. 3rd Symposium on Ion Selective Electrodes (ed. E.Pungor), Matrafured, 1980, Akademiai Kiado, Budapest, 1981.
- W.E.van der Linden and G.J.M.Heijne in Ion-selective Electrodes (ed. E.Pungor), Akademiai Kiado, Budapest, 1978, p.445.
- 8. G.Nakagawa, H.Wada and T.Sako, Bull. Chem. Soc. Japan, 53, 1303 (1980).
- 9. G.Nakagawa, H.Wada and T.Hayakawa, Bull. Chem. Soc. Japan, 48, 424 (1975).
- 10. A.Hulanicki, T.Krawczynski vel Krawczyk and A.Lewenstam, Anal. Chim. Acta, 158, 343 (1984).
- 11. R.Blum and H.M.Fog. J. Electroanal. Chem., 34, 485 (1972).
- 12. E.H.Hansen, C.G.Lamm and J.Ruzicka, Anal. Chim. Acta, 59, 403 (1972)
- 13. A.Jyo, A.Nagamoto, T.Khono and A.Ohyoshi, Bull. Chem. Soc. Japan, 56, 3062 (1983).
- 14. H. Wada and Q. Fernando, Anal. Chem., 43, 751 (1971).
- 15. J.Pick, K.Toth and E.Pungor, Anal. Chim. Acta, 61, 169 (1972)
- 16. A.Avdeef, J.Zabronsky and H.H.Stuting, Anal. Chem., 55, 298 (1983).
- 17. M.Cromer-Morin and J.P.Scharff, C.R.Hebd, Seances Acad. Sci. Ser. C, 283, 621 (1976).
- 18. J.Ruzicka and E.H.Hansen, Anal. Chim. Acta, 63, 115 (1973)
- 19. A. Yuchi, H. Wada and G. Nakagawa, Anal. Chim. Acta, 149, 209 (1983).
- 20. E.H.Hansen and J.Ruzicka, Anal. Chim. Acta, 72, 365 (1974).
- 21. H.M.Brown, J.P.Pemberton and J.D.Owen, Anal. Chim. Acta, 85, 261 (1976).
- 22. A. Craggs, G.J. Moody and J.D.R. Thomas, Analyst, 104, 412 (1979).
- A.Craggs, G.J.Moody, J.D.R.Thomas and B.J.Birch in *Ion-selective Electrodes* (ed.E.Pungor), Akademiai Kiado, Budapest, 1978.
- 24. J.Ruzicka, E.H.Hansen and J.C.Tjell, Anal. Chim. Acta, 67, 155 (1973).
- 25. M.Otto, P.M.May, K.Murray and J.D.R.Thomas, Anal. Chem., 57, 1511 (1985).
- 26. A. Yuchi, H. Wada and G. Nakagawa, Analyt. Sciences, 1, 19 (1985).
- 27. H. Wada, A. Yuchi and G. Nakagawa, Anal. Chim. Acta, 149, 291 (1983).
- 28. C.N.Reilley and R.W.Schmid, Anal. Chem., 30, 947 (1958).
- 29. C.N.Reilley, R.W.Schmid and D.W.Lamson, Anal. Chem., 30, 953 (1958).
- 30. C.N.Reilley and R.W.Schmid, J.Am. Chem. Soc., 78, 2910, 5513 (1956).