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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, 2-(carbamoylmethylamino)ethanesulfonic acid], HEPES [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 $\alpha_{X(N)} \gg \alpha_{X(H)}$, 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.

3.2. 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.

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