A NEW APPROACH TO STABILIZE THE PH IN FLUID-PRESERVED NATURAL HISTORY COLLECTIONS

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Abstract.—The maintenance of a neutral pH is, besides avoiding evaporation and decreasing alcohol concentration, the third and most complicated aspect regarding the curation of preservation fluids in natural history collections. Both the measurement and the subsequent adjustment of the pH inside the specimen jars are fraught with considerable theoretical and methodological difficulties. We propose a new approach to avoid the problem altogether by stabilizing the desired pH with substrate-bound ion-exchange materials, e.g., an ampholyte provided with positively and negatively charged groups in form of pellets, sheets or sticks. Alternatively a combination of separate acidic and basic ion-exchange substrates could be employed.

INTRODUCTION

Curatorial problems with fluid preserved natural history collections deal with various aspects such as containers, lids and labels but most importantly with the preservation fluid itself. Ethanol, which constitutes today the preferred medium in natural history collections, has been in use as a preservation fluid since the 17th century (Down 1989, Moore 1998). The respective methodology is nonetheless still based almost exclusively on empirical knowledge instead of scientific expertise (Moore 1998, Waller and Simmons 2003).

The situation may seem simple at first glance: a jar containing the specimens, some labels, a certain volume of air at the top, and – of course – the preservation fluid. However, the specimen jar with its contents constitutes a more or less closed system that is subjected to a variety of changes during years of storage, due to interaction with its environment (especially evaporation) as well as interaction amongst the various contents, such as leaching or oxidation (von Endt 1994, Marte et al. 2003, Oberer 2008). As a result, the preservation fluid may soon change its properties regarding volume, alcohol concentration, solved substances, as well as pH. These changes, in turn, may lead to serious damage or decomposition of the specimens. It is therefore necessary to monitor the collection and reconstitute the desired properties by curatorial measures regularly.

While it is theoretically possible to monitor not only the fluid level and colour but also its alcohol concentration with little effort today (e.g., with a portable density meter), the monitoring and maintenance of the pH is still problematic in theory as well as in practice. In this paper we address specifically the problems of maintaining the desired pH.

STATEMENT OF PROBLEM

Values below pH 6.5 can cause decalcification of bony structures and otoliths, hardening of specimens, as well as protein embrittlement and dissociation (Thede 1996, Gotte and Reynolds 1997, Moore 1998, van Guelpen 1999, Hargrave et al. 2005). Alkaline conditions substantially above pH 7.0 on the other hand cause clearing of soft tissues, as proteins and lipids are leached from the specimens (Taylor 1977, Dingerkus 1982, Stoddard 1989, Gotte and Reynolds 1997, Hargrave et al. 2005).

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Recent surveys reveal that the pH in natural history collections may indeed reach well into problematic ranges on the acidic as well as the alkaline side. For example, Dingerkus (1982) found values ranging from pH 2 to pH 9 in an ichthyological collection. Other surveys resulted in ranges of pH 5.4–8.2 (Simmons and Waller 1993) and pH 4.5–7, pH 5–6 or pH 5.2–7.6 (Waller and Simmons 2003) for herpetological collections and pH 5–7 (Cato 1990) and 4.8–8.9 (Palmer 1996) for mammal collections, depending on the applied measuring method.

An extensive screening across a wide range of taxa in the wet collections of two large European museums (Naturhistorisches Museum Basel, Zoologische Staatssammlung München, Kotrba et al. in preparation) revealed a range of pH 4.5–9.5 for both institutions, with 14% of the samples ranging at pH 6 or smaller and 14% ranging at pH 8 or larger. This study also showed that the pH of samples a priori classified as ''probably OK'' is not necessarily better than that of samples classified as ''probably problematic.''

Although the enumerated facts clearly show that problems with the pH in fluid preserved natural history collections exist and cannot be neglected, no study has yet come up with suggestions for practicable standard procedures for the maintenance of a desired (neutral) pH.

Open problems remain regarding the measurement and interpretation of the actual pH in the preservation fluid, which is generally ethanol with a water content of 30% or less (tap or deionised) and the addition of some denaturizing agents. The low water content as well as contaminations with proteins, lipids and other substances seriously limit the accuracy of pH measurements (Waller and Simmons 2003, Sound and Becker 2007).

A second, even larger challenge is the reconstitution of the desired pH, if unacceptable values are detected. Standard curatorial measures, i.e., topping up with alcohol to restore alcohol levels and concentration, generally have no effect to the improvement of the pH (Cato 1990, Kotrba et al. in preparation). Titration is unfeasible for various reasons starting with the above-mentioned difficulties with the pH measurement and the related time effort. Also it is usually not possible to appropriately stir the fluid without disturbing the specimens. Moreover titration generally involves the risk of precipitations forming deposits on the specimens.

At present, the recommended procedure is to completely exchange the entire preservation fluid repeatedly (e.g., Dingerkus 1982). However, this procedure may considerably disturb the specimens and lead to additional leaching.

Dealing with the accounted difficulties surpasses the physico-chemical expertise of the average curator. Appropriate standard procedures are not available and their development would require the help of a specialized chemist or analyst. Therefore the most common curatorial approach today is to ignore the problem altogether.

New Approach

It is here suggested to circumvent the related problems by stabilizing the desired pH in the preservation fluid from the very start by buffering the system with the help of a solid ion-exchange material.

The use of buffering agents is already commonplace with respect to formalin fixation of biological specimens and the storage of such formalin fixed material. While some authors suggest the use of sodium borate, i.e., borax (Miller 1952, Taylor 1967) others explicitly advise against this practice (Dingerkus 1982, Taylor 1977). Gotte and Reynolds (1997) recommend the use of a sodium phosphate monobasic / sodium phosphate dibasic buffer, and Taylor (1977) suggests the use of ground limestone.

The physico-chemical advances of the last decades allow us to propose a different approach for stabilizing the pH in ethanol based preservation fluids with the help of a substrate-bound ion-exchange material such as a substrate-bound ampholyte. This concept is similar to a method proposed by Eugster and Righetti (1993) for long term pH control in solutions for medical purposes.

A substrate-bound ampholyte is a polymeric substrate provided with positively and negatively charged groups. Appropriate negative immobile groups are carboxyl groups, sulphuric acid groups or phosphoric acid groups and the positive immobile groups are generally various types of amino groups. If the suggested ampholytic material is not available, alternatively a combination of an acidic and an alkaline ion-exchange substrate, each in a separate batch, can be applied.

The polymeric substrate may be shaped into pellets, sheets or sticks. It may be composed of any polymeric material which is permeable and chemical resistant to the preservation fluid. Unfortunately some commonly used substrates such as polystyrene are unsuitable for our purpose, because they are not resistant to methyl ethyl ketone. The latter is commonly used as a denaturizing agent in alcohol and is known to cause swelling and decomposition of many synthetic polymeric materials. There are, however, good long-term experiences with paper labels in historical collections, therefore cellulose as substrate for the ion-exchange material might be considered as an alternative and is already known as a possible material (e.g., Wade and Brown 1979).

A further step would be to combine the ion-exchange substrate with a colour pH indicator that reveals exhaustion of its capacity (such as that proposed by Härtel and Schmidt 1981). By this measure a simple inspection would be sufficient to recognize all jars with deficient pH.

As compared to the addition of dissolved or powdery buffering agents directly to the preservation fluid, the proposed method would have the following advantages:

1) The buffering agent and its reaction products do not interact directly with the stored specimens, e.g., by forming insoluble deposits on their surface.
2) Pellets contained in a net, sheets, or sticks can be easily retrieved from the specimen jar without disturbing the specimens.
3) The ion-exchange material can be regenerated by rinsing with acidic or alkaline solute and subsequently reused.
4) If a combination of separate acidic and alkaline ion-exchange substrates is applied, then only the exhausted ion-exchange substrate has to be replaced, once the direction of pH deviation in a specific specimen jar is detected.

Conclusion

The proposed concept for the maintenance of a stable pH in natural history wet collections now needs to be put into concrete terms, especially regarding the chemical and physical aspects. Suitable ion-exchange materials have to be identified, produced and tested with respect to the achievable buffer capacity and long term stability in preservation fluid. Moreover studies involving the preservation of standardized specimens from laboratory cultures such as lab mice, cockroaches, etc. are needed to provide quantitative information on the kinetics of pH changes in buffered and unbuffered specimen jars. Such studies could simultaneously show to which extent pH changes occur and actually cause damage to the preserved specimens and/or containers and which buffer capacity over time and which economic effort is necessary to avoid said pH changes.

Such studies are in the interest of the museum community rather than the individual researcher. We strongly encourage the societies involved with natural history conservation issues such as SPNHC, ICOM-CC, or Synthesys NA C to launch and support respective research projects.

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