A simple protocol for the routine calibration of pH meters.

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ABSTRACT

A simplified laboratory protocol for the calibration of pH meters is described and tested. It is based on the use of two analytical primary buffer solutions, potassium hydrogen phthalate and Borax (sodium tetraborate decahydrate) of precisely known concentrations and pH. The solutions may be stored at room temperature for long periods, without decomposition and used directly. The calibration of the meter can be checked with standard solutions of sodium dihydrogen phosphate, sodium carbonate, sodium benzoate, sodium salicylate or potassium oxalate. Methods for the purification of Borax and potassium chloride are also given, and a new method for the neutralization of 0.9 % saline is suggested.

Keywords: pH meters (calibration); saline (0.9%); pH standards; potassium biphthalate; Borax.

INTRODUCTION

It is well known that the accurate determination of pH, which reflects the concentration of ionized hydrogen (Bates, 1948; Spitzer, 2003), is very important, not only in Life science and in Pharmacy but also in other sciences, such as Medicine (Sinha et al., 2003), Chemistry (Osawa & Bertran, 2005), Geology, Ecology, Metalurgy, Physics, Electronics, Soil Science (Abreu Jr. et al., 2003; Osawa & Bertran, 2005), Pharmacology, Quality Control, Hydrology, Food Science (Xiong et al., 2000), Nutrition Science (Mendonça et al., 2005) and also to many industries: foods, paints and varnishes, drugs, papermaking, plastics, effluent treatment, metalwork etc.

When a coarse measurement is sufficient, natural (Terci & Rossi, 2002) or synthetic colorimetric indicator dyes or papers may be used. In special cases, high precise spectrophotometric methods are sometimes used, mainly in pH sensors coupled to scientific instruments (Pinheiro & Raimundo Jr., 2005).

The most widely used modern technique for pH determination is the potentiometric method, using digital or analog-digital modified electrometers (so-called pH meters), with glass electrodes, combined with an Ag/AgCl reference electrode (Gottardi & Pfeiderer, 2005).

To obtain exact results for physicochemical purposes, very accurate calibration of the pH meter and also standardization of electrodes are necessary (Aguilar & Hernandez, 1996; Camões et al., 1997; Sinha et al, 2003; Spitzer, 2003; Schneider et al., 2004; Cheng & Zhu, 2005).

However, in the majority of the situations commonly encountered in the laboratory, it is sufficient to calibrate the pH meter with a solution of known pH (Bates, 1948; Covington et al., 1983). Commercially available pH buffer solutions are used worldwide for this purpose, but these solutions have some disadvantages.

They are generally mixtures of salts (strong with weak Brønsted-Lowry bases and/or acids) that form buffered aqueous solutions, based on the classical Clark & Lubs (1917), Sorensen (1909) or Bates-Bower (Covington et al., 1983; Lide, 2005) buffers. Because they are mixtures (and not solutions of a single salt or compound) they are generally not very stable, and should frequently be remade or stored cold, but not for a long time. Since pH is temperature dependent (Verhappen, 1993; Camões et al., 1997; Lide, 2005), these solutions should be warmed to room temperature prior to use, which can be inconvenient.

The use of stable aqueous solutions of pure salts or compounds is desirable.

Some pure compounds have been proposed as new standards, but they are not readily available: calcium hydrogen malate (Shead, 1952), potassium hydrogen tartrate (Barbosa et al., 1994; Lide, 2005), pipermazine phosphate (Grove-Rasmussen, 1953; Covington & Rebelo, 1987).

Also, some stabilized solutions containing organic co-solvents have been suggested: solution of borax in aqueous methanol (Kozakova et al., 1980), potassium hydrogen tartrate in aqueous acetonitrile (Barbosa et al., 1994) and potassium biphthalate in formamide (Falcioni et al., 2004), but the presence of organic solvents is harmful to the electrodes or to plastic parts of the pH meter.

It is well stablished that some compounds are highly stable, easily purified and always crystallize in a rigorous reproducible stoichiometric proportion, corresponding to an exact, invariable molecular formula. For this reasons, they are used in analytical chemistry as primary standards (Analytical Standards…, 1965; Otterson, 1966; Bishop, 1969) for the determination of the exact
concentration of volumetric solutions, and may also be as pH standards.

For alkaline solutions, potassium biphthalate (potassium hydrogen phthalate) is a good choice (Jee, 1982; Covington et al., 1983; Lide, 2005). It is a classical primary standard (Falciola et al., 2004) for the calibration of sodium hydroxide volumetric solutions, and commercially available worldwide in AR or primary-standard grades.

For acid solutions, Borax or anhydrous sodium carbonate are generally used.

Borax was fully studied as a volumetric analysis primary standard by Kolthoff (1926), who suggested the use of anhydrous borax (tincal, calcined borax, anhydrous sodium tetraborate) for exact stoichiometry, but now it is known (Madej & Rokosz, 1975) that the loss of water of crystallization from the hydrated borax is very slow and its variation in composition is insignificant for analytical purposes (Covington et al., 1983, Lide, 2005), so that commercially available hydrated borax may be used directly as a primary standard, as described in Analytical Chemistry textbooks (Jeffery et al., 1989).

### MATERIALS AND METHODS

#### Chemical Materials

**Potassium hydrogen phthalate (potassium biphthalate):** AR (ACS) volumetric primary standard grade, 99.95-100.05% (RioLab, Brazil) and/or p. a. grade, 99.8%, (Merck, Germany) was dried in an oven at 105-115 °C for two hours and cooled in a desiccator over anhydrous calcium chloride.

**Sodium tetraborate decahydrate (Borax):** The ACS reagent (Baker & Adamson Company, USA) was dried/equilibrated in air for 3-12 hours and used directly. When less pure material was available (pharmaceutically dried/equilibrated in air for 3-12 hours and used directly. Also, pharmaceutically pure “sodium borate”, Henrifarma, Brazil), it was twice recrystallized from water below 50-55 °C. After the second recrystallization, it was filtered hot, allowed to cool to room temperature and then filtered again, between half and two-thirds of its volume of 95% ethanol (p. a.) was added, to precipitate another crop of crystals, which were filtered and dried. Total Yield: 57-61%.

**Activated alumina (Al₂O₃):** Aluminium oxide 90 active, neutral, for column chromatography, Brockmann activity 1, 70-230 mesh ASTM (Merck, Brazil), product number 101077, was used directly.

### Equipment

**Balance:** Materials were weighed using an precision (0.0001 g) balance, OHAUS (USA), model Adventurer AR-2140, special for Analytical Chemistry, auto-calibrating. The accuracy of the balance was checked with standard mass references (courtesy of Prof. Dr. Luís Alexandre Pedro de Freitas, Laboratory of Physics Applied to Pharmaceutical Sciences, FCFRP).

**Reference pH meter:** Marte (Brazil), model MB-10 digital pH meter, 110 V, assembled with thermal compensator, external sensor and original combined electrode, annular junction, glass/Ag/AgCl. This model is an auto calibrated pH meter (Marte, 2006). It was assembled and re-calibrated, the calibration being checked against two commercially-available standard buffers, pH = 4.00 (Analion, Brazil, code 00133) and pH = 7.00 (Analion, Brazil, code 00135) (Analion, 2006).

**Working pH meter:** Incibrás, Brazil, analog–digital pH meter, model PH-1400, 110/220 V, connected to the mains (115 V, 60 Hz) and assembled with a sealed, permanent KCl gel-junction (glass/Ag/AgCl reference) combined electrode, Analion, Brazil, model V631S7 (Analion, 2006).

### Methods

#### Storage of Solutions: Cylindrical, acrylic vials, 20x100 mm, INJEPLAST, Brazil, Model 40, were used for storage of the sample solutions, small quantities of buffers, and to immerse the electrode. Stock solutions of the standards were stored in polyethylene flasks.

#### Statistical Methods: The theoretical (as calculated, Table 1) pH values found in the literature (Camões et al., 1997) for the acidic buffer A and alkaline buffer B, are respectively 4.01 (calc. Debye-Huckel Method) and 9.20 (Pfizer Method). To test whether the mean value of 52 experimental measurements of each solution agreed with the theoretical values, a two-tailed t-test for the mean was performed at the 5% significance level. Also, 95% confidence intervals for means, based on t-distribution, were calculated for the experimental pH of both the acidic and alkaline solutions (Hogg & Craig, 1970). Linear regression models were fitted, in which the pH measurements were considered as a function of the number of days after the solutions were prepared (0-150 days). To check whether the age of the stored solutions, in the time interval considered, could affect the pH measurements, that is, if the slope of the pH vs. time plot is significantly different from zero, a two-tailed t-test was
performed on the slope at a significance level of 5% (Draper & Smith, 1981).

Methods developed

Preparation of a acidic standard solution, pH near 4.00.

An exact mass of potassium hydrogen phthalate (2.5528 g; 0.0125 mol) was dissolved in distilled water, and made up to 250 mL, in a volumetric flask. This stock solution was stored at room temperature, in a polyethylene flask, and used directly. It had an exact pH value. Checked with the Reference pH meter: 3.97-4.03 (Table 1).

Preparation of alkaline standard solution, pH nearly 9.00.

The alkaline stock solution was prepared in the same way, using 4.7671 g, (0.0125 mol) of sodium tetraborate decahydrate, in a final volume of 250 mL. This solution had an exact pH value, checked with the Reference pH meter: 9.17-9.23 (Table 1).

Method for calibrating and using the working pH meter.

The electrode was rinsed with 4-7 portions of distilled water, dried with a soft absorbent paper and immersed in 25-30 mL of the alkaline buffer, B (20-25 °C). The pH was measured, and the controls of the pH meter (gain and calibration) adjusted to the value of 9.18-9.20. The electrode was then rinsed and dried and immersed in the biphthalate buffer A, and the pH re-adjusted to 4.00-4.01.

The pH meter was then calibrated and can be used for measurements and/or switched to the standby mode.

After use, the electrode was rinsed again and maintained immersed in 25-30 mL of 3-4 mol/L (22.5% or saturated) aqueous KCl. The original volume of the solution was maintained by periodical addition of water.

Method for the preparation of neutral saline solution 0.9%.

The pH meter was calibrated as described in C, and the electrode immersed in 200 mL of a solution of NaCl, 0.9%, measuring the pH. The solution was stirred, and neutral aluminium oxide, Al₂O₃, was added in small portions. When nearly 3 g of the alumina had been added, the pH gradually rose. The addition of alumina was carefully continued until the pH was 7.00-7.40. The alumina was then decanted off and the solution filtered and stored.

RESULTS

Preparation and test of the solutions

Two common chemicals were selected and tested for making stable solutions of exactly-known concentration and nearly constant pH values.

Pure and dried potassium hydrogen phthalate was weighed, diluted, and used as the standard for the acidic range (1-6).

<table>
<thead>
<tr>
<th>RANGE OF pH</th>
<th>CHEMICAL</th>
<th>AMOUNT (g)</th>
<th>CONCENTRATION (mol/L)</th>
<th>MEASURED pH (temp. °C)</th>
<th>CALC. pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic</td>
<td>Potassium hydrogen phthalate&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10.2110</td>
<td>0.05</td>
<td>3.97 - 4.03&lt;sup&gt;d,e&lt;/sup&gt;</td>
<td>4.01&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>Alkaline</td>
<td>Sodium tetraborate decahydrate&lt;sup&gt;b&lt;/sup&gt;</td>
<td>19.0685</td>
<td>0.05</td>
<td>9.17 - 9.23&lt;sup&gt;d,f&lt;/sup&gt;</td>
<td>9.20&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Pure and dry.
<sup>b</sup> Pure (or purified) and dry.
<sup>c</sup> To be dissolved to 1000 mL, in distilled water.
<sup>d</sup> Range of 52 measurements, on different days, using the stock solutions and also freshly prepared solutions. Measured with a reference pH Meter (See Experimental).
<sup>e</sup> Lit. values: 3.97(20 °C); 3.98-4.02(20 °C); 4.001-4.011; 3.998-4.011 (Humeres et al., 1990; Schneider, 2004; Lide, 2005)
<sup>g</sup> Calculated with BATE, 2004 software, entering data taken from Humeres, et al. 1990 and/or Lide, 2005. The same values were reported as theoretical values (Camões et al., 1997).
**Protocol for pH meters calibration.**

Table 2. pH of some materials, solutions or compounds.

| ENTRY | MATERIAL | SOURCE, PURITY ETC… | MEASURED. pH OR CHARACTERISTICS | LITERATURE pH OR CHARACTERISTICS | LIT. REFERENCE | CALC. pH
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na₂HPO₄ (0.1 mol/L) (disodium hydrogen phosphate)</td>
<td>Exact concentration, prepared from dried, primary standard purity grade (Fischer Scientific) and/or ACS grade (Baker) materials.</td>
<td>8.91-9.03 (25°C)</td>
<td>9.2 (0.1 mol/L, 25°C); 4.1-4.2 (5%, 25°C); 9.1 (0.1 mol/L, 25°C)</td>
<td>Farmacopéia Bras., 1988; ACS, 2005.; Lide, 2005.</td>
<td>9.15</td>
</tr>
<tr>
<td>2</td>
<td>PhCOONa (0.1 mol/L) (sodium benzoate)</td>
<td>Pharm. grade, Henrifarma, Brazil, exact conc., from dried mat.</td>
<td>7.69 (27)</td>
<td>8</td>
<td>Farmacopéia Bras., 1988; Mendonça et al., 2003; Um et al., 2004</td>
<td>8.23</td>
</tr>
<tr>
<td>3</td>
<td>K₂C₂O₄.H₂O (0.1 mol/L) (potassium oxalate)</td>
<td>p. a., Baker, exact concentration.</td>
<td>5.94 (28) neutral</td>
<td>5.91 (rec. prep) - 6.32 (aged) (26-29)</td>
<td>ACS, 2005</td>
<td>5.12</td>
</tr>
<tr>
<td>4</td>
<td>KCl (3 mol/L) (potassium chloride)</td>
<td>p. a. or purified. See text</td>
<td>5.52 (rec. p.) - 6.12 (aged) (22-30)</td>
<td>5-8</td>
<td>ACS, 2005.</td>
<td>6.84</td>
</tr>
<tr>
<td>5</td>
<td>NaCl (0.2 mol/L) (sodium chloride)</td>
<td>Exact conc., dried, p.a./ACS (VETEC).</td>
<td>5.91 (rec. prep) - 6.32 (aged) (26-29)</td>
<td>6.7-7.3; 5.0-9.0 (5%)</td>
<td>Reber et al., 1979; Farmacopéia Bras., 1988; ACS, 2005</td>
<td>6.96</td>
</tr>
<tr>
<td>6</td>
<td>NaCl 0.9 %</td>
<td>Exact conc., dried, p.a./ACS (VETEC).</td>
<td>5.62 (f. prep), (aged) (27)</td>
<td>Considered neutral and isotonic, but rep as 6.4</td>
<td>Haidl et al., 2000</td>
<td>6.94</td>
</tr>
<tr>
<td>7</td>
<td>USP Isotonic Saline 0.9 %</td>
<td>Pham. grade, JP, Brazil</td>
<td>6.54 (26)</td>
<td>Considered neutral and isotonic, but rep as 6.4</td>
<td>Haidl et al., 2000</td>
<td>6.94</td>
</tr>
<tr>
<td>8</td>
<td>Table salt (5%)</td>
<td>Cisne, Brazil</td>
<td>5.73 (rec. prep) (30)</td>
<td>Considered neutral and isotonic, but rep as 6.4</td>
<td>Reber et al., 1979; ACS, 2005</td>
<td>6.92</td>
</tr>
<tr>
<td>9</td>
<td>NaF (0.1 mol/L) (sodium fluoride)</td>
<td>Exact conc., Pharm. Pure, Veado D’Ouro, Brazil</td>
<td>8.34(rec. prep), 7.24 (aged)</td>
<td>Slightly alkaline. Variable with the ionic strength</td>
<td>Vanderborgh, 1968; Spitzer, 2003,</td>
<td>8.06</td>
</tr>
<tr>
<td>10</td>
<td>Tap Water</td>
<td>f. collected</td>
<td>5.60-6.76 (22-30)</td>
<td>7.0</td>
<td>7.00</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Dist. water</td>
<td>F. collected. All glass still</td>
<td>6.52-7.16 (22-31)</td>
<td>7.0</td>
<td>7.00</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Ultra pure MiliQ water</td>
<td>f. collected and sonicated</td>
<td>6.97 (26)</td>
<td>7.0</td>
<td>7.00</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Sodium Salicylate (0.2 mol/L)</td>
<td>PA, Merck, exact concentration</td>
<td>5.37-5.40 (26-28)</td>
<td>Considered neutral and fully ionized</td>
<td>Farmacopéia Bras., 1988</td>
<td>5.6</td>
</tr>
<tr>
<td>14</td>
<td>NaHCO₃ (0.1 mol/L)</td>
<td>Pharm. grade, Henrifarma, exact mass</td>
<td>8.12 (27)</td>
<td>8.4</td>
<td>Farmacopéia Bras., 1988</td>
<td>8.36</td>
</tr>
<tr>
<td>15</td>
<td>Na₂CO₃ (0.1 mol/L)</td>
<td>PA (VETEC), dried, exact conc.</td>
<td>11.86 (26)</td>
<td>11.8</td>
<td>Farmacopéia Bras., 1988</td>
<td>11.56</td>
</tr>
<tr>
<td>16</td>
<td>Aspirin (susp. 5%)</td>
<td>Pharm. Grade, Henrifarma</td>
<td>2.57 (29)</td>
<td>2.3</td>
<td>Farmacopéia Bras., 1988</td>
<td>1.59</td>
</tr>
<tr>
<td>17</td>
<td>Oxalic Acid (0.1 mol/L)</td>
<td>Tech. grade, 98%, Aldrich, exact mass.</td>
<td>1.63 (25)</td>
<td>1.6</td>
<td>Farmacopéia Bras., 1988</td>
<td>1.59</td>
</tr>
<tr>
<td>18</td>
<td>Table Vinegar</td>
<td>Agrin, Red type², Castelo, Brazil.</td>
<td>3.37 (26)</td>
<td>2.71-3.44</td>
<td>Gonzalez &amp; Chozas, 1987; Xiong et al., 2000</td>
<td>3.44</td>
</tr>
<tr>
<td>19</td>
<td>NaClO₄ (0.1 mol/L) (sodium perchlorate)</td>
<td>Chemically pure, VETEC, Brazil, exact mass, not dried.</td>
<td>6.76-7.01 (27-31)</td>
<td>Considered neutral and fully ionized</td>
<td>Vanderborgh, 1968; Spitzer, 2003,</td>
<td>6.99</td>
</tr>
</tbody>
</table>
Protocol for pH meters calibration.

Table 2. pH of some materials, solutions or compounds. - Continuation

<table>
<thead>
<tr>
<th>ENTRY</th>
<th>MATERIAL (CONC.)</th>
<th>SOURCE, PURITY ETC...</th>
<th>MEASURED, pH (TEMP. °C)</th>
<th>LITERATURE pH OR CHARACTERISTICS</th>
<th>LIT. REFERENCE</th>
<th>CALC. pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>Acetic acid, (4 %)</td>
<td>PA, Mallinckrodt</td>
<td>2.54 (29)</td>
<td>acidic</td>
<td></td>
<td>2.79</td>
</tr>
<tr>
<td>23</td>
<td>Acetic acid, PA (0.01 mol/L)</td>
<td>PA, Mallinckrodt</td>
<td>3.20 (29)</td>
<td>3.40</td>
<td>Farmacopéia Bras., 1988</td>
<td>3.39</td>
</tr>
<tr>
<td>24</td>
<td>Boric Acid, 3 %</td>
<td>Ophthalmic solution ”boricated water”</td>
<td>3.96-4.00 (26-27)</td>
<td>4-5, 5.1, 5.2, 4.8-5.2</td>
<td>Weak Acid, but the pH is variable (Liu &amp; Tossel, 2005) See Discussion, c.</td>
<td>4.85</td>
</tr>
<tr>
<td>25</td>
<td>Nb2O5 susp. 10 % (niobium pentoxide)</td>
<td>High Optical Grade, CRMM, Araxá, Brazil</td>
<td>3.43 (31)</td>
<td>Slightly acidic</td>
<td>CBMM, 2005</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Acidic hydrated m Una, susp. 10 %</td>
<td>Chromatographic Grade, Merck, 90, neutral, Brockman activity 1</td>
<td>6.99 (29)</td>
<td>neutral</td>
<td>CBMM, 2005</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>Na2SiO3 (0.1 mol/L) (sodium metasilicate)</td>
<td>Tech./ind. grade</td>
<td>10.93 (30)</td>
<td>&gt; 10</td>
<td>Kooyman et al., 2001</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>Na5P3O10 (0.1 mol/L) (sodium tripolyphosphate)</td>
<td>Tech./ind. grade</td>
<td>9.32 (30)</td>
<td>8.60 (10 %)</td>
<td>Lin et al., 2005</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Picric Acid, saturated 0.9-1 %</td>
<td>PA, Baker, exact mass, but not dried</td>
<td>2.24-2.01 (25-27)</td>
<td>Below 3</td>
<td>Yoshikawa &amp; Matsubara, 1983, Um et al., 2004</td>
<td>2.23</td>
</tr>
<tr>
<td>31</td>
<td>Sodium Picrate monohydrate (0.01 mol/L)</td>
<td>Prepared by synthesis (Cordo et al., 2003)</td>
<td>6.18-6.20 (25-26)</td>
<td>Previously unknown.</td>
<td>Cordo et al., 2003</td>
<td>5.81</td>
</tr>
<tr>
<td>32</td>
<td>Piperazine (0.1 mol/L)</td>
<td>For synthesis, Merck, exact mass, hygroscopic</td>
<td>10.75</td>
<td>Classically known as a weak base. Strong alkaline solutions, easily bufferable. Considered Neutral.</td>
<td>Um et al., 2004.</td>
<td>10.07</td>
</tr>
<tr>
<td>33</td>
<td>Household common detergent 10 % in tap water</td>
<td>Ypê, Brazil</td>
<td>7.14 (rec. prepared, aged) (25)</td>
<td>6.64</td>
<td>Olsen &amp; Falholt, 1998</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>Household common detergent, 10 %, in distilled water</td>
<td>Ypê, Brazil, exact mass</td>
<td>7.04 (rec. prep.) aged</td>
<td>Optimal value 10-12</td>
<td>Olsen &amp; Falholt, 1998</td>
<td>8.57</td>
</tr>
<tr>
<td>35</td>
<td>Household kitchen soap, 1 %</td>
<td>Ypê, Brazil</td>
<td>10.28</td>
<td>Optimal value 10-12</td>
<td>Smith, 1956</td>
<td>8.57</td>
</tr>
<tr>
<td>36</td>
<td>Soap, 1 %</td>
<td>Home made with soy oil</td>
<td>10.80</td>
<td>Optimal value 10-12</td>
<td>Smith, 1956</td>
<td>8.57</td>
</tr>
</tbody>
</table>

* Range of several determinations, different days and solutions.
* Similar results with the water collected from a stainless steel still.
* Agrin type Brazilian vinegar is alcohol vinegar mixed with small amount of red wine vinegar. May contain 4 % of acetic acid.
* Calculated with Bate, 2004 software, entering data taken from Vanderborgh, 1968; Han et al., 1990; Armarego & Choi, 2003; Mendonça et al., 2003; Schneider et al., 2004; Lide, 2005. When not given, necessary data, such as constants, pK, cannot be found in the literature.
* Soaps are mixtures of sodium salts of long-chain carboxylic acids, containing some free sodium hydronide. The calculated pH was based on neutral sodium oleate, calculated with the value of the pK of oleic acid.
During our current experimental work in the laboratory, we developed an inexpensive and fast method for the routine calibration of pH meters. This was based on the use of simple aqueous solutions of pure primary standards.

The calculated and measured data for the standards (Table 1) were treated statistically. The lower and the higher pH values for the biphthalate and the sodium borate standards were, respectively, 3.986 and 4.046 and 9.177 and 9.238. The sample mean for the acidic solution was 4.0071 with standard deviation of 0.0213, and for the alkaline solution, 9.1986 with standard deviation of 0.0180. The interval obtained from the t-distribution was from -2.009 to 2.009. The values of T statistics were -0.9602 for the biphthalate solution and -0.5667 for the sodium tetraborate solution, both contained within the interval, indicating that the sample means were not significantly different from their theoretical values. The 95% confidence intervals for the means were (4.0012, 4.0130) for the biphthalate standard and (9.1936, 9.2036) for the sodium tetraborate standard.

The gradient of the plot of pH against time for the acidic solution, was 0.000025, resulting in -0.448 for the T statistics. In the case of the alkaline standard, the slope of this line was 0.000072, gives a value of -1.550 for the T statistics. In both cases, the values are within the interval (-2.009, 2.009) of the t distribution, indicating that neither slope was significantly different from zero. Thus, there is no statistical evidence that the pH of the solutions would be affected by decomposition up to 150 days of storage.

As calculated, measured (Table 1) and tested (Table 2), the solutions of: acidic potassium biphthalate (pH near 4.00) and basic hydrated borax solution (pH nearly 9.00) appear good choices as standards for the routine calibration of working pH meters (Figure 1).

It is known that the pH of acidic solutions, especially below 4, does not vary appreciably with temperature, but is rather variable with the concentration (Farmacopéia Bras., 1988; Camões et al., 1997; Lide, 2005). In contrast, alkaline solutions are more sensitive to temperature, and not so sensitive to dilution. Therefore, in
the calibration protocol, the alkaline solution should be used prior to the acidic biphthalate solution, as the latter will refine the calibration.

Also, the pH should be measured in moderately dilute solutions, in order to minimize errors that may occur mainly in the alkaline region (Baumann & Buchanan, 1991), with extremely dilute or highly concentrated solutions (Camões et al., 1997; Schneider, 2004; Lide, 2005).

This dilution effect was checked by measuring the pH of the standards, previously diluted to concentrations of 0.01 and 0.02 mol/L. In the case of the biphthalate buffer, the measurements of the pH become erratic. In the case of Borax, the pH not vary. However, in both cases, the solutions were less stable and decomposed or suffered changes in their pH upon storage. In this light, the use of concentrations lower than those indicated in Table 1, are not recommended.

We found that when the pH meter was maintained switched on in standby mode after calibration, even when not in use, its calibration remained stable for months.

During the development of these methods, it was observed that the use of small plastic (acrylic) vials (Figure 1) as recipients for the solutions is advantageous. They are inert and do not transfer alkali impurities to the solutions.

When not in use, the electrodes are stored immersed in nearly saturated potassium chloride. The acrylic vials do not suffer from the efflorescence phenomena (commonly observed on glass or Pyrex flasks). Simple addition of distilled water to the vial to complete the volume is sufficient to restore and re-activate the KCl electrolyte, which should not be frequently re-prepared (Figure 1).

Analytically pure KCl was used, or pharmaceutical grade KCl, previously purified by three successive recrystallizations from distilled water.

The recrystallization methods were also modified. As occurs with sodium chloride, potassium chloride has fairly similar solubilities in cold and boiling water, lowering the yields of the purification steps (Armarego & Chai, 2003). Ethanol was therefore used to precipitate the KCl from the aqueous solutions, considerably improving the yields of the purified salt.

The main advantages of these simple standard solutions, over the commercially available buffers are: they are completely stable (only two components, water and a single salt) and do not require refrigeration. Samples have been stored in the laboratory for months, at room temperature, without decomposition; they are simply prepared, from inexpensive chemicals; they are ideal ready-to-use standards, in stock solutions. They may be used directly.

The calculations of pH (Tables 1 and 2) were carried out using the software Bate, 2004, by entering general data (pK, equilibrium constants, among others) taken from Humeres et al. (1990); Camões et al., 1997; Armarego & Chai (2003); Schneider et al. (2004); Lide (2005); Mendonça et al. (2005). Sometimes, more specific data were used: e. g. Vanderboorgh (1968), for sodium fluoride.

The measured values agreed with the literature experimental values, but in some cases differed from the calculated values. It is important to remember that calculated theoretical pH values of common materials (not standards) are fully valid only for ideal solutions and frequently differ from the experimental values (Camões et al., 1997; Bate, 2004).

From the measurements displayed in Table 2, some interesting observations can be made:

The solution of sodium dihydrogen phosphate (Entry 1) is a good choice to “check” the calibration. In fact, the compound is known as a primary standard (Camões et al., 1997; Lide, 2005). Sodium carbonate (Entry 17) solutions are also good. We found that, although not commonly used as standards, sodium benzoate (Entry 2), sodium salicylate (Entry 15) and neutral potassium oxalate (Entry 3) may also be used as “check” buffers.

Sodium metasilicate (Entry 28) and sodium tripolyphosphate (Entry 29) are important compounds. They are strongly alkaline materials, the active ingredients of glassware cleaning agents (type Extran) and also used in powder detergents for dish washers or washing machines (Lakatos-Osório & Oliveira, 2001). Aqueous solutions of polyphosphates contain only ionized phosphates. The formula shown in Entry 29 is only valid for the solid salt. Also, sodium metasilicate may be partially or fully ionized in aqueous solutions.

Boric acid, H3BO3 (Entry 24) is a special case: it is a very weak triacid, with 3 pK values, but it is not ionized in water. Instead, it adds one molecule of water (Liu & Tossel, 2005) to form the ionic salt [B(OH)4]-+H, and this can liberate a proton, acting as a weak monoacid (Jeffery et al., 1989). The solution (variable pH) may contain a complex mixture (Liu & Tossel, 2005) of molecular species (metaboric acid, pyroborates, polyborates and boron clusters). In the extensive published data, the reasons for their “weak acid pH” is the subject of much controversy. In the Table 2, the pH was calculated using the “average” pK = 9.42, giving an approximate pH value.

Solutions of alkali metal (strong base) salts with strong acids are expected to be neutral. Solutions of KCl, NaCl can be nearly neutral (pH 7). However, when freshly prepared, KCl and NaCl solutions are acidic.

This is due to a complex set of phenomena (“Pfizer Theory”) related to ionic strength, removal or adsorption of solvation water, speed of ionization, differences in the number and concentration of ions, dissolved CO and proton ions and temperature. This field is known in the literature by the overall term “Solution Activity” (Vanderboorgh, 1968; Camões et al., 1997; Mendonça et al., 2003, Spitzer, 2003; Lide, 2005).

In a greatly simplified approach, for example, in freshly prepared KCl solutions, the very small protons (H+) may be de-solvated faster than the chloride ions or the potassium cations. The opposite is true in NaF, since OH is a strong base, stronger than the acidity of hydrofluoric
Protocol for pH meters calibration.

ACKNOWLEDGEMENTS

The authors thank to CNPq, FAPESP and CAPES for financial support and bursary grants. To FCFRP - USP, for special financial support of this work.

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