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RECOMMENDATIONS FOR THE ELECTROMETRIC DETERMINATION OF THE pH OF ATMOSPHERIC WET DEPOSITION (ACID RAIN)

(Technical Report)

Prepared for publication by

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Recommendations for the electrometric determination of the pH of atmospheric wet deposition (acid rain) (Technical Report)

Abstract

International studies to ascertain the extent of the environmental problems associated with the pH of atmospheric wet deposition (acid rain) are ongoing. Unfortunately, the measurement of pH in unbuffered, low ionic strength solutions, such as wet deposition, is prone to a variety of experimental difficulties which can compromise the validity of the data. Consequently, it is essential that all investigators use measurement procedures that are consistent and reproducible. This document provides recommendations on all aspects of the analytical process, including collection, handling and analysis of acid rain samples, to assure the quality and comparability of the resulting pH data.

INTRODUCTION

The pH of wet deposition, atmospheric precipitation, or, commonly, "acid rain" (which includes rainwater, snow, dew, sleet and hail), has become an environmental problem of international proportions. Extensive efforts are continuing to determine the extent of the problem and to ascertain spatial and temporal trends. To achieve these goals, international networks have been established to monitor and record accurately the composition of rainfall. Unfortunately, discrepancies in data often occur due to differences in instrumentation and analytical methodologies. These discrepancies limit the conclusions that can be drawn from these data. This is especially true of historical data sets which do not include sufficient documentation on the methods, accuracy, precision and quality assurance procedures to ascertain the validity of the data.

To this end, the purpose of this document is to provide a set of recommended procedures for the collection, handling and analysis of acid rain samples and for assuring the quality of the resulting pH data. The conscientious use of these procedures should result in greater comparability between laboratories and, consequently, improved reliability in data interpretation. As noted in the discussions below, there is still some disagreement among experts on some of the procedures listed. Accordingly, the recommended procedures represent the best compromise consistent with the current knowledge in this area. Furthermore, depending on the monitoring objectives, the frequency of sampling will vary. For example, weekly sampling may be appropriate for long-term trend evaluation, whereas sequential sampling within a single wet deposition event may be necessary to obtain information on scavenging processes.

The concept of pH, definition of pH scales, assignment of standard reference values, operational measurement, and recommended terminology have been discussed in detail in a previous IUPAC recommendation [1]. The present document differs only in describing the unique considerations relevant to pH measurements in unbuffered, very low ionic strength ($\leq 10^{-4}$ mol/L) solutions such as atmospheric wet deposition and boiler feed waters. Measurements of pH in these systems has been the subject of numerous research and review articles [2-11], and the purpose of this document is to bring together the best approaches, irrespective of national predilections. The most serious error in the measurement is associated with the residual liquid junction potential which includes an intrinsic bias term resulting from the operational definition of pH and an additional bias error associated with the method of construction and history of the liquid junction. By performing measurements on a quality control standard of dilute acid, a correction can be made to approximately compensate for these bias terms.

SUMMARY OF THE METHOD

The pH measurement system (pH/millivolt meter and associated electrodes) is calibrated with two reference buffer solutions that approximately bracket the anticipated sample pH range. The pH of the wet deposition sample is determined from this calibration and a quality control standard. The quality control standard is necessary in this application to evaluate the residual liquid junction potential bias and to correct for this bias. In addition, a test procedure is given to verify the proper functioning of the electrodes for measurement in dilute, unbuffered solutions. This procedure is capable of providing measurements of pH with an absolute accuracy of ± 0.03 and a precision of ± 0.02 .

SIGNIFICANCE OF THE PH MEASUREMENT AND ITS USE

The accurate measurement of pH in atmospheric wet deposition is an essential and critically important component in the monitoring of atmospheric wet deposition for trends in the acidity and overall air quality. However, special precautions, as detailed in this method, are necessary to ensure accurate pH measurements in low ionic strength, unbuffered solutions. Emphasis must be placed on the reference electrode and minimizing the effect of the residual liquid junction potential bias.

This method is strictly applicable only to the measurement of pH in atmospheric wet deposition. Its use in other applications may result in inaccuracies.

INTERFERENCES

The pH meter and the associated electrodes reliably measure pH in nearly all aqueous solutions and are generally not subject to solution interferences from color, turbidity, oxidants, or reductants.

The electromotive force between the glass and the reference electrodes is a function of temperature as well as pH of the solution. If measurements cannot be performed under constant-temperature conditions, e.g., in the field, temperature effects can be approximately compensated for automatically or manually depending on the type of pH meter used.

Although usually not a serious problem with acid rain samples, organic materials dispersed in water may foul the glass electrode surface, particularly when analyzing low ionic strength solutions. Difficulty encountered in standardizing the electrodes, erratic readings, or excessive response times may be an indication of contamination of the glass bulb or the liquid junction of the reference electrode.

The residual liquid junction potential can lead to very large errors in the measurement of low ionic strength samples. This error occurs when the junction potential of the sample differs from that of the standards. These conditions frequently occur in wet deposition analyses when the electrodes are calibrated with conventional standard reference buffers of moderate ionic strength. Other factors which influence the liquid junction potential are the junction configurations (free flowing vs. constrained), electrolyte leak rate, junction resistance, and flow-rate or "streaming" effects caused by solution flow past the electrodes [12].

To speed electrode equilibration, the sample should be agitated prior to taking a pH reading. Care must be taken, however, to avoid an error that can occur between stirred and unstirred wet deposition samples. It is recommended that this error be eliminated by agitating all calibration, quality control, and wet deposition solutions thoroughly to speed electrode equilibration and then allowing each solution to become quiescent before taking a pH reading. If magnetic stirring is used, take care not to contaminate the sample when inserting the stirring bar. Provide insulation or maintain an air space between the surface of the stirring motor and the sample container to prevent heating of the test solution.

APPARATUS AND EQUIPMENT

pH Meter -- The meter may have either an analog or digital display with a pH readability of at least 0.01. A meter that has separate calibration and slope adjustment features and is electrically shielded to avoid interferences from stray currents or static charge is necessary. It may be battery or AC line powered; if battery powered, the meter must have a battery check feature. A temperature compensator control for measurements at temperatures other than 25 °C is desirable.

pH Electrode -- Select a general purpose glass electrode which has a useful pH range of 2-11. This electrode should be used exclusively for atmospheric wet deposition measurements.

Reference Electrode -- The preferred reference electrode for wet deposition analysis is one equipped with a free-diffusion junction with cylindrical symmetry but, for the pragmatic reasons of availability and ease of operation, quartz-fiber and ceramic-frit junction electrodes are also recommended provided they meet the acceptance testing criteria (minimum performance characteristics) given below. Mercury/calomel and Ag/AgCl internal reference elements are satisfactory for these applications, although the calomel reference electrode is more prone to temperature hysteresis effects and care should be taken to avoid the formation of insoluble chlorides in the frit when used in dilute solutions [12]. This electrode should also be used exclusively for atmospheric wet deposition measurements.

Combination pH/Reference Electrode -- The combination electrode combines the indicating and reference elements in a single unit. A ceramic reference junction is recommended as noted above. Since sample volume requirements are often a consideration when analyzing limited-volume wet deposition samples, combination electrodes are more convenient than separate glass and reference electrodes. This electrode should be used exclusively for atmospheric wet deposition measurements.

Temperature Control -- Use either a constant temperature water bath, a temperature compensator, or a thermometer to verify that all standards and samples are maintained at temperatures within ± 2 °C of one another.

Stirrer (optional) -- This device may be electric, water- or air-driven. If an electric stirrer is selected, leave an air gap or place an insulating pad between the stirrer surface and the solution container to minimize heating of the sample. Use a thoroughly cleaned fluorocarbon-coated stirring bar. Alternatively, solutions may be manually stirred or swirled to enhance the rate of equilibration.

Electrode Storage -- When not in use, electrodes should be stored in a solution which maintains conditioning. It is recommended that glass electrodes be stored in a dilute acid or dilute buffer solution such as 10^{-4} M hydrochloric acid (ca. pH 4.00) or a 1:100 dilution of the pH 4.00 phthalate buffer. For ceramic-frit reference electrodes and combination electrodes storage in a KCl solution (≥ 3.5 mol/L and <saturated) containing ca. 5% of the diluted phthalate buffer (or dilute HCl) is recommended to maintain conditioning of the glass, to prevent the formation of a salt concentration gradient in the frit and to minimize the precipitation of calomel or silver chloride in the liquid junction pores [12]. Reference electrodes with free diffusion liquid junctions may be stored in more dilute KCl, e.g., 0.1 mol/L, since the junction is flushed prior to use.

REAGENTS AND MATERIALS

Purity of Reagents -- Use reagent grade chemicals for all solutions.

Purity of Water -- Use water conforming to ASTM Specification D 1193, Type II [13], or equivalent. Filters (0.2 micrometer) are recommended for all faucets supplying ASTM Type II water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions.

Buffer Solutions -- IUPAC phthalate reference value standard and 1:1 phosphate primary standard [1] or their commercially available equivalents must be used for calibration. These buffer solutions have nominal pH values of 4 and 7, the exact pH for the measurement temperature being provided by IUPAC [1] or by the supplier of the specific buffer. Store the reference buffer solutions in polyethylene or chemical-resistant glass bottles and replace after one year or sooner if a visible change such as the development of colloidal or particulate materials is observed.

Quality Control Sample (QCS) -- Quality control samples may be prepared by dilutions of stock volumetric acids with water.

Solutions of strong acids containing 0.1 to 1.0 mol/L, intended as volumetric standards and certified to $\pm 0.1\%$, are commercially available. They may be diluted to provide a 10^{-4} mol H⁺/L solution using gravimetrically calibrated pipettes and volumetric flasks. The pH of these solutions has been found not to be affected by the trace quantities of preservative (usually HgCl₂) which the volumetric acids sometimes contain. The final solution should be accurate to $\pm 0.2\%$, with a pH specified to ± 0.005 . The pH of these solutions is 4.005 for 10^{-4} mol/L HCl or HNO₃ and 4.006 for 5×10^{-5} mol/L H₂SO₄, assuming the solution is in equilibrium with atmospheric CO₂. The pH with respect to the calibration buffers is higher than p_{H+} according to the value of the residual liquid junction potential. Recent measurements under idealized conditions [8,14,15] indicate that the true pH is 4.035 ± 0.01 . Although measured at 20 °C, this value should be good for the range from 10 to 30 °C.

Other dilutions of acid may be made to prepare solutions in the pH range of 4 to 5. The p_{H+} of these solutions can be calculated from a knowledge of activity coefficients and the solubility of CO₂, but the pH, referred to standard buffer solutions, must be determined empirically, as consensus values have not yet emerged. As the pH approaches 5, its precise value becomes more sensitive to the partial pressure of CO₂, thereby reducing the reliability of the solution as a QCS.

The solutions should be stored at room temperature in a high-density polyethylene (HDPE) or polypropylene (HDPP) container. Various factors may affect the stability of these solutions which, due to their extreme dilution, have poor buffer capacities. The pH of the chosen quality control sample should be verified against the phthalate reference value standard on a daily basis.

Alternatively, quality control samples of verified pH in an atmospheric wet deposition matrix are available from the U.S. National Institute of Standards and Technology as Standard Reference Material (SRM) 2694, "Simulated Rainwater" [10,16].

SAMPLE COLLECTION, PRESERVATION AND STORAGE

Although darkened, borosilicate glass bottles have been recommended for the collection and storage of natural freshwater to prevent photosynthesis and gas exchange [5], rainwater normally contains minimal microbial populations and the low pH (≤ 5) precludes significant CO₂ effects. Consequently, it is recommended that wet deposition samples be collected in high-density polyethylene containers that have been thoroughly rinsed with distilled water. Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample. Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection bottles after cleaning to prevent contamination from airborne contaminants; air dry collection buckets in a laminar-flow clean air workstation (if available) and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any

residual rinse water and bag the buckets immediately. Do not dry the bucket interior by any method other than air drying in a clean air workstation.

The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from subevent to monthly sampling periods. However, collection periods of more than one week are not recommended since sample integrity may be compromised by longer exposure periods. For detailed siting and sample collection recommendations, refer to: "Analysis of Wet Deposition (Acid Rain): Determination of the Major Anionic Constituents by Ion Chromatography" [17].

The dissolution of particulate materials and the presence of microbial activity will affect the activity of hydrogen ions (pH) in wet deposition samples [5,18]. This source of error becomes more significant as the sample acquisition time increases. Samples which can not be analyzed immediately after collection should be refrigerated at 4 °C. This will minimize, but not prevent, changes in the hydrogen ion content.

For samples collected over longer periods or where particulate contamination is a problem, filtration of samples through a water-leached 0.45 micrometer membrane is effective at stabilizing pH values that are influenced by the dissolution of alkaline particulate matter [19].

CALIBRATION

Turn on the pH meter and allow it to stabilize according to the manufacturer's instructions.

If necessary, add filling solution to the reference electrode before using. Maintain the filling solution level at least 2 cm above the level of the sample surface to ensure an adequate flow of electrolyte through the constrained liquid junction. For a free-diffusion junction, before contacting the sample solution, flush the junction with the salt bridge electrolyte to provide a fresh liquid junction interface with the sample solution.

Bring the nominal pH 4 and 7 buffers, the QCS solution, and all wet deposition samples to the same temperature, to within 2 °C.

Caution: Take extreme care to avoid cross contamination, i.e., carryover, of the solutions.

Calibration Function:

- a) Rinse the electrodes with three aliquots of distilled water or with a flowing stream from a wash bottle. Dispense two aliquots of the buffer with the higher pH (i.e., pH = 7) into separate, clean sample cups. Insert the electrodes into one aliquot with agitation for 30 seconds.
- b) Remove the electrodes from the first aliquot and insert directly into the second. Allow sufficient time for the pH reading to stabilize within ± 0.01 for 30 seconds.
- c) Adjust the calibration control until the reading corresponds to the temperature-corrected value of the reference buffer solution.

Slope Function:

a) Rinse the electrodes with three aliquots of distilled water or with a flowing stream from a wash bottle. Dispense two aliquots of the second reference buffer solution into separate, clean sample cups. Insert the electrodes into one aliquot with agitation for 30 seconds.

b) Remove the electrodes from the first aliquot and insert directly into the second. Allow the system to equilibrate as directed above.

c) Adjust the slope function until the reading corresponds to the temperature corrected value of the reference buffer solution. The slope function should be between 98% and 102% of the theoretical Nernstian response.

Note - Some of the possible causes for deviation from Nernstian response include [12]:

- i) improper calibration procedure,
- ii) old, contaminated or improperly prepared buffer solutions,
- iii) insufficient rinsing of the electrodes between solutions,
- iv) fouled reference junction,
- v) defective electrode(s),
- vi) defective meter.

It may be necessary to replace one or both of the electrodes if the non-Nernstian behavior persists even with accurately and freshly prepared buffer standards.

Calibration Check:

Remove the electrodes from the second buffer, rinse thoroughly, and place into the first reference buffer solution. If the pH does not read within ± 0.01 of the temperature-corrected value, repeat the calibration procedure until the buffer readings agree.

QUALITY CONTROL

It is recommended that electrodes used for the measurement of wet deposition samples should not be used for other sample types. Strongly acidic or basic solutions may cause electrode contamination or degradation and result in biased measurements and/or slow response in wet precipitation samples. Similarly, samples containing high concentrations of organic matter may leave a residue on the pH glass membrane surface resulting in slow electrode response.

Individual laboratory quality control practices should establish the limits of acceptable bias and establish the conditions under which the correction for bias need not be applied. It is recommended that the data obtained from the QCS checks be plotted on a control chart for routine assessment of bias and precision.

QCS measurements should be made after every ten samples or after completion of a batch of samples consisting of less than ten. If the measured pH of the QCS has changed by more than 0.03, reanalyze all samples since the last QCS check.

VERIFICATION OF ELECTRODE PERFORMANCE

After the meter and electrodes have been calibrated, measure the pH of the quality control sample (QCS). This sample of dilute HNO_3 (see Reagents Section above) should be freshly prepared each day. Verify the pH of the QCS by direct comparison with the phthalate reference buffer solution. The difference between the measured pH of the QCS and reference value constitutes the bias of the pH measurement system. All measured values of the pH of subsequent wet deposition samples should be corrected for this bias by subtracting this difference from the measured value. If the pH bias exceeds 0.1, the electrodes are not acceptable for wet deposition measurements and should be replaced.

In addition, the pH readings should be relatively independent of solution stirring effects. If a pH shift of more than 0.02 is observed between a stirred and quiescent dilute acid solution, it is likely due to a malfunction of the reference electrode. If, after attempted rejuvenation (refill with fresh KCl solution and soak the junction for several hours in concentrated KCl), the electrode still exhibits an excessive pH shift upon stirring, the reference electrode should be discarded.

MEASUREMENT PROCEDURE

Bring all solutions to the same temperature (± 2 °C).

Calibrate the electrode assembly with two reference buffer solutions as described above.

After the electrodes and meter are calibrated, determine the bias by analyzing a QCS sample using the same procedure as given below for rainwater samples.

Sample Analysis:

a) Rinse the electrodes with three aliquots of water or with a flowing stream from a wash bottle. Dispense two aliquots of atmospheric wet deposition sample into separate, clean sample cups. Insert the electrodes into one aliquot and agitate for 30 seconds to condition the electrodes.

b) Remove the electrodes from the first aliquot and insert directly into the second, once again agitating for 30 seconds, then allowing the solution to become quiescent (approximately 30 seconds) and the pH reading to stabilize. The pH electrode response time is typically three to five minutes for acid rain samples. Record the pH measurement when readings differ by no more than ± 0.01 within a 30 second period. Record the pH and the temperature of the sample. Correct for the bias and report the corrected value as the pH of the wet deposition sample.

SUMMARY

The measurement of pH in low ionic strength, unbuffered solutions such as atmospheric wet deposition is prone to a variety of experimental difficulties which can compromise the validity of the data. However, if the procedures discussed above are conscientiously followed, the reliability of the data acquired will be considerably increased permitting valid intercomparisons of results.

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