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ACTIVITY/PROJECT SPECIFIC PROCEDURE

SP 12-14
USE OF pH METERS AND ELECTRODES
Revision 4

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1.0 Purpose and Scope

This document describes the Sandia National Laboratories (SNL) Waste Isolation Pilot Plant (WIPP) procedure for use of pH meters and electrodes. Calibration and operation guidelines are included in the procedure. This SP is in support of activities described in several WIPP Test Plans (TPs). Both SNL and contractor personnel will use this SP.

Acronyms and definitions for terms used in this procedure may be found in the Glossary located at the Sandia National Laboratories (SNL) WIPP Online Documents web site.

2.0 Implementation Actions

Several different models and brands of pH meters and electrodes will be used for the experimental work in support of the WIPP-related studies. This document is not meant to substitute for the manufacturer instruction manuals for the pH meters and electrodes. The user is responsible for reading and understanding the appropriate manuals. Guidelines for implementing and documenting quality assurance (QA) procedures are presented in this document, and follow the general guidelines given in Nuclear Waste Management Procedure (NP) 12-1 "Control of Measuring and Test Equipment."

2.1 Safety and Training

The activities described in this SP shall conform with SNL Environmental Safety and Health programs (ES&H). This document does not address ES&H issues. Laboratory ES&H procedures and specific instrument hazards are described in laboratory-specific TWDs and JSAs, which can be found at the WIPP Online Documents website.

2.2 Responsibility

The Principal Investigator (PI), or designee, whose activities warrant the use of this procedure, is responsible for implementing the requirements of this procedure.

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The PI or designee is responsible for performing the calibrations and measurements following the requirements of this procedure, documenting calibrations, and assuring that the latest revision of this document is followed.

2.3 pH Meter and Electrode Selection

The PI or designee will ensure that the pH meter and electrode are of the proper type, design, range, accuracy, and tolerance to accomplish their required function.

2.4 Identification

The pH meters and electrodes are identified by manufacturer, model number, and serial number, if applicable. When not supplied with a serial number, the electrodes will each be assigned a permanent number that will be recorded in the laboratory notebook, when that electrode is used.

2.5 Electrode Preparation

The electrode must be upright and the level of the electrode fill solution must be at least one inch above the sample level on immersion. Only use the electrode filling solution that is specified by the electrode manufacturer (refer to specific electrode operating instructions).

2.6 Calibration

2.6.1 Standards

Calibration will be performed using commercially obtained pH standard buffer solutions that are traceable to NIST or other nationally recognized standards. The identity, manufacturer, lot number and expiration date of the standards used shall be recorded. A minimum of two standards shall be used for the pH meter calibration, unless specified by the instrument manual.

A pH standard buffer solution will not be used past its expiration date listed on the container by the manufacturer.

The pH buffer solutions are chosen so that their values bracket the values of the samples to be measured. If the pH values of the samples exceed those of the standards by more than 0.1 pH unit, the meter must be recalibrated with the appropriate buffer or a justification to not recalibrate must be recorded.

2.6.2 Temperature

Under normal operating conditions pH measurements are made under ambient room temperature and recording of the temperature is not required.

However, if the instrument requires entering a temperature or if measurements are being conducted at temperatures other than ambient room temperature, a calibrated or calibration-checked thermometer shall be used to measure the room temperature and the value recorded in the Scientific Notebook. Samples and buffers shall be given sufficient time to equilibrate to this temperature. The temperature of a solution will be re–measured and recorded, if it suspected that it has changed (e.g. stirring bar). The temperature will be entered into the pH meter (if required), and/or the temperature corrected values of the pH buffers will be used.

2.6.3 Frequency

The instrument will be calibrated on the day of use, prior to use. It will also be calibrated immediately before use if instrument irregularities are observed.

Alternatively, if the user desires to maintain precision over the course of an experiment that lasts more than one day, the user can perform a performance test using a minimum of two pH buffers that bracket the expected pH range. These performance tests will be documented in the applicable scientific notebook as well as noting the use of the previous calibration (i.e. the slope). All requirements of this procedure apply including that a performance test will be performed every two hours as applicable (Section 2.6.5).

2.6.4 Acceptance Criteria

The pH meter calibration is acceptable when the slope response of the instrument is between 92 and 102%.

2.6.5 Performance Test

A performance test will be performed immediately after calibration. The performance test is performed by measuring the pH of an appropriate pH standard buffer solution. The pH meter will be recalibrated if the performance test shows that the difference between the pH of the measurement and the known pH of the buffer is greater than 0.1. If the analysis lasts for more than two hours, the calibration will be verified by performing another performance test. The start and stop time of the pH analysis will be recorded in the scientific notebook.

2.6.6 Troubleshooting

If the pH meter and electrode cannot meet the acceptance criteria (see Section 2.6.4), the pH standard buffer solution is replaced and a subsequent calibration is attempted. If the pH meter still does not meet the acceptance criteria, the filling solution of the electrode will be replaced or another electrode will be used. If the pH meter still cannot meet the acceptance criteria, the meter will be either repaired or replaced and labeled accordingly.

2.7 pH Measurement

The electrode shall be rinsed with de-ionized water and gently patted dry with a lint–free tissue prior to measurement.

The sample will be gently stirred to obtain an optimum equilibrium between the electrode and sample to be tested. The electrode is dipped in the sample. The pH can be read off the pH meter after stabilization of the system, indicated by most pH meter models. If the pH meter is not equipped with a readiness indicator, the pH value is collected when visual stabilization of the pH value is obtained. The minimum acceptable equilibration time is 30 seconds.

2.8 pC_{H+} Correction

The pC_{H+} (negative logarithm of H^+ concentration) is a critical parameter used for calculating geochemical equilibria in electrolyte solutions, especially the high ionic strength brines relevant to the WIPP geochemistry model. The H^+ concentration is typically determined via pH measurements in the solutions of interest. However, the measurement of pH in high ionic strength solutions using standard National Bureau of Standards (NBS) operational methods does not provide an accurate measure of the H^+ concentration due to a number of factors such as potentially large liquid-junction potentials and

the formation of species such as HSO_4^- and $H_2B_4O_7$ that can consume H^+ during electrode standardization (see Roselle, 2011, and references therein).

Rai et al. (1995) have shown that the H^+ concentration in unknown samples of a given electrolyte (e.g. NaCl) at a fixed molarity can be estimated using the following relation:

$$pC_{H+} = pH_{obs} + A \quad (1)$$

where pH_{obs} is the measured pH reading of the unknown sample with a calibrated combination glass electrode, and A is obtained empirically through a modified Gran titration. Based on the summary of Roselle (2011) for multiple Gran titrations in brines relevant to the WIPP geochemistry studies one of two expressions can be used to determine the pC_{H+} correction factor (A). For NaCl-dominated brines, $MgCl_2$ brines or more complex brines (i.e. GWB, ERDA-6) that do not contain significant concentration of Na_2SO_4 the following expression is to be used:

$$A_{NaCl} (\pm 0.47) = 0.186\ I_M - 0.105 \quad (2)$$

where A_{NaCl} is the correction factor to be used in Equation (1) and I_M is the molar ionic strength of the solution. This expression is valid for ionic strengths up to 8.0 M. For Na_2SO_4 –dominated brine the appropriate expression is:

$$A_{Na2SO4} (\pm 0.09) = 0.0332\ I^2_M - 0.203\ I_M - 0.016 \quad (3)$$

where A_{Na2SO4} is the correction factor to be used in Equation (1) and I_M is the molar ionic strength of the solution. This expression is valid for ionic strengths up to 6.0 M.

These expressions are valid for all makes of combination glass pH electrodes. If a new pH electrode is obtained it may be checked against the above expression using the procedure outlined in Appendix A at the discretion of the Principal Investigator (PI), or designee.

The procedure outlined in Appendix A may also be used to determine a pC_{H+} correction factor (A) for brines not covered by Equations (2) and (3). In this case all titration data and pertinent data analysis shall be documented in a scientific notebook.

2.9 Maintenance

The pH meters shall be stored so as to minimize their exposure to dusty, corrosive, or excessively humid environments, temperatures outside the range of 0–40ºC, and mechanical shock and vibration.

The pH standard buffer solutions shall be stored in containers that do not alter the pH of the solutions (e.g. polyethylene). The solutions must be protected from the sunlight and stored at temperatures between 15º C and 30º C (as per manufacturer recommendations). Containers shall have lids and caps to prevent spillage and evaporation.

The electrode shall be stored by soaking it in commercial electrode storage solution or if storage solution is not available, use 200 mL pH 7 buffer to which about 1 gram of KCl has been added, as a temporary substitute. When not in use, the cap covering the filling solution hole of the electrode shall be covered at all times unless re-filling of the electrode is required.

2.10 References

Rai, D., Felmy, A.R., Juracich, S.P., and Rao, F. (1995) *Estimating the hydrogen ion concentration in concentrated NaCl and Na_2SO_4 electrolytes*. SAND94-1949, Albuquerque, NM: Sandia National Laboratories.

Roselle, G.T. (2011) *Determination of pC_{H+} Correction Factors in Brines*. Milestone Report, December 1, 2011. Carlsbad, NM: Sandia National Laboratories. ERMS 556532.

3.0 Records

The following records generated through implementation of this procedure shall be prepared and submitted to the WIPP Records Center in accordance with NP 17-1, “Records”.

QA Record

- Scientific Notebook

4.0 Appendices

Appendix A: Determination of the pC_{H+} Correction Factor

Appendix A
Determination of the pC_{H+} Correction Factor

A.1 Equipment and Materials Required

- pH meter equipped to read out in pH units to a precision of at least 0.01 units.
- Combination glass pH electrode
- pH buffer solutions to cover range of measurements (typically pH 2 to 10)
- Standardized HCl or NaOH solutions, 0.01 M to 1.0 M
- Class A (or equivalent) pipette, 50.0 ± 0.1 mL
- Titration vessel with cover
- Burette or pipette capable of delivering titrant accurate to 0.005 mL
- N_2 gas for sparging

A.2 Determination of pH Electrode Response in Brines

A.2.1 Calibrate pH electrode and meter using pH according to requirements in Section 2.6 of this procedure. Record calibration results in the appropriate Scientific Notebook.

A.2.2 Deliver 50.0 ± 0.1 mL brine into a titration vessel for each calibration. Sparge with an inert gas (e.g. N_2) for 5 minutes before beginning titration. Continue sparging throughout the titration procedure. In addition, the solution should be continuously stirred.

A.2.3 Add standardized HCl to the titration vessel containing the sparged brine solution until an appropriate pH change is observed. Select the molarity of the HCl so that:

A.2.3.1 the volume of acid added can be accurately measured to observe pH changes and

A.2.3.2 the total volume of acid used by the end of the titration is far less than 10% of the original volume of the brine used for titration. This ensures that the addition of the titrant will not significantly alter the brine composition during the titration.

A.2.4 Add HCl titrant in increments of approximately 50 to 100 μL. Record both the measured pH and the corresponding volume addition of standardized HCl for each step in the appropriate Scientific Notebook.

A.2.5 Rai et al. (1995) showed that the correction factor A can also be determined using modified Gran titrations with NaOH as the titrant. In this case follow steps A.2.1 through A.2.5 substituting NaOH for HCl. It should be noted that the presence of OH^- consuming species in brines for which A is to be determined using base titrations will require special consideration similar to sulfate and borate for acid titrations. For WIPP-relevant brines (especially GWB) the presence of significant quantities of magnesium will result in precipitation of $Mg(OH)_2$, which must be accounted for if base titrations are used.

A.3 Calculation of pC_{H+} Correction Factor (A)

The pC_{H+} correction factor, A, can be obtained from the Gran titration data by plotting the moles of added free H^+ per liter ($H^+_{free,add}$) against the observed H^+_{obs} (i.e., 10^{-pHobs}). The logarithm of the slope of this curve is the correction factor A needed to convert the measured pH reading to pC_{H+}. The following sections explain the method of calculating the added free H^+ per ($H^+_{free,add}$) for different brine

types. A plot of H^+_{obs} versus $H^+_{free,add}$ should result in a linear trend. However, the presence of small amounts of impurities such as soluble bicarbonate may consume minor amounts of H^+ at the beginning of a titration resulting in non-linear behavior at low values of $H^+_{free,add}$. These portions of the plots should not be used in determining the slope of the data trend.

A.3.1 *NaCl Dominated Brines* - In brines dominated by NaCl and without significant concentrations of other species (e.g. SO_4^{2-} or $B_4O_7^{2-}$) that can consume added H^+ during an acid titration, the amount of acid added during titration should correspond to the free H^+ added ($H^+_{free,add}$). The free H^+ added in moles per liter can then be determined with the following formula:

$$H^+{}_{free,add} = \frac{V_{add} N}{V_i + V_{add}} \tag{A1}$$

where V_i is the volume of brine added to the titration vessel (ml), V_{add} is the volume of standardized acid addition (ml), and N is the normality of the standardized HCl solution.

A.3.2 *Na_2SO_4 Brines* – In brines containing Na_2SO_4 the addition of HCl results in the formation of bisulfate ions (HSO_4^-). The concentration of HSO_4^- that is formed is dependent on the total sulfate concentration of the brine and the amount of acid added. Because bisulfate formation can consume a significant quantity of added H^+ and it becomes necessary to account for bisulfate formation when determining the correct value of $H^+_{free,add}$. In this case the amount of free H^+ added to solution is calculated using the equation:

$$H^+{}_{free,add} = \frac{H^+{}_{add}}{1 + K_{app}\left[SO_4{}^{2-}\right]} \quad H^+_{free,add} = \frac{H^+_{add}}{1+K_{app}[SO_4^{2-}]} \tag{A2}$$

where H^+_{add} is calculated according to Eq. (A1) for borate-free brines or Eq. (A4) for borate-containing brines, $[SO_4^{2-}]$ is the molar free sulfate concentration of the brine and K_{app} is the apparent molar equilibrium constant for the bisulfate formation reaction:

$$H^+ + SO_4{}^{2-} = HSO_4{}^- \tag{A3}$$

K_{app} is determined for the Na_2SO_4 concentration of interest using the Pitzer thermodynamic model. The method used to calculate K_{app} is discussed in Section A.4.

A.3.3 *Borate Brines* –As with sulfate brines, the addition of acid to brines containing borate will result in significant consumption of added H^+ due to the formation of $H_2B_4O_7$. Here again the consumption of added HCl by borate complexes must be accounted for when calculating $H^+_{free,add}$. Because the formation of borate species is rather complex the "K_{app}" method used for sulfate brines is not practical and an empirical approach is used. In this case the equivalence point for $H_2B_4O_7$ formation must be determined in a separate titration using the same volume of brine and standardized acid concentration as will be used in the Gran titration. This is done by adding an indicator solution (e.g. methyl orange) to the brine and titrating acid into the brine until a color change of the indicator is observed. In some cases the equivalence point was determined empirically based on a visual estimate of the inflection point in a plot of solution pH versus amount of acid added. The equivalence point occurs at a pH of approximately 5 for ERDA-6 brines and 3 for GWB brines. From this equivalence point determination the volume of acid required to reach the equivalence point is used to calculate $H^+_{free,add}$ as follows:

$$H^{+}{}_{free,add} = \frac{(V_{add} - V_{eq})N}{V_i + V_{add}} \tag{A4}$$

where V_{eq} is the volume (ml) of acid added to reach the equivalence point and all other variables are as defined for Eq. (A1).

A.3.4 *Borate Brines* –When NaOH is used as a titrant a different formulation must be used to calculate $H^{+}_{free,add}$ that accounts for the dissociation of water. The amount of NaOH added during the titration is converted to $H^{+}_{free,add}$ through the equation:

$$H^{+}{}_{free,add} = \frac{K_w}{OH^{-}{}_{add}} \tag{A5}$$

where K_w is concentration-dependent dissociation constant of water and OH^{-}_{add} is determined by:

$$OH^{-}{}_{add} = \frac{V_{add} N}{V_i + V_{add}} \tag{A6}$$

where V_i is the volume of brine added to the titration vessel (ml), V_{add} is the volume of standardized base addition (ml), and N is the normality of the standardized NaOH solution. K_w is determined for the brine concentration of interest using the Pitzer thermodynamic model. The method used to calculate K_w is discussed in Section A.4.

A.4 Calculation of Apparent Equilibrium Constants

The determination of $H^{+}_{free,add}$ for acid titrations in brines containing sulfate and for all titrations using NaOH requires the calculation of appropriate equilibrium constants. This includes the equilibrium constant for bisulfate formation via the reaction given in Eq. (A3) and the dissociation constant of water, both of which are dependent on the composition of the brine. The Pitzer thermodynamic model is used to calculate these constants for each brine of interest with the EQ3/6 version 8.0a geochemical modeling program. The bulk composition of each brine is input into EQ3 in molal units, which then calculates the equilibrium distribution of the various chemical species in the brine. The needed equilibrium constants are then calculated from the results using the following relations for bisulfate formation and water dissociation, respectively:

$$K_{app} = \frac{[HSO_4^{-}]}{[H^{+}][SO_4^{2-}]} \tag{A7}$$

$$K_w = [H^{+}][OH^{-}] \tag{A8}$$

where the values in brackets are the molar concentrations of the indicated species. It should be noted that the EQ3 program reports the concentration data for each species in units of mole per kilogram water (molal). However, the Gran titration method requires the use of molar (mole/L) values for calculating the equilibrium constants. In order to calculate the appropriate K_{app} and K_w values the molar to molal ratio (M/m) reported by EQ3 for each brine is used to convert the concentrations of the species of interest from molal to molar.

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