PLANT OPERATIONS MANUAL

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CHEMISTRY INSTRUCTION

DEVELOPMENT AND USE OF CALIBRATION CURVES FOR CHLORIDE DETERMINATIONS UTILIZING CHLORIDE ELECTRODES

SAFETY RELATED

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1.0 PURPOSE

For development and use of calibration curves for chloride determinations using the Graphic Controls ultra-sensitive (or eqivalent) and the Lazar micro chloride eletrodes. This instruction pertains to chloride concentration from 20 ppb to 1000 ppm.

2.0 REFERENCES

2.1 Standard Methods, 15th Edition, 1980

2.2 Chemistry Procedure 08-S-03-1, Qualification of Chemistry Program

2.3 Chemistry Instruction 08-S-04-109, Operation of Orion 701 Ion Analyzer

2.4 Chemistry Instruction 08-S-04-466, Potassium Chloride Standard

2.5 Applicable Manufacturer's Technical Manuals for Instruments and Electrodes

2.6 Chemistry Instruction 08-S-04-443, Ionic Strength Adjuster (ISA) and Filling Solution with FSIE and Double Junction Reference Electrode

2.7 Chemistry Instruction 08-S-04-468, Potassium Nitrate

3.0 DEFINITIONS

3.1 Immersion Depth - Immersion depth, with the Lazar micro ion electrode, should be adjusted to conform to the sample size. For samples of 1 ml or greater, the electrode sensing element can be completely immersed. For extremely small samples, the electrode can just barely be immersed to allow contact between the solution being measured and the electrode sensing element.

3.2 Ionic Strength Adjuster (ISA) - ISA should be added to both samples and standards whenever possible. If sample size is in the low microliter range, making the addition of ISA very difficult, then standards should not contain any ISA.

3.3 Standard Solutions - Volume of standards should be close to that of the samples.

3.4 Stirring - Stirring with a stirring bar becomes impractical for samples below 10 ml and, therefore, should not be done. Response time in unstirred solutions will be somewhat longer than in stirred solutions. If sample solutions are not stirred, then standard solutions should not be stirred.

3.5 Shaking - Shaking is possible when using the chloride analysis chamber in conjunction with the Lazar electrodes. Also, sample and standard solutions in micro dishes may be gently agitated except where there is a possibility of radioactive concentration, should a high radiation sample be spilled.

4.0 PREREQUISITES

4.1 Apparatus Required

4.1.1 Graphic Controls (or equivalent) ultra-sensitive chloride electrode and Orion (or equivalent) double junction reference electrode

4.1.2 Lazar micro chloride electrode and Lazar micro, double junction reference electrode

4.1.3 pH/mV meter

4.1.4 Orion electrode swit h

4.1.5 Chloride analysis chamber

4.1.6 Beakers, various sizes

4.1.7 Micro dishes

4.1.8 Pipets, various sizes

4.2 Reagents Required

4.2.1 Potassium nitrate, KNO_3, 10% (pH adjusted to 12 with KOH)

4.2.2 Sodium nitrate, $NaNO_3$, 5M

4.2.3 Ultrex nitric acid, HNO_3, concentrated

4.2.4 Chloride standards, 20 ppb to 1000 ppm

4.2.5 Demineralized water

4.3 Attachments

4.3.1 Attachment I - Orion 90-02 Double Junction Reference Electrode

4.3.2 Attachment II - Lazar DJM-146 Micro Double Junction Reference Electrode

5.0 PRECAUTIONS

5.1 The outer solution (10% KNO_3) of the double junction reference electrode must be changed daily. Check pH of outer solution (pH = 12). Initial card attached to instrument for daily verification.

NOTE

The KNO_3 for the Lazar electrode is a special gelled KNO_3.

5.2 The Cl- and reference electrodes must be stored separately.

5.2.1 Store the Cl-electrodes in a solution made from 100 ml demineralized H_2O and 100 λ ultrex HNO_3.

5.2.2 Store the Graphic Controls' reference electrode in demineralized H_2O.

5.2.3 Store the Lazar's reference electrode in 10% KNO_3.

5.3 Do not use the Cl-electrodes in the presence of silver or sulfide.

5.4 The Graphic Controls, or equivalent, electrode is designed for very low levels of chloride. It should not be used in samples or dilutions if the chloride concentration is expected to be greater than 1 ppm. Instead, dilute farther, or use the Lazar micro electrode.

5.5 Exercise care when handling the electrodes to prevent contaminating the electrodes with chloride or greasy substances.

6.0 INSTRUCTIONS

6.1 Refill the chambers of the Orion (or equivalent) double junction reference electrode as follows:

6.1.1 Outer Chamber (Refill Daily When in Use)

a. Tip the electrode so that the filling solution moistens the green O-ring (see Attachment I) on the electrode's body.

b. Holding the electrodes by the cap in one hand, push the outer sleeve up into the cap with the other hand, allowing the filling solution to drain out.

c. With the outer sleeve pushed up into the cap, flush the chamber once or twice with 10% KNO_3 through the outer chamber filling hole.

d. Assure the outer sleeve is flush with the inner cone.

e. Fill the outer chamber with 10% KNO_3.

NOTE

The level of the outer chamber filling solution must be at least one inch above the sample solution in the beaker, and the level of the inner solution must always be at least one inch above the level of the outer solution.

6.1.2 Inner Chamber (Refill weekly when in use)

a. Unscrew the electrode cap and remove the two springs and contact assembly.

NOTE

It is not necessary to remove the outer sleeve to drain the inner chamber.

b. Remove the inner chamber filling solution by:

(1) Inserting the spout of a partially emptied flip-spout bottle into the inner chamber filling hole, holding the bottle upright, the electrode upside down with the vent hole pointed in the desired direction of dispersal, and squeezing the flip spout bottle to cause the inner solution to spurt out of the chamber vent, or

(2) Turn the electrode upside down, insert the needle of a hypodermic syringe into the filling hole and withdraw the filling solution into the syringe.

c. Refill the inner chamber through the filling hole with fresh 90-00-02 Orion (or equivalent) filling solution.

d. Replace the syringe and contact assembly, then screw the cap on to finger tightness.

6.2 Refill the outer chamber of the Lazar double junction reference electrode as follows:

6.2.1 Remove the silicone gasket and wash the bottom chamber with deionized or distilled water (see Attachment II).

6.2.2 With the electrode held upside down, slowly add the jelled KNO_3 filling solution to the bottom chamber, being careful not to trap air bubbles.

6.2.3 Fill the chamber to approximately 1/8 of an inch from the opening.

6.2.4 Remove the cap from the electrode tip and carefully replace the silicone gasket.

6.2.5 Using the silicone gasket in a manner similar to using a hypodermic syringe plunger, push some solution out of the electrode tip.

6.2.6 Check the teflon tubing for air bubbles and remove the air bubbles by continuing to press the gasket inward until the air bubbles are expelled, being careful not to push the gasket so deep that it becomes difficult to remove.

NOTE

If the air bubbles could not be removed without jamming the gasket, remove the filling solution from the electrode chamber and repeat steps 6.2.3 through 6.2.6 until no air bubbles are present.

6.2.7 Rinse the electrode and tip with demineralized water, wipe the tip with tissue, and insert the electrode plug into the reference electrode jack in the pH/mV meter or the appropriate jack in the Orion electrode switch.

6.3 Calibration Curves

6.3.1 Ensure startup of the Orion 701-A Ion Analyzer in accordance with Reference 2.3.

6.3.2 Verify functional check performed within the proper time frame as stated in the Calibration Functional Check Log Book.

6.3.3 Verify outer solution of the double junction reference electrode has been changed and the inner solution is at the required level.

6.3.4 Select the channel corresponding to the electrode to be used and ensure Orion 605 electrode switch is energized.

6.3.5 Rinse the specific ion and reference electrode in demineralized water.

6.3.6 Graphic Controls (or equivalent) Chloride Electrode and Orion (or equivalent) Reference Electrode

a. Place 100 ml of demineralized H_2O into a 150 ml beaker containing a magnetic stirring bar.

b. Immerse the chloride and double junction reference electrode in the water.

c. Turn the Orion 701-A selector switch to the MV position, start the magnetic stirrer, and pipet 0.100 ml of Ultrex HNO_3 into the water. Stir for 30 seconds. The solution is now adjusted to a pH of approximately 2.0.

NOTE

The curve can be generated up to 1 ppm; however, as the amount of standard is added to the beaker, the volume and, consequently, the pH of the solution may be affected. To preclude problems in this area, limit the curve to 1 ppm.

NOTE

The lower limit of the curve should be that level that can be proven repeatable. The electrode is most reproducible at a lower level of 20 ppb, therefore the lower chloride concentration should be established there.

d. At exactly 30 seconds after step 6.3.6.c, pipet 0.100 ml of the 20 ppm chloride standard to the breaker of step 6.3.6.c.

e. Stir for 30 seconds and record mV.

NOTE

Each additional 0.100 ml increases the Cl- concentration by 20 ppb.

f. Repeat steps 6.3.6.d and 6.3.6.e over the range desired.

Example:

1st addition of 0.100 ml of 20 ppm Cl- to the solution = 20 ppb

2nd addition of 0.200 ml of 20 ppm Cl- to the solution = 60 ppb

3rd addition of 0.200 ml of 20 ppm Cl- to the solution = 100 ppb

4th addition of 0.500 ml of 20 ppm Cl- to the solution = 200 pbb

g. Plot the mV potential versus concentration on appropriate graph paper, with mV reading along the X-axis, and concentration along the Y-axis.

6.3.7 Lazar Micro Chloride and Reference Electrodes

a. Do steps 6.3.1 through 6.3.4.

b. Soak the chloride electrode in a 100 ppm chloride solution for 10 minutes.

c. Rinse the electrodes in demineralized water.

NOTE

Calibration curves using larger volumes (to 100 ml) than those that follow may be generated simply by adjusting, proportionately, the volume of Ultrex HNO_3. When total volume of sample plus Ultrex HNO_3 is 10 ml, add 0.2 ml of ISA (5M $NaNO_3$). Increase the addition of ISA proportionately with increasing volume.

NOTE

The purpose of the Chloride Analysis Chamber (CAC) is to prevent exposing high radiation samples to the atmosphere. When preparing a calibration curve for the CAC, the steps performed should duplicate those steps taken during the analysis.

NOTE

If the calibration curve to be generated is to be done using a micro dish, proceed to step 6.3.7.e.

d. Using the CAC

(1) Assure that the pH/mV meter is set to STANDBY.

(2) Screw the cap containing the Lazar chloride electrode and reference electrode onto the CAC.

(3) Using a 0.025 to 0.100 ml pipet, carefully add 1 drop of Ultrex HNO_3 through the pipet port of the CAC.

(4) Place a rubber septa onto the pipet port.

(5) Using a gas tight syringe, evacuate 0.100 cc (or greater) of air from the chamber.

NOTE

Always evacuate a volume of air equal to or greater than the volume of sample.

(6) Using the gas tight syringe, pipet 0.100 ml of the 0.15 ppm standard into the CAC.

(7) Note the time or start a timer.

(8) Gently shake the CAC to mix the standard with the Ultrex HNO_3

(9) Turn the select switch to mV and allow 3 minutes (starting with step 6.3.7.d(7)) for the mV reading to stabilize.

NOTE

Stabilization time allowance must be exactly the same for all standards and samples.

(10) Record the reading, remove the septa and rinse the CAC with demineralized water.

(11) Repeat steps 6.3.7.d(2) through 6.3.7.d(9) over the range desired.

(12) Do step 6.3.6.g.

NOTE

To avoid rinsing the micro dish between each measurement, use as many micro dishes as necessary to cover the desired range.

e. Using Micro-Dishes

(1) Using a micro pipet, carefully pipet 1 drop of Ultrex HNO_3 and 0.100 ml of the 0.15 ppm chloride standard into the micro dish.

(2) Note the time or start a timer.

NOTE

If a high radiation sample is to be analyzed, skip step 6.3.7.e(3) to avoid possible contamination.

(3) Agitate gently, being careful not to spill any of the solution.

(4) Lower the electrodes into the solution, wait at least 5 minutes from step 6.3.7.e(1), then read the mV value (see note following step 6.3.7.d(9)).

(5) Record the mV reading.

(6) Repeat steps 6.3.7.e(1) through 6.3.7.e(5) over the desired range.

(7) Do step 6.3.6.g.

6.4 Sample Analysis

6.4.1 Graphic Controls (or equivalent) Chloride Electrode and Orion (or equivalent)

a. Do steps 6.3.1 through 6.3.5.

NOTE

High conductivity water may indicate a pH that will not be adjusted to pH 2 with the addition of 0.100 ml of Ultrex HNO_3. This sample must first be pH tested, then an appropriate quantity of HNO_3 must be added to separate sample to adjust the pH to 2 (pH measurements add chloride, therefore, the same sample cannot be used).

b. Measure the 20 ppb standard as per section 6.3.6 and adjust the mV reading to the value taken from the most recent calibration curve for this standard.

c. Rinse the electrodes thoroughly with demineralized water.

d. Add 100 ml of sample or sample dilution to a clean 150 ml beaker and start the stirrer.

e. Add 0.100 ml of Ultrex HNO_3, note the time and lower the electrodes into the solution.

f. At exactly 30 seconds after the previous step, observe and record the mV reading.

g. Convert mV to ppb Cl- by using the calibration curve.

6.4.2 Lazar Electrodes

a. Using the CAC

(1) Do steps 6.3.1 through 6.3.4.

(2) Do step 6.3.7.b.

(3) Rinse the electrodes in demineralized water.

(4) Using a standard with a chloride concentration approximating that of the expected concentration of the sample, do steps 6.3.7.d(1) through 6.3.7.d(9).

(5) Adjust the mV reading to the specific value of the standard's known concentration as taken from the most recent calibration curve generated for this analysis.

(6) Remove the septa and rinse the CAC with demineralized water.

(7) Using a 0.100 ml aliquot of the sample in lieu of the standard, do steps 6.3.7.d(3) through 6.3.7.d(10).

(8) Read ppm chloride from the calibration curve.

b. Using a Micro Dish

(1) Do steps 6.3.1 through 6.3.4.

(2) Do step 6.3.7.b.

(3) Rinse the electrodes with demineralized water.

(4) Using a standard with a chloride concentration approximating that of the expected concentration of the sample, do steps 6.3.7.e(1) through 6.3.7.e(4).

(5) Do step 6.4.2.a(5).

(6) Using a 0.100 ml aliquot of the sample in lieu of the standard, do steps 6.3.7.e(1) through 6.3.7.e(5).

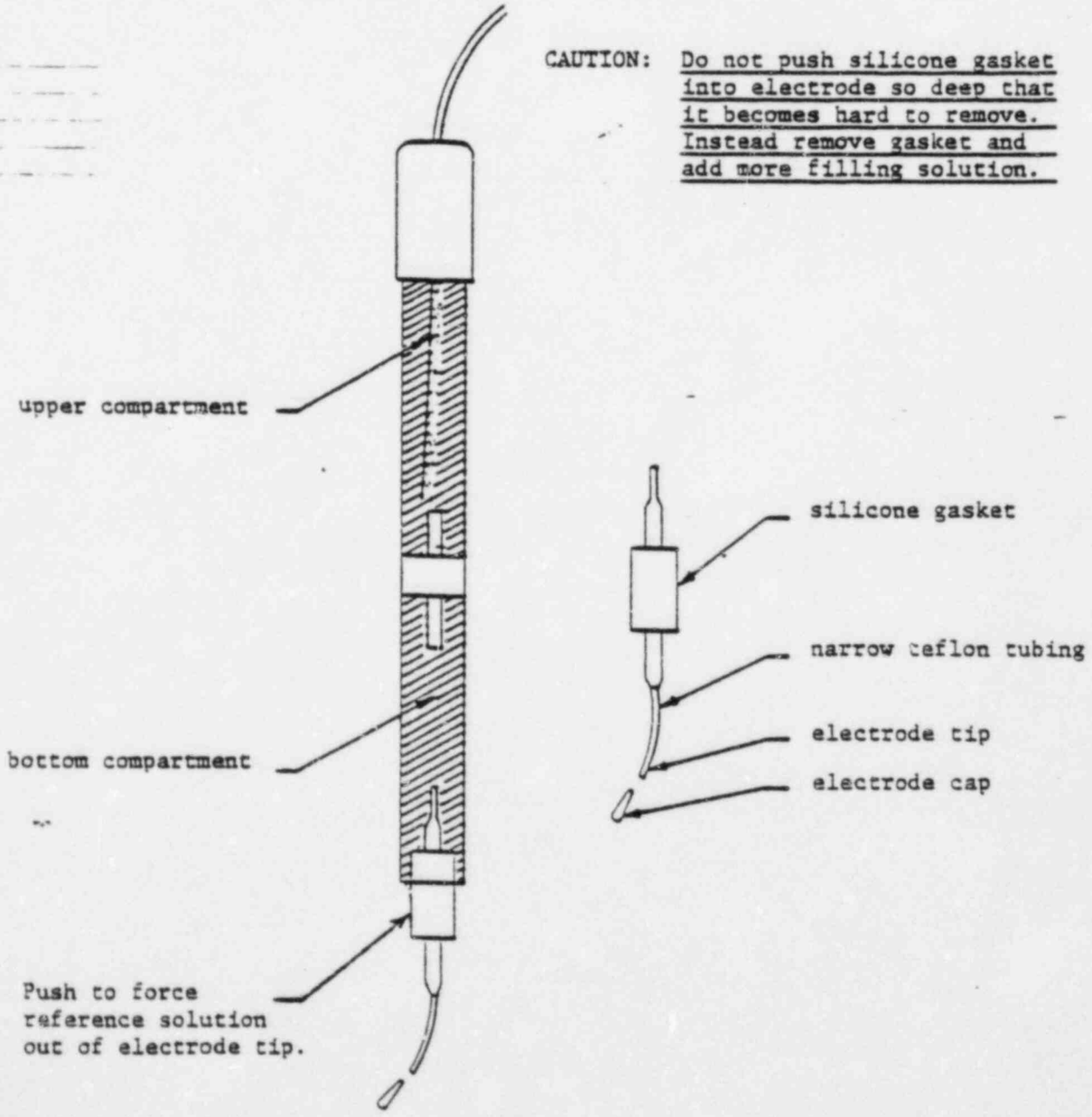
(7) Read ppm chloride from the calibration curve.

7.0 DOCUMENTATION/CORRECTIVE ACTION

Document results on appropriate reporting forms as per Chemistry Procedure 08-S-03-10. Process completed forms in accordance with Chemistry Procedure 08-S-03-3, Document Control.

LAZAR DJM-146 MICRO DOUBLE JUNCTION REFERENCE ELECTRODE

CAUTION: Do not push silicone gasket into electrode so deep that it becomes hard to remove. Instead remove gasket and add more filling solution.



ORION 90-02 DOUBLE JUNCTION REFERENCE ELECTRODE