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CHEMISTRY INSTRUCTION

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

SAFETY RELATED

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Technical Review Independent Review

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Approved: _____
Plant Chemist

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Attachment I

List of TCN's Incorporated:

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0	None
1	None
2	None
3	None

Title: Develop. & Use of Calibration Curves for Chlor. Deter. Utilizing Chlor. Electr.	No.: 08-S-04-316	Revision: 4	Page: 1

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, 14th Edition, 1975

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

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 one 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 also not contain any ISA.

3.3 Standard solutions - Volume of standards should be close to that of the samples. Standard solutions which are as much as an order of magnitude larger in volume than samples will not greatly effect results.

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 also not be stirred.

NOTE

When using the Chloride Analysis Chamber in conjuntion with the Lazar electrodes, sample and standard solutions can be shaken for mixing. Also, sample and standard solutions in micro dishes may be gently agitated except where there is a possibility of radioactive contamination, should a high radiation sample be spilled.

4.0 PREREQUISITIES

4.1 Apparatus Required

4.1.1 Graphic Controls Ultra-Sensitive Chloride electrode and Reference electrode

4.1.2 Lazar Micro Chloride electrode and Lazar Micro Reference electrode

4.1.3 pH/mV meter

4.1.4 Orion Electrode switch

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%

4.2.2 Sodium Nitrate, $NaNO_3$, 5M

4.2.3 Ultrex Nitric Acid, HNO_3, concentrated

4.2.4 Chloride Standards, ~~0~~ 20 ppb to 1000 ppm

4.2.5 Demineralized water

4.3 Attachments

Attachment I - Lazar DJM-146 Micro Double Junction Electrode

5.0 PRECAUTIONS

5.1 The outer solution of the double junction reference electrode must be changed daily (10% KNO_3). 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 ml ultrex HNO3

5.2.2 Store the double junction electrodes in demineralized H_2O.

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 if the chloride concentration is expected to be greater than 1 ppm. Instead, use the Lazar Micro electrode, or another procedure.

6.0 INSTRUCTIONS

6.1 Calibration Curve for the Graphic Controls, or equivalent, electrode

6.1.1 Ensure startup of the Orion 701-A Ion analyzer in accordance with Reference 2.3.

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

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

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

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

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

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

6.1.8 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 pH of approximately 2.0.

6.1.9 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.

6.1.10 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.

6.1.11 From the 20 ppm chloride standard [illegible] pipet with Eppendorf (or equivalent) pipets, 0.100 ml to the beaker of step 6.1.8. Stir for 30 seconds and record MV. Each additional 0.100 ml increase chloride concentration by 20 ppb.

6.1.12 Repeat step 6.1.11 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 1.500 ml of 20 ppm Cl- to the solution = 200 ppb

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

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

NOTE

Exercise care to prevent contaminating the electrode tip with chloride from hands.

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

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.

6.3 Calibration Curve for the Lazar Micro electrode

6.3.1 Do steps 6.1.1 through 6.1.4.

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

Rinse the electrode in demineralized water.

6.3.3

NOTE 1

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 2

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

NOTE 3

If the calibration curve to be generated is to be done using a micro dish, proceed to step 6.3.5 .

6.3.4 Using the CAC

a. Screw the cap contiuing the Lazar chloride electrode and reference electrode onto the CAC.

b. Using a 0.025 to 0.100 mL pipet, carefully add 1 drop of Ultrex HNO_3 through the pipet port of the CAC.

c. Place a rubber septa onto the pipet port.

d. Using a gas tight syringe, evacuate ~~0.05~~ 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.

e. Using the gas tight syringe, pipet 0.100 ml of ~~teh~~ the 0.15 ppmm standard into the CAC.

f. Note the time or start a timer.

g. Gently shake the CAC to mix the standard wtih Ultrex HNO_3

h. Allow 5 minutes for the mV reading to stabilize.

NOTE

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

i. Record the reading, remove the septa and rinse the CAC with demineralized water.

j. Repeat steps 6.3.4 b through 6.3.4.i over the range desired.

k. Do step 6.1.13.

NOTE

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

6.3.5 Using micro-dishes

a. Using a micro pipet, carefully pipet 1 drop of Ultex HNO_3 and 0.[illegible] of the 0.15 ppmpm chloride standard into the micro dish.

b. Note the time or start a timer.

NOTE

If a high radiation sample is to be analyzed, skip Step 6.3.5.c to avoid possible contamination

c. Agitate gently, being careful not to spill any of the solution.

d. Lower the electrodes into the solution, wait at least 5 minutes from step 6.3.5.a, then read the mV value. (See Note following step 6.3.4.h)

e. Record the mV reading.

f. Repeat steps 6.3.5.a through 6.3.5.e over the desired range.

g. Do step 6.1.13.

6.4 Sample Analysis

6.4.1 Graphic Controls (or equivalent) Electrodes

a. Do steps 6.1.1 through 6.1.4.

NOTE

High conductivity water may indicate a pH that will not be adjusted to 2 with the addition of a 100 ml of ultrex HNO_3. This sample must first be pH tested, then an appropriate quantity of HNO_3 must be added to a separate sample to adjust the pH to 2 (pH measurements add chloride, therefore, the same sample cannot be used).

b. Prior to running an analysis, standardize the meter/electrode by analyzing the 20 ppb standard. Adjust the standardization knob for the respective electrode channel to the reading of the standard.

c. Rinse the electrodes thoroughly with demin water. Immerse the electrodes in 100 ml of sample to which you have added 100 ml Ultrex HNO_3.

d. Stir for 30 seconds and record the MV reading.

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

6.4.2 Lazar Electrode

a. Using the CAC

(1) Do steps 6.1.1 through 6.1.4.

(2) Do step 6.3.2.

(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 6.3.4.a through 6.3.4.h

(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 6.3.4.b through 6.3.4.i.

(8) Read ppm chloride from the calibration curve.

b. Using a micro dish

(1) Do Steps 6.1.1 through 6.1.4.

(2) Do Step 6.3.2.

(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 6.3.5.a through 6.3.5.e.

(5) Do step 6.4.2.a(5)

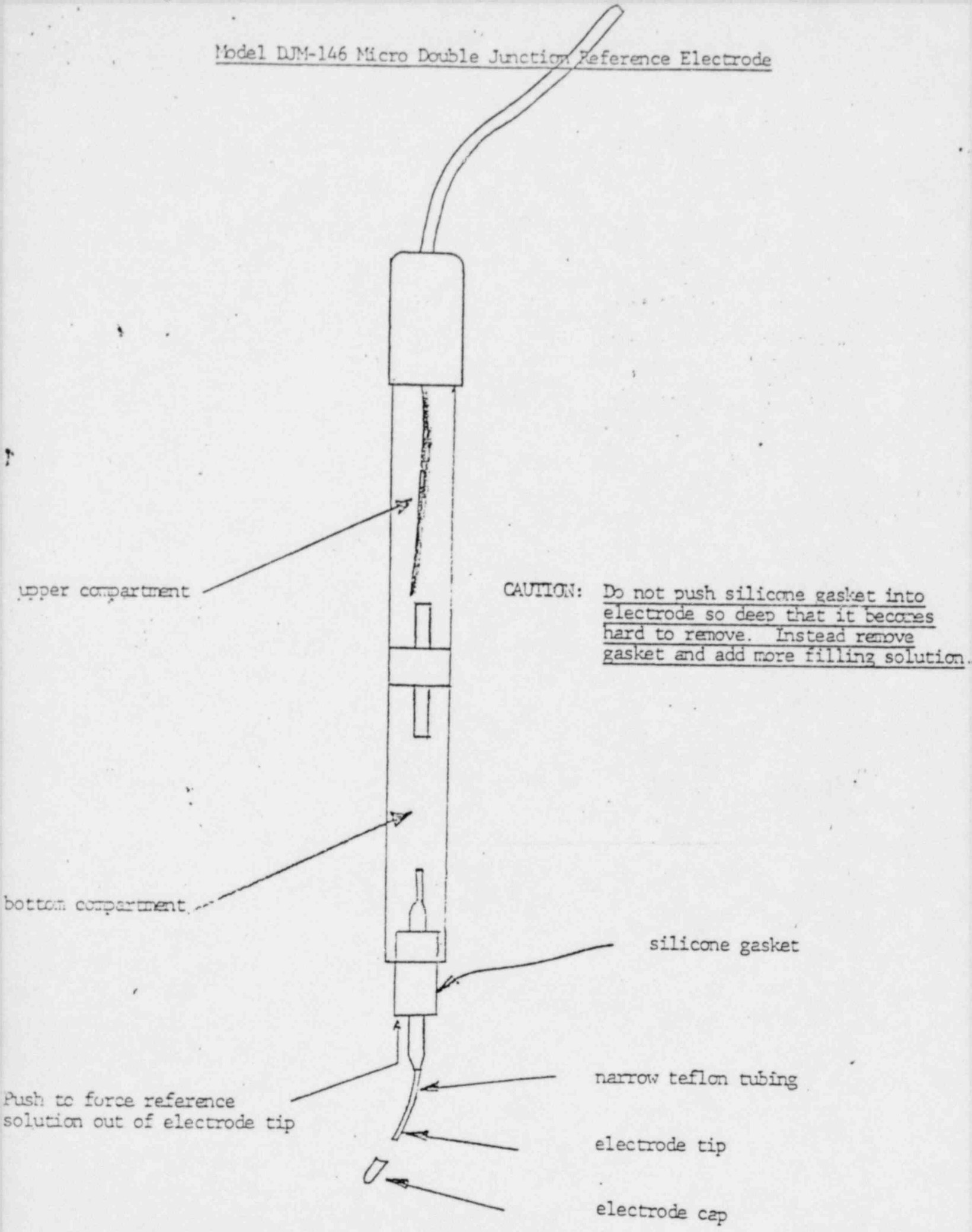
(6) Using a 0.100 ml aliqnot of the sample in lieu of the standard, do steps 6.3.5.a through 6.3.5.e.

(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.

Model 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.