MINISTRY OF ENVIRONMENT AND CLIMATE CHANGE
LABORATORY SERVICES BRANCH

METHOD TITLE: THE DETERMINATION OF CHEMICAL OXYGEN DEMAND (COD) IN WATER BY PHOTO-ELECTROCHEMICAL MEASUREMENT

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SECTION: INORGANIC CHEMICAL ANALYSIS

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APPLICABLE REGULATIONS/PROGRAMS:

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AUTHORIZATION DATE: _____FEBRUARY 5, 2016_____

This method is deemed fit for purpose as of the date shown on this cover page by the data provided in section 1.6 (Analytical Performance Summary).

* The approval of this document is valid for two years at which time it will be subject to review to determine if any updates or modifications are warranted.*

Note: Equivalent suppliers to those stated in the method are acceptable. Reference to a particular brand does not constitute an endorsement by the Ontario Ministry of Environment.*

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THE DETERMINATION OF CHEMICAL OXYGEN DEMAND (COD) IN WATER BY PHOTO-ELECTROCHEMICAL MEASUREMENT

1.0   SUMMARY

Chemical oxygen demand (COD) is a measure of the oxygen requirement of the oxidizable component of organic matter by a strong chemical oxidant. The test is most widely used in measuring waste loadings of treatment plants and in evaluating the efficiency of treatment processes.

1.1   Principle of Method

The COD is determined following a photo-electrochemical measurement of chemical oxygen demand. The sample enters a microcell which contains UV activated TiO2 nanoparticles. Under UV light an electrical signal is generated by the TiO_2 nanoparticles, which is directly proportional to the amount of oxidizable species being present. As the organic matter in the cell gets oxidised, electrons are released, with the signal converted into an equivalent COD measurement.

1.1.1   Relationship to Other Methods.

Method E3515 was in-house validated using a PeCOD® COD Analyser. E3515 replaces the standard dichromate methods E3170 and E3246. An inter-comparison between the standard dichromate methods and the new method in terms of performance is provided in a validation report which is available on file (Reference 1.7.8). Method E3515 eliminates environmentally hazardous waste and the use of harmful and toxic reagents.

1.2   Parameters Measured

The procedure determines the oxygen demand of that portion of the chemical constituents in a sample which are oxidized under the conditions of the test. The LIMS Product Code is COD E3515. Results are reported in mg/L as O_2.

1.3   Sample Matrices

This procedure is routinely used on precipitation (WP), sludge (SL), effluent (TE), industrial waste (TI), raw sewage (TR), groundwater (WG), leachate (WL), surface water (WS).

1.4 Sample Requirements

1.4.1 Specifications.

Glass, polyethylene (PET) or polystyrene (PS) containers are acceptable. A minimum sample volume of 100 mL is required for analysis. Samples are to be stored at 5±3°C.

Sample holding time is 7 days for unpreserved samples.

All samples are refrigerated at 5°C ± 3°C upon receipt at the laboratory.

NOTE: An in house stability study was performed using sulphuric acid and nitric acid as preservatives. 0.2 ml of acid was added per 100ml of sample. These samples were held in clear containers for the duration of the study. The study showed that unpreserved samples were stable for 7 days from sampling and preserved samples were stable for 21 days from preservation date (Refer to 1.7.8)

NOTE: If unpreserved samples are not submitted to the lab to allow time for analysis within their holding time, the samples may be preserved with sulphuric acid or nitric acid to pH<2 (Use 0.2 mL of acid per 100 mL of sample). Preserved samples have a holding time of 21 days from preservation date. Indicate on the sample bottle if sample has been acidified.

1.4.2 Contingencies.

Unpreserved samples may be preserved with sulphuric or nitric acid to pH < 2 upon receipt in the lab and/or before the holding time of the sample is expired. Samples having a pH >10 will be analysed and results will have a LIMS remark code. UPH (unreliable pH>10).

Acidified samples will have the LIMS remark code PPS (test performed on preserved sample).

Any sample that has been analyzed after the acceptable holding time will have LIMS remark code UAL (Unreliable: Sample Age Exceeds Normal Limit) accompanying the result.

Solid sludge samples are diluted with Pure-DW to a liquid state and the result will have the LIMS remark code RDS (Result obtained on diluted solution).

1.5 Shortcomings

1.5.1 Interferences.

The PeCOD® measurement is not affected by the presence of chloride at concentrations lower than 400 mg/L. If the sample is suspected to have a higher concentration of chloride, dilute the sample so that concentration of chloride in

the sample is less than 400 mg/L. NOTE: The central sensor element appears black in colour. If the sensor becomes white, it indicates that chloride tolerance has been lost. Refer to Aqua diagnostic A visual guide to PeCOD® sensors (section 1.7.5).

Some inorganic cations and anions may interfere with COD readings (Reference 1.7.8). It was observed during the analysis of some preserved samples, prepared outside of our laboratory, that results may be biased high due to a possible addition of other preserving chemicals.

1.5.2   Biases.

The suitable pH range for samples is from pH 4-10.

Samples having a pH>10 will have results biased low. Samples with pH >10 will be analysed and remark code UPH (unreliable ph>10) will accompany the results. (Refer to sec 1.7.9, 1.7.10)

1.5.3   Limitations.

PeCOD® measures total soluble COD, which does not include proteins, macromolecules or cellulose. Dichromate COD provides total COD, so differences may be observed for some samples (mainly influent) between E3515 and historical data from E3170 and E3246.

1.6   Analytical Performance Summary

1.6.1   Method Performance, Within-Run Precision (Duplicates)
        (February 2013 to January 2016)

        Sample duplicates are analysed in every batch to monitor method precision. The performance data covers the period February 2013 to January 2016.

        Table 1.6.1   Duplicates

Number of Data Pairs	Range (mg/L as O_2)	Standard Deviation	% Coeff of Var
23	0 - 15	0.56	11.3
11	15 - 30	0.98	4.2
13	30 - 75	1.91	4.4
20	75 - 150	3.42	3

1.6.2   Instrument Performance, QC Calibration Control Standards.

Two levels of QC calibration control standards are analysed in every batch to check if the calibration is valid before samples are analysed. Table 1.6.2 shows the instrument performance covering the period February 2013 to January 2016.

Table 1.6.2   **Calibration Control**

	Number of Data Points	**Expected Concentration (mg/L as O_2)**	**Mean Concentration (mg/L as O_2)**	**Mean Bias (mg/L as O_2)**	**Standard Deviation**
A:	78	100	97.59	-2.41	4.07
B:	78	40	37.48	-2.52	2.75

1.6.3   Method Detection Limit (MDL) - Verified January 2016

MDL was established by analysing eight replicates of a low level standard at the lower 5% of the working range. The data is shown in Table 1.6.3 supports an estimated MDL value of 0.8 mg/L. The reporting method detection limit is 1.0 mg/L.

Table 1.6.3 MDL

	Target Value (mg/L)	**n**	**Average mg/L**	**Standard Deviation mg/L**	**LIMS Reported MDL (mg/L)**
COD	5	8	4.24	0.27	1.0

SD (Standard Deviation); MDL = $t_{(.01,8)}$ x SD = 2.998 x SD

1.7   Bibliography

Note: The most current version of Branch and Section SOPs and Forms are available through LaSB desktop.

1.7.1   Zhang, S., Jiang, D., Zhao, H. Development of chemical oxygen demand on-line monitoring system based on a photoelectrochemical degradation principle. *Environ. Sci. Technol.* **2006**, *40*, 2363–2368.

1.7.2   Zhang, J., Zhou, B., Zheng, Q. Li, J., Bai, J., Liu, Y., Cai, W. Photoelectrocatalytic COD determination method using highly ordered TiO_2 nanotube array. *Water Research*. **2009**, *7*, 1986-1992.

1.7.3   Zhao, H., Jiang, D., Zhang, S., Catterall, K., John, R., Development of a direct photoelectrochemical method for determination of chemical oxygen demand.

Anal. Chem. **2004**, *76*, 155-160.

1.7.4   Government of Ontario. (2002). O. Reg. 169/03- Ontario Drinking-Water Quality Standards, *Safe Drinking Water Act (SDWA)*, *2002.*

1.7.5   PeCOD® COD Analyser L100 User manual. Mantech Inc.

1.7.6   Systematic Comparison of PeCOD®® and Dichromate Methods of COD Measurement for a Suite of 34 Organic Species (Michael Esler, Kumiko Chinen, Heather Higginbotham and Priyanka Reddy; 23 February 2010)

1.7.7   Aqua diagnostic. A visual guide to PeCOD® sensors

1.7.8   Furdui, V. and Palmer, D. (2014). *Validation Report for Method E3515*. (Internal Report). Ontario Ministry of the Environment, Laboratory Services Branch, Toronto.

1.7.6   List of Supporting Branch/Sectional SOPs

      LSBSOP.035   Staff Training
      ICASOP.007   Procedure for Control Charting
      ICASOP.009   Procedure for Records Management

1.7.7   List of Supporting Forms and Logbooks

      FRM_ICA_010   Preparation of Stock Standard Solution
      FRM_ICA_012   Preparation of Working Standard Solutions
      FRM_ICA_017   Run Review Cover Sheet
      FRM_ICA_021   Analyst Method Proficiency Checklist, ICA

      FRM_LSB_031   Staff Orientation /Training / Updated Training
      FRM_LSB_047   Analyst Method Proficiency Testing
      FRM_LSB_048   Analyst Method Proficiency Summary

      PeCOD® Binder 1   Equipment List, Reagent Preparation
      PeCOD® Logbook 1   Maintenance/Troubleshooting/Corrections

1.8   History of Changes/Revisions

1.8.1   February 2014, Version 1.0

New method.

1.8.2   February 2016 – Version 2.0

Section 1.6 performance data updated. Reference to FRM_3515_001 Control Charting for Method E3515, Green Range, not used as posted form was removed. Minor typographical/editorial changes throughout the document applied.

2.0   SAMPLE PREPARATION

2.1   Labwares

2.1.1   Tubes, disposable centrifuge tubes 50 mL plastic
2.1.2   Racks, centrifuge tube
2.1.3   Pipettes, Eppendorf, various sizes
2.1.4   Dilution Tubes, 50 mL glass

2.2   Reagents

2.2.1   Pure Water that has been further deionized, Pure-DW.

2.3   Equipment

2.3.1   Centrifuge, set at 1500 RPM.

2.4   Procedure

2.4.1   From LIMS (Laboratory Information Management System), view or print an enhanced worklist of the samples to be analyzed. For hold times, print a worklist sample holding time report

2.4.2   Create a workgroup file in LIMS for analytical department 5318. Use the dci-eLab function "enhanced modify workgroup" to sequence samples in ascending order by matrix and dci the workgroup to e-lab. Print an enhanced workgroup report.

2.4.3   If samples are to be preserved, add 0.2ml of concentrated sulphuric acid for every 100ml of sample.

> **NOTE:** The System automatically checks the pH of each sample. For samples with pH<4, the pH will automatically be adjusted to pH 4-10 with NaOH. The appropriate dilution factor will automatically be applied. For samples with pH >10, the results will have remark code UQC (Unreliable: Possible Lab QC Problems).

2.4.4   Pour samples into clean, dry tubes, filling to approximately 45 mL level.

2.4.5   If the samples contain significant amount of particulates, centrifuge at 1500 RPM for 10 minutes. Enter LIMS Remark Code, FAQ (Fraction of Sample Analyzed: Aqueous Phase only).

2.4.6   Analyse one duplicate for every 30 samples, to a maximum of 3 duplicates. Record the sample numbers of the duplicate samples on the bench sheet.

2.4.7   If samples suspected to be high, perform a dilution and record dilution factor on worksheet. A minimum sample volume of 5 mL is to be used. For example, for a 10 times dilution: dilute 5 mL of room temperature sample to 50 mL with Pure-DW.   Enter LIMS Remark CODE, RDS (result obtained on diluted solution). NOTE: Ensure volumetric traceability as per LSBSOP021.

3.0   ANALYTICAL PROCESSING

No further processing of the samples is required before introducing them to the Detection System.

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4.0   DETECTION SYSTEM

4.1   Labwares

    4.1.1   Volumetric flask, class A, 1L

    4.1.2   Pipettes, class A, various sizes

    4.1.3   Pipettes, eppendorf, various sizes

    4.1.4   Graduated cylinders, various sizes

4.2   Reagents

    4.2.1   Pure Water that has been further deionized, Pure-DW (milli-Q water)

    4.2.2   1 N sodium hydroxide – Expiry one year from preparation date.
           Dissolve 40 g NaOH in 800 mL Pure-DW. Dilute to 1 L with Pure-DW.

    4.2.3   PeCOD® Technology Electrolyte Solution. Green range (<150 mg/L, and Blue
           range <25 mg/L) – Expiry as stated by the manufacturer.

    4.2.4   Electrolyte Blank solution – Expiry one year from preparation date.
           Mix equal quantities electrolyte with milli-Q water and add to the blank storage
           bottle (water: electrolyte is a 1:1 ratio).
           NOTE: Ensure sufficient blanking solution for duration of analytical run.

4.3   Equipment

    4.3.1   pH/PC titrate equipment
           - PC-titrate burivar I/2 Buret PC-1104-00
           -Interface Module PC-1055-00
           -Variable Stirrer control PCH-4000-149
           -Mantech titrasip module X 2 PC1300-475
           -Mantech PC titrate titra-dose / A module X 2 PC-1000-550
           -pH probe PCE-80-PH1012

    4.3.2   Autosampler- Mantech, 73 tube capacity

    4.3.3   PeCOD® Unit –L 100

    4.3.4   PC-Titrate™ V3.0.0.718 software and Lab term – Labview v8.5.

4.4   Procedure

    4.4.1   In LIMS, create a Workgroup of appropriate length, according to the standard
           LIMS procedure. The run format is 15 samples followed by an in-run QC check
           and the last tube is a pH 4 buffer solution. Note: the pH 4 buffer solution is
           automatically analysed in the last auto sampler position. There is no need to add
           this to the sample table. Record the Workgroup number. Upload the workgroup

to e-lab. Copy the workgroup created in e-lab onto an USB drive. This allows the workgroup to be downloaded into the run schedule at the PC-Titrate system.

4.4.2   Turn **ON** the automated titration system at the power bars (Consisting of the computer, Burivar I/2 Buret Module, Titra-Sip Titration Modules, Gilson auto sampler) if necessary.

4.4.3   On the computer desktop, double click the icon "PC-Titrate for Windows" to activate the PC-Titrate system.

4.4.4   Set up the reservoir (the 20L collapsible container) for the wash-waste system with Pure-DW, dilution water bottle and the 4L container for the electrolyte titra-sip.

4.4.5   Ensure there is enough pH adjusting solution (1N NaOH) in the container.

4.4.6   Ensure that all the tubing is properly connected and free from contaminants.

4.4.7   Examine the positions of the pH electrode, stirrer, and the tips in the vessels. Ensure that they are firmly held by the cover. The titration vessel should be free from grease or dirt. If necessary, remove the three screws that are holding the cover in position. Wipe clean the inside of the vessel with a clean tissue and then rinse with Pure-DW for a few times. Do the same with care to the pH electrode, stirrer, temperature probe and the dispensing tips.

4.4.8   Examine the PeCOD® sensor. Refer to "Aqua diagnostic A visual guide to PeCOD® sensors" if cell appears to be worn. If white precipitate is visually noted on the sensor, analyse chloride interference check to confirm sensor functionality.

4.5   Shutdown Procedure

4.5.1   When the analyses have been completed, the results will be displayed on the screen. If a hard copy is desired, press the print icon to print the results. The auto sampler will automatically continue to position 73 where it will draw up solution to store the pH probe. The sample needle will then go back to the home position and remain suspended in air. To return the needle to the rinse station, select **Titrator** from the PC-Titrate main menu and **Manual control**. From the auto-sampler tab choose load tray from folder. Select tray file **standard tube sampler-73x50.GTY** then select **Home sampler** and **go to this location XYZ**.

5.0 CALIBRATION

5.1 Labwares

5.1.1 Flasks, volumetric, Class A, various sizes as required.

5.1.2 Pipettes, volumetric, Class A, various sizes as required

5.1.3 Weighing boat, or plastic weighing dishes.

5.1.4 Tubes, 50mL plastic disposable.

5.1.5 Pipettes, Eppendorf, various sized as required

5.3.6 Analytical Balance, readable to ± 0.0001 g.

5.2 Standards and Reference Materials

NOTE: Unless otherwise stated all dry chemicals are stored at room temperature for a period of up to three years from the date it was opened.

5.2.1 pH Calibration Solutions

pH buffers 4.00, 7.00, and 10.00 are purchased and traceable to NIST standards. Expiry date as indicated by the manufacturer on the buffers.

5.2.2 Sodium chloride, NaCl, reagent grade crystals dried 1 hour at 110 ± 5°C and stored in a desiccator.

5.2.3 Sorbitol, $C_6H_{14}O_6$ (>98%)

5.2.4 Sorbitol Stock Solution (1000mg/L). Dissolve 0.8758g in 800mL Pure-DW in a 1L volumetric flask and dilute to the mark. This solution is to be prepared every 3months or when depleted.

NOTE: The source of the calibration and quality control stock solutions must be from different suppliers. If two different sources are not available different lot numbers are ordered for calibration and quality control standards.

5.2.5 Working Calibration Standards.

Working calibration standards are prepared by diluting 120 ml of the stock calibration standards (ss. 5.2.6) to 1 L with Pure-DW.

NOTE: New calibration standards are prepared every three months or upon depletion.

5.2.6 Quality Control Stock Standard Solution, 1000 mg/L as O_2.

Using a different source than that used for the calibration stock standard, dissolve 0.8758g ± 0.0001 g of sorbitol in a 1 L volumetric flask and dilute to the mark

with Pure-DW.

NOTE: New quality control standards are prepared every three months or upon depletion.

5.2.7　Working Quality Control Standards

Dilute the following volumes of quality control stock standards (section. 5.2.8) with Pure-DW to 1L using volumetric glassware.

QC	Volume of Stock (ml)	COD concentration (mg/L)
QCB	40	40
QCA	100	100

NOTE: New QC standards are prepared every three months and verified before existing solutions are **depleted** or expired (refer to s. 5.4 Standards Verification).

5.2.8　CRM (Certified Reference Material)

A CRM is purchased externally as a concentrate and is prepared according to the manufacturer's instructions. The expiry date and storage conditions are indicated in the quality certificate of the CRM and on the label.　This is analysed quarterly.

5.2.9　Chloride Interference Check Stock Standard Solution, 1000 mg/L as Cl^-

Dissolve 1.6482g of sodium chloride in pure-DW in a 1L volumetric flask and dilute to 1L.

5.2.10　Chloride Interference Check Working Standard Solution, 50mg/L as Cl^- and 40 mg/L as O_2

Dilute 40 ml of sorbitol calibration stock standard (section 5.2.4) and 50 ml of chloride interference check stock standard (section 5.2.9) in a 1L volumetric flask and dilute to the mark with pure-DW.

5.3　Equipment

Pour buffers 4, 7, 10 into disposable 50 mL tubes and place in auto sampler positions 1, 2, and 3 respectively.　Pour the calibration solution (120 mg/l) and place into position 4. Ensure correct range is selected on the PeCOD® unit by selecting menu, set up, analysis method, and COD range using the ↑ or ↓ buttons on the PeCOD® unit.　Select green range and press enter. Ensure sufficient blanking solution is prepared.　Prime both lines on the PeCOD® unit by selecting menu, operation, prime lines, prime port A, Enter. Prime 3 times.　Select prime port B.　Prime 3 times.　In the main PC-Titrate window select daily start up.
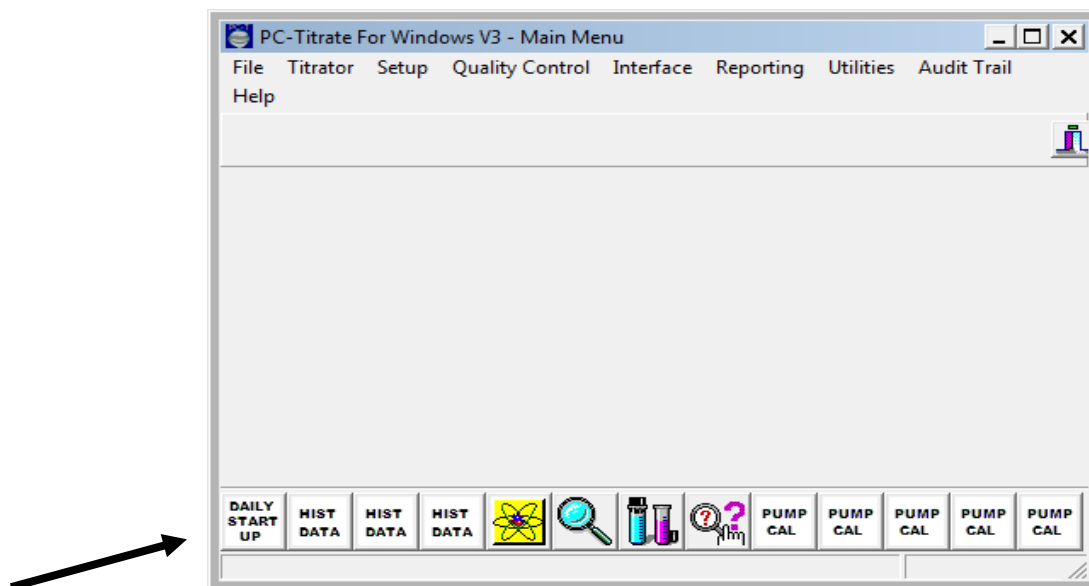
In the PC-Titrate software ensure appropriate calibration schedule is selected (green calibration). Once calibration is complete ensure pH calibration meets requirements and pass is indicated. If fail observed repeat analysis ensuring solution is covering probe and stirrer is able to stir. Ensure the PeCOD® unit calibration values fall within acceptable range. $0.02 < M < 0.06$ and $300 < C < 700$. If outside acceptable range recalibrate system. If still outside range investigate sensor performance in Lab term software.

NOTE: If the blank is contaminated the M value will be outside of acceptable range. Prepare fresh blanking solution and recalibrate system

5.4 Standards Verification

5.4.1 For working quality control standards (section. 5.2.7), the average concentration from a triplicate analysis must be within ± 2SD of QC average performance (see warning limits described in section. 6.2.1).

5.4.2 If a new working standard fails the acceptance criteria, the cause is investigated and the standard is re-analyzed. If still not met, discard the solution and prepare a new working solution. Record all results and comments on FRM_ICA_012.

6.0   RUN PROCESSING AND QUALITY ASSURANCE

6.1   Run Format

6.1.1   The following format is used

1.   QCB
2.   QCA
3.   DUP (one for every 10 samples to a maximum of 3 duplicates)
4.   CRM (quarterly)
5-20. Samples (15)
21.   In run QCB

NOTE: Repeat positions 5-20. The number of samples is limited by the number of samples
fitting into the auto sampler. If visual inspection of the sensor indicates a reduction in
chloride tolerance, run a chloride interference check (section 5.2.10)

NOTE: If pre-dilution of the sample was performed, enter the dilution factor in the weight
column.

QC(x)	Quality control standards	x = calibration control standards A,B (s. 5.2.7)
DUP(x)	Duplicate samples	x = 1 to 3 duplicates to monitor within-run precision
In run QCB	Low QC standard	Calibration quality control standard check

6.2   Run Control Operations/Limits

6.2.1   Calibration Control:

Expectation: The QC standards QCA and QCB monitor the calibration. The limits for
the individual QC results are calculated from available data (Feb 2013 to
January 2016) historical data as shown in the table below (section 1.6.2)

Calibration Control Working Solution	Expected Value (mg/L O_2)	Warning Limits (mg/L O_2)	Control Limits (mg/L O_2)
QCA	100	91.9 - 108.1	87.8 - 112.2
QCB	40	34.5 - 45.5	31.8 - 48.2

Action: Values falling outside of the control limits may be identified during the analytical run or data processing. If the control limit exceedance is identified during the run, immediately stop and repeat the run. If the control limit exceedance is identified during data processing, check the calibration results and correct any discrepancies. If no corrections can be made, either repeat the run from the beginning or qualify data in LIMS with the remark code "UQC" – Unreliable, QC failure. Consult the group leader or manager for instructions.

Values between the warning and control limits may indicate a developing problem. Examine all aspects of the calibration process, reagents, and standards to be sure all are within specification. Carry out QC trend analysis as per ICASOP.007.

The chloride spike is intended to monitor the chloride sensors tolerance. The results may be used to monitor sensor performance and aid in sensor maintenance decisions. A result outside of limits does not necessitate a run failure but may be an indicator of decreasing chloride tolerance.

6.2.2   Duplicates:

Expectation: Samples analyzed in duplicate must agree to within three standard deviations of the selected concentration span. (Values listed below are calculated based on the average standard deviation of results from 2016.)

Concentration Range (mg/L O_2)	Control Limits (mg/L O_2)
0 - 15	± 1.65
>15-30	± 2.73
>30-75	± 5.01
>75-150	± 10.05

Action: Regard a single failure as a warning that some part of the process may be out-of-control, and conduct a review of those steps which may lead to such failures, correct any problems identified and repeat analysis of sample. Regard the failure of more than one duplicate as cause to withhold the run results until the cause is identified, corrected and affected samples are identified for re-analysis. Where a cause cannot be identified with confidence, repeat the run.

6.2.3   In-run Quality Control Standards

Expectation: The In-runQCB standard monitors the performance during the run. The control limits for the In-runQCB standard are the same as that for QCB.

Expected Concentration (mg/L O_2)	Control Limits (mg/L O_2)
40	31.8 - 48.2

Action: If an In-Run exceeds the limits defined above, the data will be discarded from that point in the run and the analysis of samples repeated.

6.2.4   Certified Reference Material

The certified reference material is analyzed quarterly. The theoretical concentration and limits may change for externally purchased CRMs. Refer to the Certificate of Analysis certificate issued when purchased for theoretical concentration and control limits.

Expectation: The reference material is used to access accuracy/recovery of COD (mg/L O_2). The reference sample must fall within the acceptance limits that accompany the reference material.

Action: If the CRM falls outside the acceptance limits, check the calibration results and correct any discrepancies. Repeat analysis of the CRM. If the CRM still falls outside the limits, consult the group leader for instructions.

6.3   Calculation Procedure

6.3.1   The calculations of the results are performed by PC-Titrate™ software. No other calculations are required.

6.3.2   Import sample and QC results from the system's software to USB storage device. Plot the Control chart of the calibration control standards. The analyst must examine the results in the context of the control chart for trends which may indicate that problems are developing or can now be confirmed. Take appropriate action to correct any problem identified (see 6.2.1). This summary must be audited, with appropriate comments and approved by the group leader or manager.

6.4   Reporting

6.4.1   Chemical oxygen demand is reported in mg/L as O_2.

6.4.2   In the LIMS, the workgroup must be "moved" and a pre-APP1 approval report is audited. After assuring the quality of the results, update the status to APP1 and print an APP1 approval report.

MDL = 1.0 mg/L O_2

Flag to Y in "Replicate Data"' any results which are repeated values that require reporting. In "Update Status", set to REDO any samples transmitted with NDRR (No Data: Rerun Requested), or other samples which require repeating.

6.4.3   Attach together the 'Run Review' cover sheet (FRM_ICA_017), Control charts print out, LIMS APP1 approval report, results print out, pH calibration report, PeCOD® instrument calibration report, the enhanced work group report, holding time work list, and run sample table. Label the package with the unique run number ("R-workgroup #"), LIMS workgroup number, initial and date, and have the manager or group leader audit and initial the package. Store these records according to ICASOP.009.

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## Appendix 1

Changing the sensor

When the calibration no longer is passing and the sensor coating is depleted, the sensor should be changed.

Manually:

Set up the system for manual sample introduction. Mix equal amounts of calibration solution with electrolyte and have ready to introduce into the system.   Open the PeCOD® unit and remove the sensor. Replace with a new sensor and close the door. On the PeCOD® screen select menu, set up, enter, sensor operation, enter, new sensor. Confirm new sensor will appear on the screen. Select yes by pressing enter. The previously prepare electrolyte solution will then introduced into the system.

Automated sensor routine

Have a sample of calibration solution in position 1 of the autosampler.
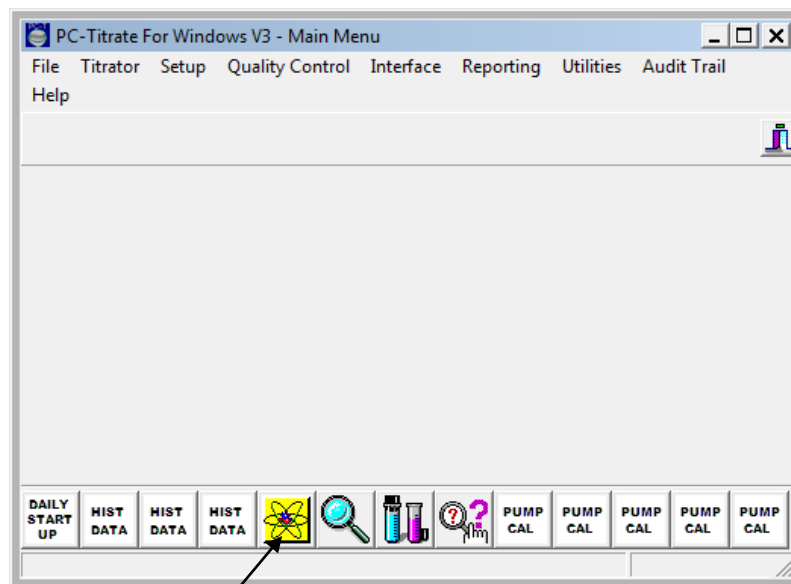
Select the new sensor routine and select the start icon. Enter the new sensor number (i.e., 11117) and select enter.

Troubleshooting

If an LED or over current error occurs the sensor may need to be conditioned. On the PeCOD® unit select menu, setup, enter, sensor operation, enter, set baseline. Reduce the baseline from 20 to 10-15. Run a calibrations or quality control solutions at this level. Gradually increase the baseline back to 20 without getting an error message.

If a communication error occurs, try removing and replacing the PeCOD® USB and rebooting the system. If the error continues it may help to erase the error logs. On the PeCOD® unit select menu, diagnostics, enter, erase logs, enter, erase event log, and enter. For the system to work an error must exist in the logs so a false error must be created. To create a false error on the PeCOD® unit select menu, operation, enter, run calibration, enter. Once it start select exit to create a false error.