OFFICIAL DOCUMENT

Albuquerque Bernalillo County

Water Utility Department

WATER RECLAMATION DIVISION
4201 2ND STREET SW, ALBUQUERQUE, NEW MEXICO 87105

WATER QUALITY LABORATORY
STANDARD OPERATING PROCEDURE APPROVAL FORM

WQL SOP **223 Phenolics**

CURRENT REVISION # **03** DATE **May 2006**

ORIGINAL ISSUE DATE **April 1998**

MODIFICATIONS AND REASONS FOR REVISION

***New WQL Management Staff**
***New SOP Numbering System**
***New QA/QC Filing System**
***Revised Quality Control Section**

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Out of Service By: _____ Date: ___/___/___

Reason:

Revision Date: ~~March 2005~~ May 2006

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STANDARD OPERATING PROCEDURE

SOP 223

PHENOLICS

SCOPE AND APPLICATION: This method is applicable to drinking, surface and saline waters, domestic and industrial wastes, and solids. The applicable range is 5 ug/L to 500 ug/L.

APPLICABLE METHOD REFERENCES:

U.S.E.P.A. METHOD 420.4
Technicon Instruments Corp., Tarrytown, New York, Industrial method 127-71W
Bran+Luebbe Inc., Buffalo Grove, IL, Method No. 696K 82W

DISPOSAL OF SAMPLES: Dispose of samples at an acid sink.

Effective Date 6/5/06

PHENOL

1.0 GENERAL DISCUSSION

1.1 Principle: The automated method for determining ortho and meta substituted phenols is based on the distillation of phenol and the subsequent reaction of the distillate with alkaline ferric cyanide and 4-aminoantipyrine to form a red complex which is measured colorimetrically at 505 nm.

1.2 Interference:

Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate. If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

Background contamination from plastic tubing and sample containers is eliminated by filling the wash receptacle by siphon and using glass tubes for the sample and standards.

Sulfur compounds interference from sulfur compounds are eliminated by acidifying the sample to a pH of 4.0 and aerating briefly by stirring.

1.3 Safety Considerations: The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Wear protective gloves, laboratory coat and eye protection. Dispose of all samples and reagents in an acid sink. Reagents used are potentially caustic or corrosive, avoid ingestion or inhalation and contact with the skin. For specific hazards consult the MSDS sheet, located in the laboratory office for the following compounds: Sodium hydroxide, Brij-35, potassium chloride, boric acid, potassium ferric cyanide,4-aminoantipyrine, sulfuric acid.

1.4 Sample Preservation & Storage: Samples should be collected in glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, typically 500mL volume is collected, which allows for replicate analysis. Samples must be preserved at time of collection with sulfuric acid to a pH of <2 and cooled to 4°C. Samples should be analyzed as soon as possible after collection. If storage is required, preserved samples are maintained at stored 4°C and may be held up to 28 days.

1.5 Sample Preparation: All samples require the distillation procedure prior to analysis.

1.6 Method Performance Criteria: The interlaboratory precision and accuracy data in table 1 **(see appendix one)** were developed using a reagent water matrix. Values are in mg Phenol/L. Single laboratory precision data can be estimated at 50 to 75% of the interlaboratory precision estimates.

2.0 APPARATUS & EQUIPMENT: Analytical balance, capable of accurately weighing to the nearest 0.0001 g. Glassware, class A volumetric flasks and pipets as required. Distillation apparatus including boiling flask, condenser

and absorber. Heating mantle which accommodates a 500mL boiling flask. Automated continuous flow analyzer (AAII Auto Analyzer), with a auto sampler, multichannel pump, reaction manifold, colorimetric detector and data collection system **(see appendix two)**.

3.0 REAGENTS & SUPPLIES:

3.1 Reagent Water: De-ionized water free of the analyte of interest.

3.2 Sodium Hydroxide 1+9 solution: Dilute 10 mL of 1N NaOH to 100 mL with reagent water.

3.3 Buffered Potassium Ferric Cyanide: Add to 400mL of reagent water, 1g of potassium ferric cyanide, 3.1g of boric acid, 3.75g of potassium chloride and 44 mL of 1N sodium hydroxide. Dissolve and dilute to 500mL with reagent water. Adjust the pH to 10.1 and add 0.5 mL of 30% Brij-35 solution.

3.4 Sulfuric acid 1+9: Slowly add 10 mL conc. sulfuric acid to 70 mL of reagent water. Cool and dilute to 100 mL with reagent water.

3.5 4-Aminoantipyrine: Dissolve 1.0g of 4-aminoantipyrine in 800 ml of reagent water. Dilute to one liter with reagent water.

3.6 Stock Phenol: Dissolve 0.50g phenol in 500mL of reagent water and dilute to 500mL Add 0.25 mL concentrated sulfuric acid as preservative. 1.0 mL = 1.0 mg phenol.

4.0 QUALITY CONTROL PROCEDURE:

4.1 Calibration Blank (CB) are to be used at a frequency of one per each calibration curve produced and precede each CCVS used. The CB is a volume of reagent water fortified with the same matrix as the calibration standards but without the analyte. The CB must have be quantified less than the method detection limit. If the acceptability limit is exceeded, then a new calibration blank must be prepared and re-calibration must be instituted.

4.2 Initial Calibration Standard (ICAL) is a solution prepared from the primary dilution standard solution or stock standard solution. The ICAL solutions are used to calibrate the instrument response with respect to analyte concentration. A minimum of three ICALs are to be used to establish a valid calibration curve. The ICALs must be of concentrations that represent the high range, mid-range and low range of the calibration curve.

4.3 Continuing Calibration Verification Standards (CCVS) a mid-range ICAL (500 ppb) used to verify continued calibration, are to be conduct with a frequency of one CCVS per ten samples, with a minimum of one CCVS for less than ten samples. A CCVS must be run last in each series of ten samples and must always be included at the end of any batch run regardless of the number of samples run or number of CCVS's used, ie. use a 'End of Run CCVS'. CCVS's must have a percent difference of no greater than 5%. If the 5% acceptability limit is exceeded, then re-calibration must be instituted. The samples subsequent to the last successful CCVS must be re-tested with a reinstated calibration curve.

4.4 Initial Calibration Verification Standard (ICVS) is a solution of method analyte of known concentration that is used to validate calibration curves. The ICVS is obtained from a source external to the laboratory and different

from the source of calibration standards. ICVS is to be used at a frequency of one per each calibration curve produced. The ICVS must have a percent difference of not greater than 5%. If the 5% acceptability limit is exceeded, then re-calibration must be instituted, using freshly prepared ICAL's and verified with a ICVS.

4.5 Laboratory Reagent Blank (LRB) is an aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, that are used with other samples. The LRB is used to determine if method analytes or other interference are present in the laboratory environment, the reagents, or the apparatus. The laboratory must analyze at least one LRB with each batch of samples. Data produced are used to assess contamination from the laboratory environment. When the LRB value is 2.2 times the analyte MDL, a fresh aliquot of the sample/s must be prepared and analyzed again for the affected analyte after the source of contamination has been corrected and acceptable LRB values have been obtained. If the affected samples are beyond their holding time or lack adequate volume to retest, these samples will not be reanalyzed. The results of the affected samples will be corrected by subtracting out the measured level of contamination and reporting the difference. The corrected samples will require text to qualify the data. The text should state the sample has been corrected due to a LRB greater than 2.2 times the MDL.

4.6 Laboratory Control Sample (LCS) is an aliquot of reagent water or other blank matrices to which known quantities of method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The laboratory must analyze at least one LCS with each batch of samples. Calculate accuracy as percent recovery. If the recovery of any analyte falls outside the required control limits of 85-115%, that analyte is judged out of control, and the source of the problem should be identified and resolved, any corrective action taken must be documented in the bound work sheet book concomitant with the analysis data. The laboratory must use LCS analyses data to assess laboratory performance against the required control limits of 85-115%. When sufficient internal performance data become available, usually a minimum of 20-30 analyses, optional control limits can be developed from the percent mean recovery (X) and the standard deviation (S) of the mean recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = X + 3S
LOWER CONTROL LIMIT = X - 3S

After each five to ten new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations included in the LCS. These data must be kept on file and be available for review. If the LFB is not within its control limits, then the affected samples must have text to qualify the data. The text should state the percent recovery achieved for the LCS.

Calculation of percent recovery for an LCS:

$$R = \frac{LCS - LRB}{S} \times 100$$

where: R = Percent recovery

LCS = Laboratory control sample.
LRB = Laboratory reagent blank.
s = Concentration equivalent of analyte added to fortify the LRB solution

4.7 Laboratory Control Sample Duplicate (LCSD) is prepped exactly like the LCS and measures precision of the methodology.

4.8 Quality Control Calculations:

To calculate a % Difference: $$\frac{2(\text{Sample Result} - \text{Sample Result}') \times 100}{\text{Sample Result} + \text{Sample Result}'}$$

To calculate a % Recovery: $$\frac{(\text{Spiked Sample Result} - \text{Sample Result}) \times 100}{\text{Final Concentration of spike added*}}$$

* Use the dilution formula to compute the final concentration of spike added ie. $V_1 \times C_1 = V_2 \times C_2$. The volume of spike solution added should not exceed 1-2% of the final volume.

where: C_1 = Concentration of spike solution
V_1 = Volume of spike solution added to sample
C_2 = **Final Concentration of spike added**
V_2 = Volume of sample

4.9 Method Detection Limit(MDL): MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit. To determine a MDL value, take seven replicate aliquot of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

where, t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom, t = 3.14 for seven replicates.

S = Standard deviation of the replicate analyses.

MDLs should be determined biannually.

4.10 Control Charts- All quality control data will be entered in the lab share drive by analysts performing this test. Quality assurance reviews are performed weekly, for complete details of control chart performance evaluations see QA SOP-005.

5.0 INSTRUMENT CALIBRATION: Calibration is conducted by generation of a calibration curve via a data system (AACE) interfaced with the colorimeter of the flow injection analyzer. The calibration curve must be produced using four Initial Calibration Standards **(ICAL)** 1000, 500, 300,100ppb and a Calibration Blank **(CB)**. The calibration curve generated must have a regression analysis performed on the calibration curve. A correlation

coefficient, resultant from the regression analysis, must be greater than or equal to 0.995 for the calibration curve generated. A mid- range **ICVS** (500ppb) must be run to validate the calibration curve. The percent difference must be no greater than 10%. If the acceptability limits are not met for the correlation coefficient and/or the **ICVS**, then a new calibration curve must be generated which meets the acceptability criteria.

6.0 PROCEDURE PHENOLS:

6.1 Sample distillation: Measure 250 mL sample into a beaker. Adjust the pH to approximately 4 with 1+9 NaOH or 1+9 H_2SO_4 and transfer to the distillation apparatus. Distill 200 mL of sample, stop the distillation, and when boiling ceases add 50 mL of warm reagent water to the flask and resume distillation until 250 mL have been collected. If the distillate is turbid, filter through a pre-washed membrane filter.

6.2 System Equilibration: Fill and connect reagent containers and start system. Allow instrument to warm up until a stable baseline is achieved. To start the system secure end blocks of the manifold pump tubing to the pump. Place the platen cover on the pump. Place the labeled pump tube in the appropriate reagent containers and place the pump switch to the 'on' position. Place the power buttons in the 'on' position for the printer and AA3 colorimeter. Turn on the computer, power button located on the computer. Using the mouse, double click on the AACE icon. Double click on 'RUN' located on the menu bar. The drop down menu will appear, click on 'Chart'. Observe the bubble pattern, the pattern should have equally space bubbles and bubbles of the same sizes. If the bubbles are well spaced and the same size, then using the right mouse click in the chart area. A menu will appear, select 'Set Base'. Setting the base to achieve a base that is 5% of the chart can be repeated at anytime while in Charting. Using the right mouse click in the chart area. A menu will appear, select 'Auto Lamp'. Using the right mouse click in the chart area. A menu will appear, select 'Smoothing' and 16. Maximize or select [SYS 1 AA3…] bar, then double click on the 'Channel 1' icon. Using the arrow key or manually select and set the gain at a value of 151, then click on the 'OK' button. Then minimize or close the window.

6.3 Calibration & Sample analysis: Select 'Set Up' from the menu bar located at the top of the window. Click on 'Analysis' from the drop down menu a new window will appear. Click on 'data' in the left column of the page. Select or click on the 'Phenol' folder. Then select in the next column 'Phenol Template' and click on the 'Copy Run' button. Select 'Tray Protocol' by clicking on the Tray Protocol tab. Add samples and blanks (Nulls) to the sample tray template by clicking on the 'Stop icon' column and click on the 'Insert' button. Click on the 'Sample' button or 'Null' button to add sample and blanks (nulls). Click on the Sample ID column, for the peak number selected and type in the sample ID for each sample to be analyzed. When all samples and blanks have been enter in the tray, click on 'Print' at the bottom of the page to produce a hard copy with the tray numbers for loading the sample carrousel on the auto-sampler. Then click on the 'OK' button at the bottom of the page or window. The charting window will appear, if the chart has a smooth base line that is ~5%, then click on 'RUN' located on the menu bar. Load the carrousel on the auto-sampler. Click on 'Start'. The Run Start screen will appear, select the newly created file, then click on the 'OK' button. The Start screen will appear, enter analyst name and click on 'OK'. Depress the power switch on the auto-sampler to begin analysis.

6.4 Shutdown: When the last sample has been drawn by the auto sampler

Depress the power switch on the auto-sampler to turn off the auto sampler, when the draw tube has returned to the wash water reservoir. Place the reagent lines in a beaker of reagent water. Using the mouse click on the Close Window Icons for each window until the applications menu appears. Using the mouse click on 'Start' then on 'Shut Down' then on 'OK'. Depress or switch to the 'off' position the switch for the AA3 colorimeter, printer and computer. Continue to pump reagent water through the system for at least 10 minutes. Remove the reagent pump lines for the beaker of reagent water and disconnect the sample line. Allow the system to pump air through the system until all lines appear dry. Turn off the pump via the toggle switch. Remove the platen from the pump and relax the manifold pump tubing by removal of the end blocks from the end block bar.

7.0 REPORTING: All measurements and results, calibration and QC results are to be reported to three significant figures and will be transcribed from the data system report and recorded in the bound work sheet book for Phenol. The determined results for each sample tested and will be entered on the electronic data system, SQLLMS. All samples requiring qualification will be text at the sample level in SQLLMS. All analyses requiring corrective actions, control charts and instrument maintenance will be documented in the companion bound work sheet book, with the sample results, calibration and QC results. The charting and computer generated report from the analysis must have all samples, standards, QC samples identified on the chart. The date of analysis and analyst name and operating parameters must be written on the chart and report after completion of the analysis.

8.0 SYSTEM MAINTENANCE: **See appendix 3** in SOP AC-020, Nitrate-Nitrite.

9.0 SYSTEM TROUBLESHOOTING: **See appendix 4** in SOP AC-020, Nitrate-Nitrite.