Method: Carbohydrate in Produced Water (Colorimetric)

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METHOD: **Carbohydrate in Produced Water (Colorimetric)**	LBNL-2001223
TITLE:	Carbohydrate in Produced Water (Colorimetric)
ANALYTE:	D-Glucose, CAS#50-99-7 D-Mannose, CAS# 3458-28-4 D-Galactose, CAS#59-23-4 D-Lactose, CAS#63-42-3 Guar Gum, CAS#9000-30-0
INSTRUMENTATION:	PerkinElmer Lambda 35 UV/VIS Spectrophotometer

1.0 Scope and Application

1.1 This method covers the determination of mannose, guar gum and other carbohydrates in produced water samples.

1.2 Sugars have varying response factors by this method (Figure 1) and the carbohydrate used for calibration must be specified in the result.

1.3 The method is based on standard curves that are specific for mannose, one of two sugars in commercial guar gum, such that the final carbohydrate concentration is expressed as mannose, mg/L.

1.4 Commercial guar gum should not be used as a calibration standard, due to variability in chemical composition and purity.

1.5 Glucose is not a structural component of guar gum and is therefore not recommended as a calibration standard.

1.6 The method is usable in the 6 to 1000 mg/L as mannose range. Detection range may be variable according to the instrument used.

2.0 Summary of Method

Guar gum, a polysaccharide of galactose and mannose, is a common ingredient for hydraulic fracturing fluids [7]. Standard methods for measuring carbohydrates in flow-back and other produced water are needed, particularly in the context of reporting water quality data to regulatory agencies [6]. This method describes standard procedures for carbohydrate measurement that have been validated for use in produced water.

Heating produced water with sulfuric acid hydrolyzes polysaccharides and dehydrates monosaccharides to form 2-furaldehyde from pentoses and 5-(hydroxymethyl)-2-furaldehyde from D-glucose and other hexoses [2, 8]. 2-Furaldehyde and 5-(hydroxymethyl)-2-furaldehyde

reacts with anthrone to form a green colored compound [1, 2, 3, 5]. Total carbohydrate is quantified by measuring absorbance of known and unknown samples at 625 nm [2].

3.0 Definitions [10]

3.1 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL for D-Mannose is 6 mg/L.

3.2 Precision: Measure of the degree of agreement among replicate analyses of a sample.

$$Precision = \sqrt{\frac{\sum(found\ value - true\ value)^2}{(n-1)}}$$

4.0 Interferences

4.1 Sodium chloride up to 200,000 mg/L did not cause significant interference.

4.2 Aldehydes (formaldehyde, glutaraldehyde, propionaldehyde, pyruvaldehyde) up to 20 mg/L did not cause significant interferences. However, aldehydes react to form red colored compounds that may cause interferences at higher aldehyde concentrations [4].

4.3 Crude oil was not found to cause significant interferences.

4.4 Suspended solids, including bacteria, may cause significant interferences. Filtration before analysis is required. Full characterization of solids is recommended.

5.0 Safety

5.1 Safety glasses, gloves and a lab coat should be worn while performing this analysis.

5.2 Always work under the fume hood when working with sulfuric acid.

5.3 Boiling acid is inherently dangerous. Use proper glassware that is suitable for high temperature.

5.4 All glassware, including test tubes should be inspected before use and determined to be safe for use at high temperature.

6.0 Equipment and Supplies

6.1 Photometer - A spectrophotometer suitable for measurement at 625 nm.

6.2 Heat-resistant test tubes - 15 x 85 mm (length of the test tubes can vary). Tubes must be clean and lint free.

6.3 Heat block - A standard heat block suitable for maintaining temperature at 100 °C.

6.4 Filtration equipment - Glass filtering flask, glass filtering funnel, glass filter holder, aluminum clamp, GF/F filter, support screen, PTFE gasket

7.0 Reagents and Standards

7.1 Anthrone reagent: Dissolve 0.1 g of anthrone (97%) in 50 mL concentrated sulfuric acid. This will be sufficient reagent for approximately 16 samples and standards. If more volume is needed keep ratio of anthrone to sulfuric acid consistent to maintain the same concentration. Reagent solution should be prepared immediately before use. Keep the reagent solution in an ice water bath once prepared.

7.2 Standard mannose solution: Dissolve D-mannose ≥ 99% in Millipore water.

8.0 Sample Collection, Preservation, and Storage

8.1 Samples are collected in clean glass or plastic carboys or bottles.

8.2 Samples should be analyzed as soon as possible after collection. If necessary samples can be stored at 4 °C for up to 7 days until analysis or can be preserved by freezing (-18 °C) up to 14 days until analysis.

8.3 Samples are filtered through GF/F filter (pore size: 0.7 μm) prior to analysis.

9.0 Quality Control [10]

9.1 Laboratory Reagent Blank (LRB)

9.1.1 Use ultrapure water to zero the spectrophotometer and to make LRB.

9.1.2 The LRB result should be approximately 0.04 absorbance units (AU) at wavelength 625 nm after addition of reagents and completion of the reaction in comparison to ultrapure water.

9.1.3 If LRB is too high, re-zero the instrument with ultrapure water and rerun LRB. If the problem persists, consider sources of laboratory contamination, including bacterial contamination of laboratory water.

9.1.4 An LRB should be analyzed with every batch and at least once for every 20 samples.

9.2 Calibration Check (CC)

9.2.1 100 mg/L D-mannose prepared using same source as used in the standard curve.

9.2.2 Percent (%) Recovery must be within ± 25%.

$$\%\ Recovery = \frac{found\ value}{true\ value} * 100\%$$

9.2.3 When out of range, repeat to confirm. If failure persists, perform new standard curve and reanalyze samples.

9.2.4 A CC should be analyzed with every batch and at least once for every 20 samples.

9.3 Laboratory Control Standard (LCS)

9.3.1 200 mg/L D-mannose prepared using different manufacturer than CC.

9.3.2 Percent (%) Recovery must be within ± 25%.

9.3.3 When out of range, repeat to confirm. If failure persists, perform new standard curve and reanalyze samples.

9.3.4 An LCS should be analyzed with every batch and at least once for every 20 samples.

9.4 Laboratory Fortified Sample Matrix (LFSM)

9.4.1 Spike a 0.6mL sample in test tube with 20 µL of 3,000 mg/L D-mannose using the same source as CC. Final concentration is 100 mg/L.

9.4.2 Percent (%) Recovery must be within ± 25%.

$$\%\ Recovery = \frac{(LFSM\ sample\ result - sample\ result)}{known\ LFSM\ added\ concentration} * 100\%$$

9.4.3 A LFSM should be analyzed with every batch and at least once for every 20 samples.

9.5 Control Charts

9.5.1 Control chart is composed of upper and lower control limits and upper and lower warning limits around the mean of % recovery values which defines acceptable % recovery range for QA/QC (Example control chart in Section 17)

9.5.2 Control Limit (CL): When out of range, repeat to confirm. If failure persists, perform corrective action.
Upper Control Limit (UCL) = $\bar{x} + 3s$
Lower Control Limit (LCL) = $\bar{x} - 3s$

9.5.3 Warning Limit (WL): When three successive measurements are out of range, perform corrective action.
Upper Warning Limit (UWL) = $\bar{x} + 2s$
Lower Warning Limit (LWL) = $\bar{x} - 2s$

$$s = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{(n-1)}}$$

10.0 Calibration and Standardization

10.1 A new standard curve is required every 30 days, when QA samples fail quality assurance requirements and for every new analyst performing the analysis.

10.2 For each standard curve and QA/QC, record the standard source, including manufacturer, catalog number, lot number, purity, and expiration date.

10.3 Prepare minimum 5 concentrations within 6 – 1000 mg/L range for standard curve.

11.0 Procedure

11.1 Place 0.6 mL of filtered sample or calibration standard into heat-resistant test tube in test tube rack.
11.2 Place the test tube rack in ice water bath.
11.3 Using a 5 ml pipette, add 3 ml of cold anthrone reagent (7.1) into the heat-resistant test tube and mix well by swirling.
11.4 Allow to react for 5 minutes in ice water bath.
11.5 Place the tubes in heating block at 100 °C for 10 minutes.
11.6 Transfer the tubes back in to ice water bath.
11.7 Once cooled down, fill a 1-cm quartz cuvette with the sample and place the cuvette in a spectrophotometer.
11.8 Measure and record absorbance at 625 nm.

12.0 Data Analysis and Calculations

12.1 Prepare a standard curve by plotting the absorbance values of standard versus the corresponding carbohydrate concentrations.
12.2 Obtain concentration value of sample directly from prepared standard curve. Report results as carbohydrate as mannose, mg/L.

13.0 Method Performance

13.1 Precision was calculated for Millipore water matrix.

Mannose Concentration (mg/L)	Sample Number, n	Precision (mg/L)	Precision (%)
0	8	± 6.86	
10	8	± 1.98	± 19.84
25	3	± 1.64	± 6.56
30	4	± 2.65	± 8.85
50	8	± 4.45	± 8.91
70	4	± 12.52	± 17.88
100	8	± 10.60	± 10.60
200	4	± 13.94	± 6.97
400	4	± 28.12	± 7.03
600	4	± 38.31	± 6.38
800	4	± 40.73	± 5.09
1000	4	± 60.29	± 6.03

14.0 Waste Management

Wastes generated from this process contain sulfuric acid and are corrosive ($pH \leq 2$). Place all waste containing sulfuric acid in a suitable glass or plastic container. It is the responsibility of the generator to correctly characterize and remove the waste in accordance with local, state and/or federal regulations.

15.0 References

[1] Dreywood, R., "Qualitative Test for Carbohydrate Material", *Industrial & Engineering Chemistry Analytical Edition*, 1946, 499.

[2] Gerhardt, P., Murray, R. G. E., Wood, W. A., Krieg, N. R., Methods for General and Molecular Microbiology. American Society for Microbiology, Washington, D.C., 1994.

[3] Koehler, L.H., "Differentiation of Carbohydrates by Anthrone Reaction Rate and Color Intensity", *Analytical Chemistry*, 24, 10, 1952, 1576-1579.

[4] Kwon, T., Watts, B.M., "A New Color Reaction of Anthrone with Malonaldehyde and Other Aliphatic Aldehydes", *Analytical Chemistry*, 35, 6, 1963, 733-735.

[5] Morris, D. L., "Quantitative Determination of Carbohydrates With Dreywood's Anthrone Reagent", *Science*, 107, 1948, 254-255.

[6] Stringfellow, W.T., Camarillo, M.K., "Flowback verses first-flush: new information on the geochemistry of produced water from mandatory reporting", *Environmental Science-Processes & Impacts*, 21, 2019, 370-383.

[7] Stringfellow, W.T., Domen, J.K., Camarillo, M.K., Sandelin, W.L., Borglin, S., "Physical, chemical, and biological characteristics of compounds used in hydraulic fracturing", *Journal of Hazardous Materials*, 275, 2014, 37-54.

[8] Wolfrom, M.L., Schuetz, R.D., Cavalieri, L.F., "Chemical Interactions of Amino Compounds and Sugars. III. The Conversion of D-Glucose to 5-(Hydroxymethyl)-2-furaldehyde", *Journal of the American Chemical Society*, 70, 2, 1948, 514-517.

[9] EPA Drinking Water Method Format, U.S. Environmental Protection Agency, November 2017.

[10] Standard Methods for the Examination of Water and Wastewater. American Public Health Association, American Water Works Association and Water Environment Federation, Washington, D.C., 1998.

16.0 Acknowledgements

This work was funded by the California Department of Conservation under award agreement 2017-011 with Lawrence Berkeley National Laboratory.

This protocol was subject to internal review by Drs. Sharon E. Borglin, Mary Kay Camarillo, and Mark Conrad, Earth & Environmental Sciences Area, Lawrence Berkeley National Laboratory. Dr. Camarillo is also a professor at the University of the Pacific, Stockton, CA. External review was provided by the California Department of Conservation's Division of Oil, Gas, and Geothermal Resources.

17.0 Suggested Citation

Lee, J. Y. and W. Stringfellow. 2019. Method: Carbohydrate in Produced Water (Colorimetric), LBNL Report No. 2001223. Lawrence Berkeley National Laboratory, Berkeley, CA.

18.0 Tables, Diagrams, Forms, Flowcharts, and Validation Data

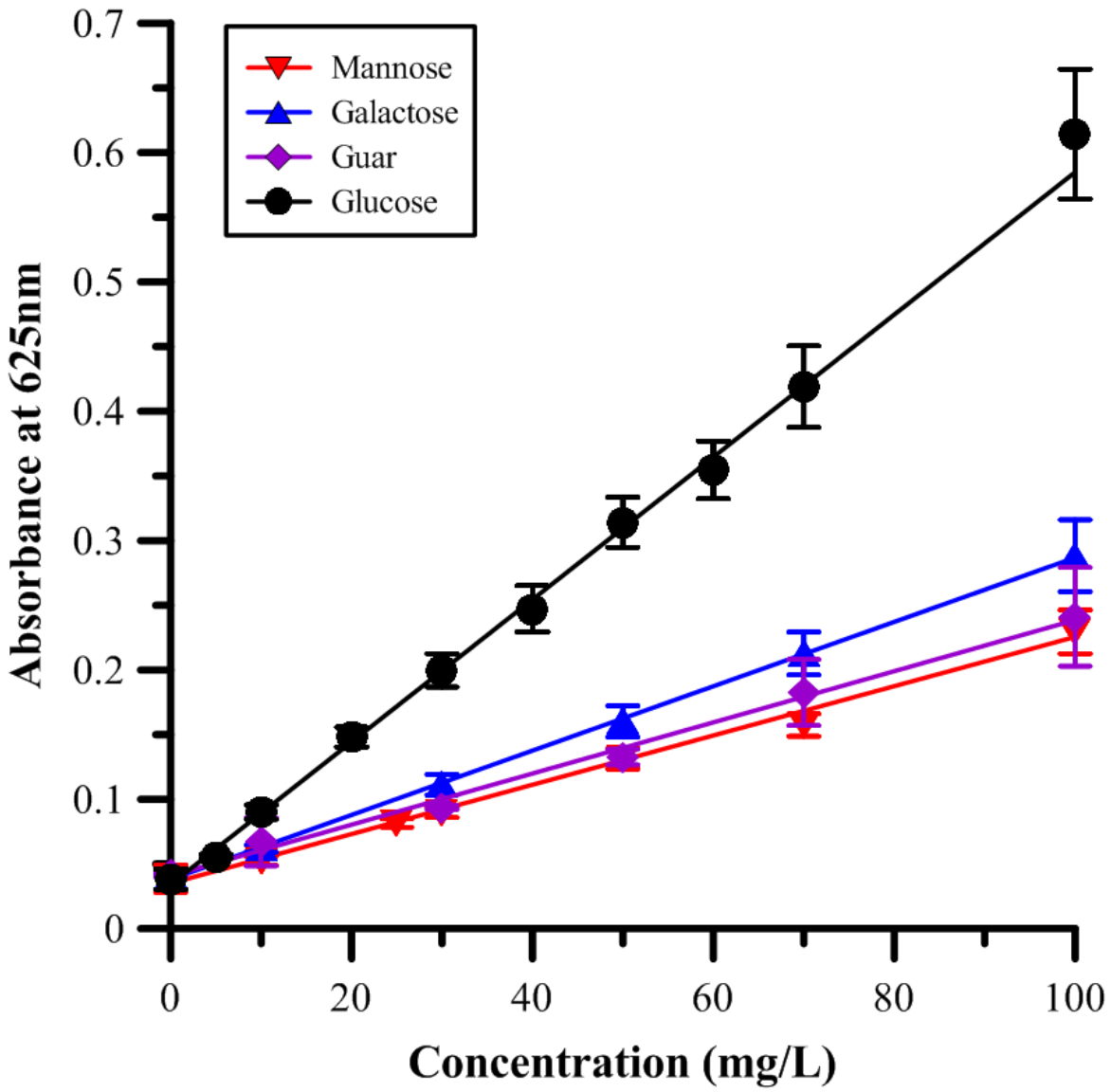

Figure 1. Standard curves for various carbohydrates.

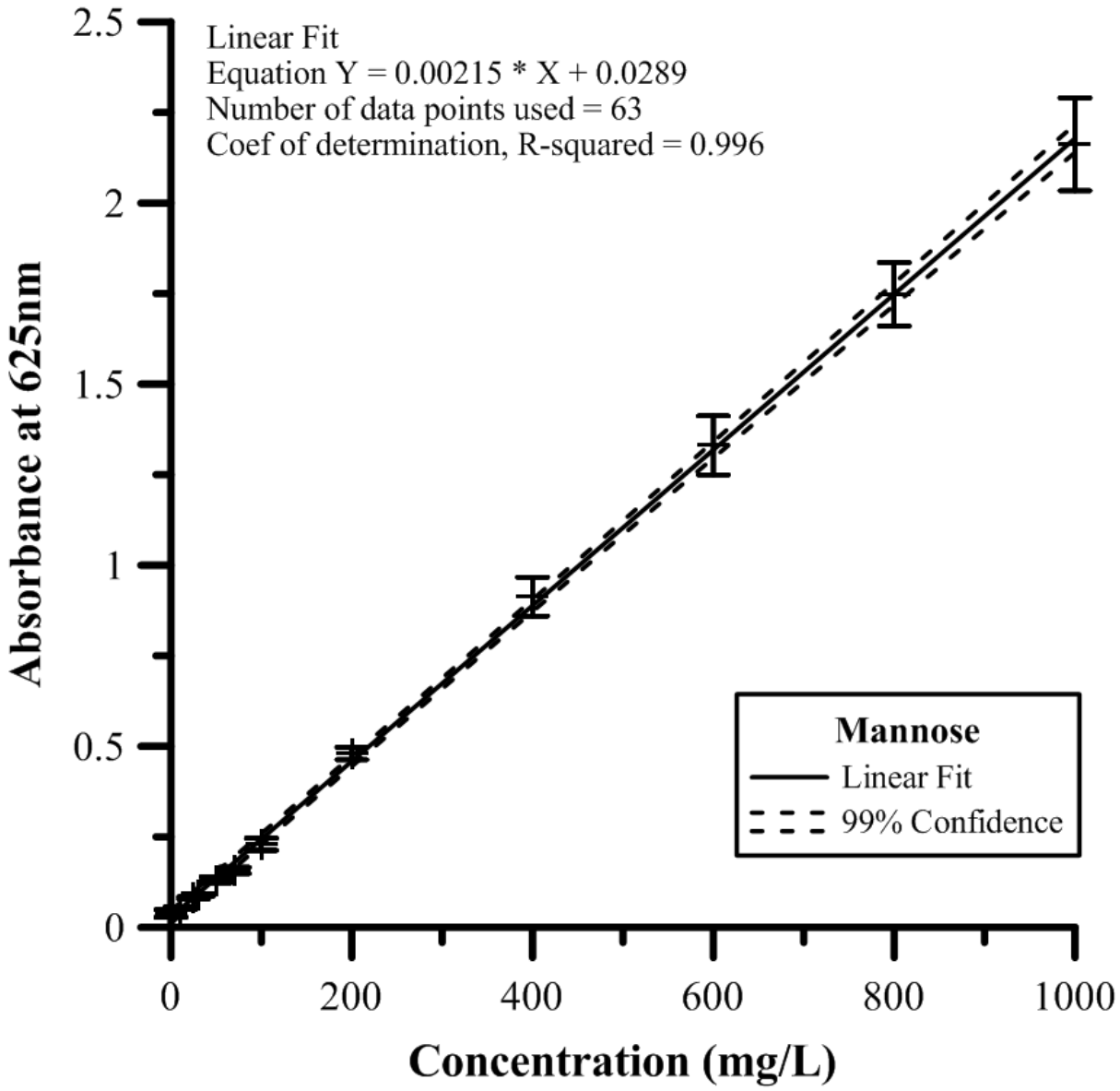

Figure 2. Example standard curve for D-Mannose.

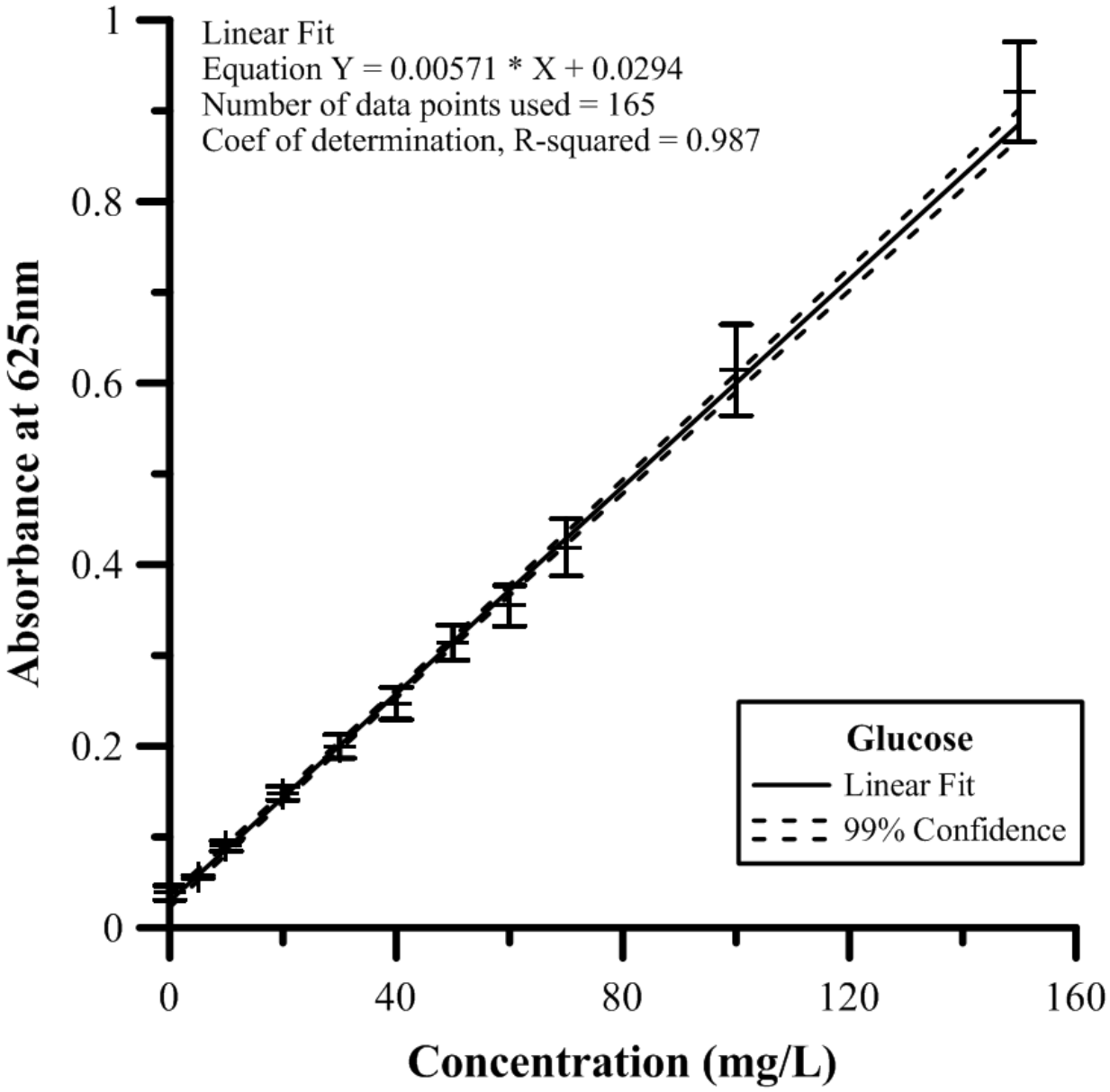

Figure 3. Example standard curve for D-Glucose. Detection Range 4 – 150 mg/L as glucose.

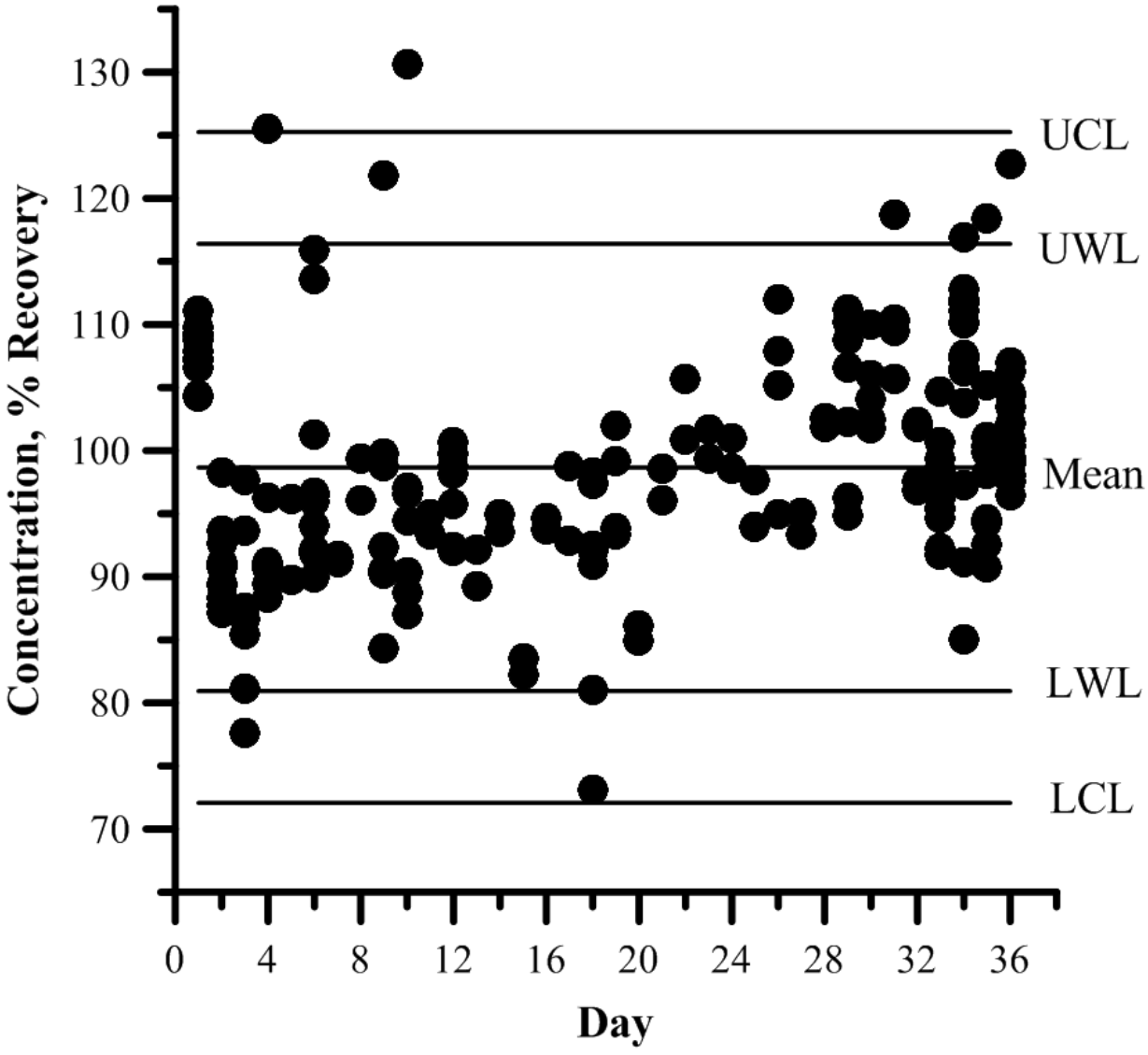

Figure 4. Control charts for carbohydrate. Mean=99%, UWL=116%, LWL=81%, UCL=125%, LCL=72%. [10]

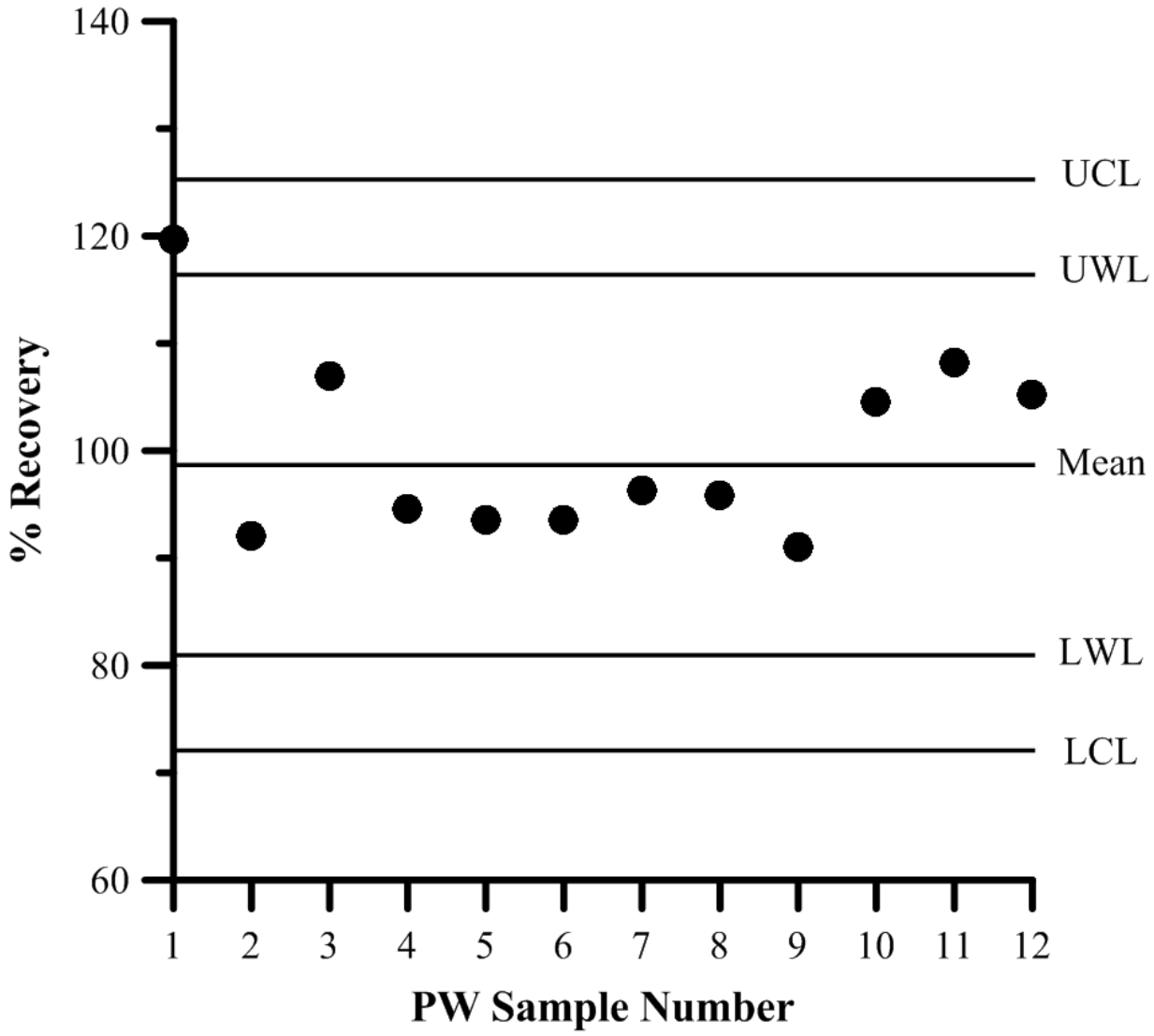

Figure 5. Percent recovery of spiked produced water (PW) samples plotted on carbohydrate control charts.