

## **Appendix 3.**

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### **Laboratory Method and Change Timeline**

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**Table 3–1.** Descriptions and uniform resource locators (URLs) for referenced publications, Web pages, and memos used to develop timelines of changes in laboratory methods and procedures.

[Abbreviations contained within the parentheses are used in the timelines to indicate from which resource the information was derived. USGS, U.S. Geological Survey]

Resource	Citation or URL	Availability
National Water Quality Lab technical memos (NWQL)	<a href="http://wwwnwql.cr.usgs.gov/dyn.shtml?techmemo">http://wwwnwql.cr.usgs.gov/dyn.shtml?techmemo</a>	USGS internal
National Water Quality Lab Rapi-Notes (Rapi-Note)	<a href="http://wwwnwql.cr.usgs.gov/rapi-note-index.shtml">http://wwwnwql.cr.usgs.gov/rapi-note-index.shtml</a>	USGS internal
National Water Quality Lab policy memos (NWQL policy)	<a href="http://wwwnwql.cr.usgs.gov/dyn.shtml?policy_memo">http://wwwnwql.cr.usgs.gov/dyn.shtml?policy_memo</a>	USGS internal
Office of Water Quality technical memos (OWQ) [previously Quality of Water Branch (QWB Tech Memo)]	<a href="http://water.usgs.gov/admin/memo/QW/">http://water.usgs.gov/admin/memo/QW/</a> (Office of Water Quality Web site),	Publicly accessible
	<a href="http://phoenix.cr.usgs.gov/www/references.html">http://phoenix.cr.usgs.gov/www/references.html</a> (Phoenix Web site),	USGS internal
	<a href="http://pubs.usgs.gov/dds/wqn96cd/html/wqn/qasure/qasure.htm">http://pubs.usgs.gov/dds/wqn96cd/html/wqn/qasure/qasure.htm</a> (Digital Data Series-37 report [DDS-37])	Publicly accessible
Open-File Report 00–170	Patton, Charles, J., and Truitt, Earl P., 2000, U.S. Geological Survey Open-File Report 00–170, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Ammonium Plus Organic Nitrogen by a Kjeldahl Digestion Method and an Automated Photometric Finish that Includes Digest Cleanup by Gas Diffusion, p. 31. <a href="http://pubs.usgs.gov/of/2000/0170/report.pdf">http://pubs.usgs.gov/of/2000/0170/report.pdf</a>	Publicly accessible
Open-File Report 92–146	Patton, Charles, J., and Truitt, Earl P., 1992, U.S. Geological Survey Open-File Report 92–146, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Total Phosphorus by a Kjeldahl Digestion Method and an Automated Colorimetric Finish that Includes Dialysis, p. 11. <a href="http://nwql.usgs.gov/Public/pubs/OFR92-146/OFR92-146.pdf">http://nwql.usgs.gov/Public/pubs/OFR92-146/OFR92-146.pdf</a>	Publicly accessible
Open-File Report 92–480	Brenton, Ronald W., and Arnett, Tony, L., 1992, U.S. Geological Survey Open-File Report 92–480, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Dissolved Organic Carbon by UV-Promoted Persulfate Oxidation and Infrared Spectrometry, p. 12. <a href="http://pubs.usgs.gov/of/1992/0480/report.pdf">http://pubs.usgs.gov/of/1992/0480/report.pdf</a>	Publicly accessible
Open-File Report 97–380	Burkhardt, Mark R.; Kammer, James, A.; Jha, Veirendra, K.; O’Mara-Lopez, Peggy, G.; and Woodworth, Mark T., 1997, U.S. Geological Survey Open-File Report 97–380, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Nonpurgeable Suspended Organic Carbon by Wet-Chemical Oxidation and Infrared Spectrometry, p. 12. <a href="http://nwql.usgs.gov/pubs/OFR/OFR-97-380.pdf">http://nwql.usgs.gov/pubs/OFR/OFR-97-380.pdf</a>	Publicly accessible
Open-File Report 94–351	U.S. Geological Survey Approved Inorganic and Organic Methods for the Analysis of Water and Fluvial Sediment 1954-94 by Marvin Fishman, Jon Raese, Carol Gerlitz, and Richard Husband; 1994; “Table 1. Approved inorganic and organic methodology, 1954–1994, in alphabetical order.” <a href="http://nwql.usgs.gov/pubs/OFR/OFR-94-351.html">http://nwql.usgs.gov/pubs/OFR/OFR-94-351.html</a>	Publicly accessible
Water-Resources Investigations Report 03–4174	Patton, Charles, J., and Kryskalla, Jennifer, R., 2003. Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Evaluation of Alkaline Persulfate Digestion as an Alternative to Kjeldahl Digestions for Determination of Total and Dissolved Nitrogen and Phosphorus in Water. USGS Water-Resources Investigations Report 03–4174. <a href="http://nwql.usgs.gov/Public/pubs/WRIR03-4174/WRIR03-4174.pdf">http://nwql.usgs.gov/Public/pubs/WRIR03-4174/WRIR03-4174.pdf</a>	Publicly accessible
Scientific Investigations Report 2012–5281	Rus, David L.; Patton, Charles J.; Mueller, David K., and Crawford, Charles G., 2012. Assessing Total Nitrogen in Surface-Water Samples—Precision and Bias of Analytical and Computational Methods. USGS Scientific Investigations Report 2012–5281. <a href="http://pubs.usgs.gov/sir/2012/5281/sir12_5281.pdf">http://pubs.usgs.gov/sir/2012/5281/sir12_5281.pdf</a>	Publicly accessible

**Table 3-1.** Descriptions and uniform resource locators (URLs) for referenced publications, Web pages, and memos used to develop timelines of changes in laboratory methods and procedures.—Continued

[Abbreviations contained within the parentheses are used in the timelines to indicate from which resource the information was derived. USGS, U.S. Geological Survey]

Resource	Citation or URL	Availability
Techniques and Methods 5-B8	Patton, C.J., and Kryskalla, J.R., 2011, Colorimetric determination of nitrate plus nitrite in water by enzymatic reduction, automated discrete analyzer methods: U.S. Geological Survey Techniques and Methods, book 5, chap. B8, 34 p. <a href="http://pubs.usgs.gov/tm/05b08/">http://pubs.usgs.gov/tm/05b08/</a>	Publicly accessible
NWQL Catalog, 2014	<a href="http://wwwnwql.cr.usgs.gov/USGS/catalog/index.cfm">http://wwwnwql.cr.usgs.gov/USGS/catalog/index.cfm</a>	USGS internal
Techniques of Water-Resources Investigations 5-A1	Fishman, Marvin, J., and Friedman, Linda, C., 1989, Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, p. 12. <a href="http://pubs.usgs.gov/twri/twri5-a1/">http://pubs.usgs.gov/twri/twri5-a1/</a>	Publicly accessible
Clow and Mast, 1999	Clow, D. W., and M. A. Mast, 1999, Long-term trends in stream water and precipitation chemistry at five headwater basins in the northeastern United States, Water Resources Research, 35(2), 541–554, doi: 10.1029/1998WR900050. <a href="http://onlinelibrary.wiley.com/doi/10.1029/1998WR900050/full">http://onlinelibrary.wiley.com/doi/10.1029/1998WR900050/full</a>	Publicly accessible
Aiken and others, 2002	Aiken, G., L. A. Kaplan, and J. Weishaar, 2002, Assessment of relative accuracy in the determination of organic matter concentrations in aquatic systems, Journal of Environmental Monitoring, 4(1), 70–74, doi:10.1039/b107322m. <a href="http://pubs.rsc.org/en/content/articlehtml/2002/EM/B107322M">http://pubs.rsc.org/en/content/articlehtml/2002/EM/B107322M</a>	Publicly accessible

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**Table 3-2.** National Water Quality Lab (NWQL) method and procedure changes for nitrogen parameters. Abbreviations are defined in table 3-1.<sup>1</sup>

[?, start and (or) end year is unknown; °C, degree Celsius; EPA, U.S. Environmental Protection Agency; mg/L, milligram per liter; ~, approximate year or date]

Year	NWQL method and procedure changes
<b>Total nitrogen (unfiltered)</b>	
1970–current	Calculated. “total, as NO <sub>3</sub> ” from 1970 and “total” from 1977. [OFR 94–351] Positive bias in total nitrogen (TN) when calculated as nitrate+nitrite and ammonia+organic nitrogen due to nitrate interference in the Kjeldahl digestion method. TN calculated as the sum of dissolved nitrogen and particulate nitrogen is currently the only non-biased method for determining TN. [WRIR 03–4174; SIR 2012–5281; OWQ 13-01]
2004–current	Direct determination by alkaline persulfate digestion. Older calculation methods still available. [Rapi-Note 03-040, WRIR 03–4174] Negative bias in TN determinations using this method due to the incomplete digestion of suspended sediment. [OWQ 09-03; SIR 2012–5281; OWQ 13-01]
<b>Nitrate + nitrite (filtered)</b>	
1970–75	Colorimetry, hydrazine reduction-diazotization, segmented flow. [OFR 94–351]
1973–2014	Colorimetry, cadmium reduction-diazotization, segmented flow. [OFR 94–351; Rapi-Note 14-014]
1982–86	Colorimetry, hydrazine reduction-diazotization, discrete. [OFR 94–351]
1986–current	Colorimetry, cadmium reduction-diazotization, segmented flow, low-ionic strength waters. [OFR 94–351; Rapi-Note 14-014]
2012–current	Colorimetry, enzymatic reduction, automated discrete analyzer. [Rapi-Note 11-021, Rapi-Note 12-001, T&M 5-B8, NWQL Catalog, 2014]
?–1971	Preserved by uncertain means but may have included the addition of HgCl <sub>2</sub> or H <sub>2</sub> SO <sub>4</sub> and (or) chilling. [DDS-37, table 8]
1972–81	Preserved by chilling to 4 °C. [OWQ 72-09]
1981–95	Preserved by adding HgCl <sub>2</sub> and chilling to 4 °C. [QWB Tech Memo 80-26; OWQ 94-16]
1995–current	Preserved by chilling to 4 °C; samples collected for EPA compliance may have also have had H <sub>2</sub> SO <sub>4</sub> added during this time. [OWQ 94-16]
<b>Nitrate (filtered)</b>	
1969–76	Colorimetry (brucine). [OFR 94–351]
1972–current	Calculated from nitrate+nitrite and nitrite analyses. [OFR 94–351; NWQL Catalog, 2014]
1981–2000	Ion chromatography, low-ionic strength. [OFR 94–351, NWQL 00-06]
1985–90 or 2000	Ion chromatography. [OFR 94–351 indicates 1990 end date; NWQL 00-06 indicates 2000 end date]
<b>Nitrite (filtered)</b>	
1956–76	Colorimetry, diazotization. [OFR 94–351]
1974–2006	Colorimetry, diazotization, segmented flow. [OFR 94–351; Rapi-Note 06-016]
1981–?	Ion chromatography, low-ionic strength. [OFR 94–351]
1982–86	Colorimetry, diazotization, discrete. [OFR 94–351]
1985–90	Ion chromatography. [OFR 94–351]
1986–2006	Colorimetry, diazotization, segmented flow, low-ionic strength. [OFR 94–351; Rapi-Note 06-016]
2006–current	Colorimetry, diazotization, segmented flow. New instruments at lab negate the need to distinguish regular and low-level analyses. [Rapi-Note 06–016]
?–1971	Preserved by uncertain means but may have included the addition of HgCl <sub>2</sub> or H <sub>2</sub> SO <sub>4</sub> and (or) chilling. [DDS-37, table 8]
1972–81	Preserved by chilling to 4 °C. [OWQ 72-09]
1981–95	Preserved by adding HgCl <sub>2</sub> and chilling to 4 °C. [QWB Tech Memo 80-26; OWQ 94-16]
1995–current	Preserved by chilling to 4 °C; samples collected for EPA compliance may have also have had H <sub>2</sub> SO <sub>4</sub> added during this time. [OWQ 94-16]
<b>Ammonia (filtered)</b>	
?–?	Calculation. [OFR 94–351]
>1971–?	Electrometric, ion-selective electrode. [Fishman and Friedman, TWRI 5-A1, 1989; OFR 94–351]
1956–76	Colorimetry, distillation-nesslerization. [OFR 94–351]

**Table 3-2.** National Water Quality Lab (NWQL) method and procedure changes for nitrogen parameters. Abbreviations are defined in table 3-1.<sup>1</sup>—Continued

[?, start and (or) end year is unknown; °C, degree Celsius; EPA, U.S. Environmental Protection Agency; mg/L, milligram per liter; ~, approximate year or date]

Year	NWQL method and procedure changes
1973–83	Colorimetry, indophenol, segmented-flow. [OFR 94–351]
1984–86	Colorimetry, salicylate-hypochlorite, discrete. [OFR 94–351]
1984–current	Colorimetry, salicylate-hypochlorite, segmented-flow [OFR 94–351, NWQL Catalog, 2014]. In 2006, new instruments at lab negate the need to distinguish regular and low-level analyses. [Rapi-Note 06-016]
1986–2006	Colorimetry, salicylate-hypochlorite, segmented-flow, low-ionic strength. [OFR 94–351]
1998	Minimum reporting level changed to 0.02 mg/L. Data released prior to this date will not be modified, but it is suggested that concentrations < 0.2 mg/L as nitrogen be interpreted as such. [NWQL 97-10]
?–1971	Preserved by uncertain means but may have included the addition of HgCl <sub>2</sub> or H <sub>2</sub> SO <sub>4</sub> and (or) chilling. [DDS-37, table 8]
1972–81	Preserved by chilling to 4 °C. [OWQ 72-09]
1981–95	Preserved by adding HgCl <sub>2</sub> and chilling to 4 °C. [QWB Tech Memo 80-26; OWQ 94-16]
~1985	HgCl <sub>2</sub> tablets used for preservation of nutrient samples may be randomly contaminated with ammonia. [OWQ 85-07]
1995–current	Preserved by chilling to 4 °C; samples collected for EPA compliance may have also have had H <sub>2</sub> SO <sub>4</sub> added during this time. [OWQ 94-16]
<b>Total Kjeldahl nitrogen (ammonia + organic nitrogen, unfiltered)</b>	
1973–78	Colorimetry, digestion-distillation-indophenol, segmented flow. [OFR 94–351]
1976	May be analyzed using a new provisional method. [OWQ 76-16]
1978–91	Colorimetry, block digester, salicylate-hypochlorite, segmented flow. [OFR 94–351]
~1983–85	Low precision in determinations from Atlanta and Denver labs. [OWQ 86-02]
1984–86	Colorimetry, block digester, salicylate-hypochlorite, discrete. [OFR 94–351]
1986–92	Semi-automated, block digester method. Digestion blanks (= 0.1 mg/L) were not subtracted from concentrations using this method. Determinations are biased high and a step-change decrease in Kjeldahl nitrogen concentration of 0.1 mg/L on 10/1/1991. [OFR 00–170]
1992–current	Colorimetry, microblock digester, salicylate hypochlorite. [OFR 94–351; NWQL catalog, 2014]
?–1971	Preserved by uncertain means but may have included the addition of HgCl <sub>2</sub> or H <sub>2</sub> SO <sub>4</sub> and (or) chilling. [DDS-37, table 8]
1972–81	Preserved by chilling to 4 °C. [OWQ 72-09]
1981–95	Preserved by adding HgCl <sub>2</sub> and chilling to 4 °C. [QWB Tech Memo 80-26; OWQ 94-16]
~1985	HgCl <sub>2</sub> tablets used for preservation of nutrient samples may be randomly contaminated with ammonia. [OWQ 85-07]
1995–98	Preserved by chilling to 4 °C; samples collected for EPA compliance may have also have had H <sub>2</sub> SO <sub>4</sub> added during this time. [OWQ 94-16]
1999–current	Preserved by adding H <sub>2</sub> SO <sub>4</sub> and chilling to 4 °C. [OWQ 99-04]

<sup>1</sup>These timelines documenting the history of changes at the National Water Quality Laboratory are not definitive. They were pieced together using disparate technical memos, reports, and Rapi-Notes. They may be missing one or more important changes.

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**Table 3-3.** National Water Quality Lab (NWQL) method and procedure changes for phosphorus parameters. Abbreviations are defined in table 3-1.<sup>1</sup>

[est, estimated year range based on available information; °C, degree Celsius; EPA, U.S. Environmental Protection Agency; mg/L, milligram per liter; ?, start and (or) end year is unknown]

Year	NWQL method and procedure changes
<b>Total phosphorus (unfiltered)</b>	
1973–91	Colorimetry, phosphomolybdate, segmented-flow. [OFR 94–351] Possible negative bias during this period because of an error in the implementation of the method that resulted in incomplete digestion. For most samples negative bias was between 0.01 and 0.03 mg/L, but bias was especially evident for samples with >50 mg/L of suspended sediment, for which negative bias was between 0.04 and 0.18 mg/L. The memo pertaining to this bias issue states, “There is no general way to make scientifically defensible corrections to the data for either period.” An updated method with dilution was used from May 1990 and September 1991 to address bias introduced by error in methods; bias was still present. [OWQ 92-10]
1985–86	Colorimetry, phosphomolybdate, discrete. [OFR 94–351]
1991–99	Colorimetry, phosphomolybdate, segmented-flow, low-ionic strength. [OFR 94–251]
1991–2004 (est)	Colorimetry, phosphomolybdate, block digester (micro-Kjeldahl digestion), segmented-flow [OFR 94–351, Rapi-Note 03-040]. Higher relative total phosphorus concentrations from micro-Kjeldahl digestion method compared to samples before 1991 (one source indicates 0.003 to 0.3 mg/L; another indicates 0.02 to 0.04 mg/L of relative bias). The relative difference increases with increasing phosphorus concentration. This relative difference is due to the error in the older methods discussed above. No statistically significant difference in dissolved phosphorus concentrations was observed. [OWQ 92-10; OFR 92–146]
1991–98	Change in reporting level for phosphorus in 1998. Historical phosphorus data reported as < 0.03 mg/L as phosphorus since the new method was implemented on 10/1/1991 should be recensored to <0.05 mg/L as phosphorus. [NWQL 98-07]
1999	Change in field treatment protocols and bottle types. [OWQ 99-04]
1999–current	U.S. Environmental Protection Agency method 365.1 for low-concentration samples (0.004 to 0.200 mg/L). Method was swapped by NWQL to the micro-Kjeldahl digestion method if sample concentration was > 0.2 mg/L as phosphorus, but method was not swapped if micro-Kjeldahl digestion method was requested and sample concentration was <0.2 mg/L as phosphorus. [NWQL 99-05]
2004–current	U.S. Environmental Protection Agency method 365.1 or alkaline persulfate digestion for all samples. [Rapi-Note 03-040; WRIR 03–4174]
?–1971	Preserved by uncertain means but may have included the addition of HgCl <sub>2</sub> or H <sub>2</sub> SO <sub>4</sub> and (or) chilling. [DDS-37, table 8]
1972–81	Preserved by chilling to 4 °C. [OWQ 72-09]
1981–95	Preserved by adding HgCl <sub>2</sub> and chilling to 4 °C. [QWB Tech Memo 80-26; OWQ 94-16]
1995–98	Preserved by chilling to 4 °C; samples collected for EPA compliance may have also have had H <sub>2</sub> SO <sub>4</sub> added during this time. [OWQ 94-16]
1999–current	Preserved by adding H <sub>2</sub> SO <sub>4</sub> and chilling to 4 °C. [OWQ 99–04]
<b>Dissolved phosphorus (filtered)</b>	
1956–74	Colorimetry, phosphomolybdate, manual. [OFR 94–351]
1973–91	Colorimetry, phosphomolybdate, automated, segmented-flow. [OFR 94–351] Possible negative bias during this period because of an error in the implementation of the method that resulted in incomplete digestion. For most samples negative bias was between 0.01 and 0.03 mg/L, but bias was especially evident for samples with >50 mg/L of suspended sediment, for which negative bias was between 0.04 and 0.18 mg/L. The memo pertaining to this bias issue states, “There is no general way to make scientifically defensible corrections to the data for either period.” [OFR 94–351, OWQ 92-10] Updated method with dilution was used from May 1990 and September 1991 to address bias introduced by error in methods; bias was still present. [OFR 94–251; OWQ 92-10]
1985–86	Colorimetry, phosphomolybdate, discrete. [OFR 94–351]
1991–98	Colorimetry, phosphomolybdate, segmented-flow, low-ionic strength. [OFR 94–351; NWQL 99-05]
1991–2004 (est)	Colorimetry, phosphomolybdate, block digester (micro-Kjeldahl digestion), segmented-flow [OFR 94–351; Rapi-Note 03-040]. Positive bias in total phosphorus determinations from micro-Kjeldahl digestion method (one source indicates 0.003 to 0.3 mg/L; another indicates 0.02 to 0.04 mg/L of bias). The bias increases with increasing phosphorus concentration. This bias is due to the error in the older methods discussed above. No statistically significant difference in dissolved phosphorus concentrations was observed. [OWQ 92-10; OFR 92–146]

**Table 3-3.** National Water Quality Lab (NWQL) method and procedure changes for phosphorus parameters. Abbreviations are defined in table 3-1.<sup>1</sup>—Continued

[est, estimated year range based on available information; °C, degree Celsius; EPA, U.S. Environmental Protection Agency; mg/L, milligram per liter; ?, start and (or) end year is unknown]

Year	NWQL method and procedure changes
1991–98	Change in reporting level for phosphorus in 1998. Historical phosphorus data reported as < 0.03 mg/L as phosphorus since the new method was implemented on 10/1/1991 should be recensored to <0.05 mg/L as phosphorus. [NWQL 98-07]
1999–current	U.S. Environmental Protection Agency method 365.1 for low-concentration samples (0.004 to 0.200 mg/L). [NWQL 99-05] Method was swapped by NWQL to the micro-Kjeldahl digestion method if sample concentration was > 0.2 mg/L as phosphorus, but method was not swapped if micro-Kjeldahl digestion method was requested and sample concentration was <0.2 mg/L as phosphorus.
2004–current	U.S. Environmental Protection Agency method 365.1 or alkaline persulfate digestion for all samples. [Rapi-Note 03-040; WRIR 03–4174]
?–1971	Preserved by uncertain means but may have included the addition of HgCl <sub>2</sub> or H <sub>2</sub> SO <sub>4</sub> and (or) chilling. [DDS-37, table 8]
1972–81	Preserved by chilling to 4 °C. [OWQ 72-09]
1981–95	Preserved by adding HgCl <sub>2</sub> and chilling to 4 °C. [QWB Tech Memo 80-26; OWQ 94-16]
1995–current	Preserved by chilling to 4 °C; samples collected for EPA compliance may have also have had H <sub>2</sub> SO <sub>4</sub> added during this time. [OWQ 94-16]
<b>Orthophosphate (filtered)</b>	
1956–76	Colorimetry, phosphomolybdate, manual. [OFR 94–351]
1965–76	Manual calculation. [OFR 94–351]
1973–?	Automated calculation or colorimetry, phosphomolybdate, segmented flow. [OFR 94–351]
1981–2000	Ion chromatography. [OFR 94–351, NWQL 00-06]
1985–90 or 2000	Ion chromatography. [OFR 94–351 indicates 1990 end date; NWQL 00-06 indicates 2000 end date]
1985–86	Colorimetry, phosphomolybdate, discrete. [OFR 94–351]
1986–?	Colorimetry, phosphomolybdate, segmented flow, low-ionic strength. [OFR 94–351]
?–2006	Colorimetry, phosphomolybdate, continuous flow. [Rapi-Note 06-016]
2006–current	Colorimetry, phosphomolybdate, discrete. New instrument at lab negates the need to distinguish regular and low-level analyses. [Rapi-Note 06-016]
?–1971	Preserved by uncertain means but may have included the addition of HgCl <sub>2</sub> or H <sub>2</sub> SO <sub>4</sub> and (or) chilling. [DDS-37, table 8]
1972–81	Preserved by chilling to 4 °C. [OWQ 72-09]
1981–95	Preserved by adding HgCl <sub>2</sub> and chilling to 4 °C. [QWB Tech Memo 80-26; OWQ 94-16]
1995–current	Preserved by chilling to 4 °C; samples collected for EPA compliance may have also have had H <sub>2</sub> SO <sub>4</sub> added during this time. [OWQ 94-16]

<sup>1</sup>These timelines documenting the history of changes at the National Water Quality Laboratory are not definitive. They were pieced together using disparate technical memos, reports, and Rapi-Notes. They may be missing one or more important changes.

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**Table 3-4.** National Water Quality Lab (NWQL) method and procedure changes for major ion parameters. Abbreviations are defined in table 3-1.<sup>1</sup>

[?, start and (or) end year is unknown; mg/L, milligram per liter]

Year	NWQL method and procedure changes
Chloride	
1967-?	Colorimetry, ferric thiocyanate, segmented flow. [OFR 94-351]
1981-88	Colorimetry, ferric thiocyanate, discrete. [OFR 94-351]
1981-?	Ion chromatography, low-ionic strength. [OFR 94-351]
1985-Dec. 1992	Ion chromatography. [OFR 94-351]
1990-1992	Ion chromatography using a Dionex OMNIPAX-500 column. [NWQL 94-03]
1990-1993	NWQL had difficulty with determinations of chloride, sulfate, and fluoride at various times for different reasons over the past several years. Problem appears to be with different methods. [NWQL 93-03; NWQL 94-03].
1992-current	Only filtered samples to be used for chloride, sulfate, and fluoride determinations. Previous practice of substituting unfiltered samples is discontinued. [NWQL 92-07]
1993	Photometric method. [NWQL 93-03; NWQL 94-03]
1994-current	Ion chromatography using standard Dionex AS4A columns. [OFR 94-351, NWQL 94-03]
Sulfate	
1954-76	Titrimetry, thiorin. [OFR 94-351]
1976-83	Colorimetry, complexometric, methylthymol blue, segmented flow. [OFR 94-351]
1981-?	Ion chromatography, low-ionic strength. [OFR 94-351]
1983-90	Turbidimetry, barium sulfate, discrete. [OFR 94-351] Positive bias of 2 mg/L observed in sulfate determinations (those typically < 75 mg/L) from the turbidimetric method because a blank correction was not applied to the determinations. No nationwide adjustment was applied. Regional adjustments were suggested, but it is unclear if these occurred. [OWQ 90-04]
1985-current	Ion chromatography. [OFR 94-351]
1986-89	Positive bias was identified due to the omission of “a background sample-absorbance adjustment when using the turbidimetric analysis method.” [Clow and Mast, 1999, Water Resources Research 35(2)]
1990-92	Ion chromatography using a Dionex OMNIPAX-500 column. [NWQL 94-03]
1990-93	NWQL had difficulty with determinations of chloride, sulfate, and fluoride at various times for different reasons over the past several years. Problem appears to be with different methods. [NWQL 93-03; NWQL 94-03]. Positive bias on the order of 0.5-3 mg/L for samples with sulfate concentrations of 15-75 mg/L. [DDS-337]
1992-current	Only filtered samples to be used for chloride, sulfate, and fluoride determinations. Previous practice of substituting unfiltered samples is discontinued. [NWQL 92-07]
1994-current	Ion chromatography using standard Dionex AS4A columns. [NWQL 94-03]
1995-mid-1996	Negative bias; cause unknown. [Clow and Mast, 1999, Water Resources Research 35(2)]

<sup>1</sup>These timelines documenting the history of changes at the National Water Quality Laboratory are not definitive. They were pieced together using disparate technical memos, reports, and Rapi-Notes. They may be missing one or more important changes.



**Table 3-5.** National Water Quality Lab (NWQL) method and procedure changes for pH, alkalinity, and carbon parameters. Abbreviations are defined in table 3-1.<sup>1</sup>

[UV, ultra-violet; ?, start and (or) end year is unknown; DOC, dissolved organic carbon; OC, organic carbon; MRL, method reporting level; ~, approximate year or date;  $\mu\text{S}/\text{cm}$  at 25 °C, microsiemen per centimeter at 25 degrees Celsius]

Year	NWQL method and procedure changes
<b>Total organic carbon</b>	
1970–current	Wet oxidation. [OFR 94–351]
1986–current	UV-promoted persulfate oxidation and infrared spectrometry. [OFR 92–480]
1986–current	Most oxidation methods found to under-report particulate (suspended) organic carbon, which will affect total organic carbon analyses as well. [Aiken and others, 2002]
10/1/2009	New instrument used for all determinations requesting total organic carbon. No significant difference in determinations between instruments was reported. [Rapi-Note 09-016]
<b>Dissolved organic carbon</b>	
1970–?	Wet oxidation. [OFR 94–351]
1986–current	UV-promoted persulfate oxidation and infrared spectrometry. [OFR 94–351, OFR 92–480]
1992–current	Dohrmann analyzer approved for organic carbon determination. [OFR 92–480]
2000	Filtration of DOC samples with glass-fiber or supor filters instead of silver filters was approved. [OWQ 00-08, OWQ 00-05]
2003	Discontinued dissolved organic carbon lab codes that used silver filters. [Rapi-Note 02-025]
<b>Suspended (particulate) organic carbon</b>	
1970–current	Wet oxidation. [OFR 94–351]
1970– 6/1/1997	Low bias for suspended organic carbon due to incomplete carbon oxidation. [OFR 97–380]
6/1/1997	Wet oxidation methods found to have low bias in suspended OC recovery. New method implemented that included a sonication step to disrupt filtered material to give greater recovery. Historical data were not adjusted by the NWQL. [OFR 97–380, NWQL 97-12]
6/1/2000	High-temperature combustion method (U.S. Environmental Protection Agency method 440.0) introduced for four new constituents, including particulate organic carbon (POC). POC is given same parameter code as suspended organic carbon (SOC) and will ultimately replace older SOC method (wet oxidation with silver filter). POC determined as the difference between total particulate carbon and particulate inorganic carbon, both new constituents determined using new method. [OWQ 00-05, OWQ 00-08, NWQL policy 00-04]
12/1/2002	Discontinued lab codes that used silver filters, including suspended organic carbon. [Rapi-Note 02-025]
~5/16/2003	New lot of filters had different background carbon levels that could result in low bias. [Rapi-Note 03-015]
~6/22/2004	New lot of filters had different background carbon levels that could result in low bias. [Rapi-Note 04-013]
<b>Total particulate carbon/particulate inorganic carbon</b>	
6/1/2000	High-temperature combustion method (U.S. Environmental Protection Agency method 440.0) introduced for four new constituents, including total particulate carbon and particulate inorganic carbon. [OWQ 00-05, OWQ 00-08, NWQL policy 00-04]
~5/16/2003	New lot of filters had different background carbon levels that could result in low bias. [Rapi-Note 03-015]
~6/22/2004	New lot of filters had different background carbon levels that could result in low bias. [Rapi-Note 04-013]
<b>Alkalinity</b>	
1954–?	Electrometric fixed endpoint titration. Switched from manual to automated in 1972. [OFR 94–351]
1982	Parameter codes created for field incremental titration in WATSTORE. [OWQ 82-06]
1986	National Stream Quality Accounting Network (NASQAN) and Hydrologic Benchmark Network (HBN) implement field incremental titration of alkalinity, used codes 99430 and 99440 for alkalinity and bicarbonate, respectively. Used program developed by Texas District. [OWQ 85-19]
1986	Guidance was to perform alkalinity on filtered samples, but only “whole water” parameter codes were available. [OWQ 86-10]

## 10 Appendix 3

**Table 3-5.** National Water Quality Lab (NWQL) method and procedure changes for pH, alkalinity, and carbon parameters. Abbreviations are defined in table 3-1.<sup>1</sup>—Continued

[UV, ultra-violet; ?, start and (or) end year is unknown; DOC; dissolved organic carbon; OC, organic carbon; MRL, method reporting level; ~, approximate year or date;  $\mu\text{S}/\text{cm}$  at 25 °C, microsiemen per centimeter at 25 degrees Celsius]

Year	NWQL method and procedure changes
1986	Parameter codes were consolidated and updated. OWQ indicates that it is not necessary to use separate parameter codes to distinguish fixed endpoint versus incremental endpoint alkalinity titration methods. [OWQ 87-01]
1988	Alkalinity results moved to modern parameter codes to distinguish all permutations of filtered/unfiltered, lab/field, and fixed versus incremental end-point titration. A comparison of lab and field alkalinity values found difference >10 percent in about 18 percent of samples. [OWQ 88-05]
1994	NWQL discontinues routine analysis of alkalinity and encourages the measurement of alkalinity in the field. [NWQL 95-01]
2/10/2003– 3/7/2003	Some alkalinity samples (filtered and unfiltered) have a high bias during this time. [Rapi-Note 03-027]
6/6/2005	New instrument for alkalinity determinations and increase in MRL. [Rapi-Note 05-022]
pH	
10/1/1980	Introduced separate parameter codes for field and laboratory values. [OWQ 80-27]
1982–87	Samples with conductivities <100 $\mu\text{S}/\text{cm}$ at 25 °C were analyzed by hand to allow for longer stabilization time, but this process did not continue after 1987. [NWQL 93-07]
1987	No hand determinations of pH for samples with conductivities < 100 $\mu\text{S}/\text{cm}$ at 25 °C. All pH determinations for LC68 (even low conductivity samples) were only performed on the automated system. Low conductivity samples were also processed using LC1268 which has led to inconsistent handling of these types of samples. [NWQL 93-07, OFR 94–351]
11/1/1992– 12/14/1992	Samples with conductivities <1,200 $\mu\text{S}/\text{cm}$ at 25 °C had unacceptable determinations due to a slow responding electrode. [NWQL 93-07]
12/14/1992	Beginning on 12/14/1992 samples with conductivities < 1,200 $\mu\text{S}/\text{cm}$ at 25 °C were determined by hand, after 12/21/1992 equipment was repaired, and pH determinates are once again acceptable between 100 and 1,200 $\mu\text{S}/\text{cm}$ at 25 °C. Unclear if after this time samples with <100 $\mu\text{S}/\text{cm}$ at 25 °C are being processed by hand for pH determination using LC68. [NWQL 93-07]
12/10/1993	Manual determinations are discontinued for LC68. All lab pH determinations will include an “E” remark code because pH is actually best measured in the field. [NWQL 94-02]
7/1/2010	Began reporting “E” remark code for pH with specific conductance levels < 100 $\mu\text{S}/\text{cm}$ at 25 °C that requested LC68. [Rapi-Note 10-018]

<sup>1</sup>These timelines documenting the history of changes at the National Water Quality Laboratory are not definitive. They were pieced together using disparate technical memos, reports, and Rapi-Notes. They may be missing one or more important changes.

**Table 3-6.** National Water Quality Lab (NWQL) method and procedure changes for pesticide parameters. Abbreviations are defined in table 3-1.<sup>1</sup>

Year	NWQL method and procedure changes
1992	C-18 solid phase extraction with identification and quantification by gas chromatography/mass spectrometer (GC/MS) method. [Schedule 2001/2010; OFR 95-181; NWQL 97-03; WRIR 01-4098]
2003	New field spike solutions or field spike containers. [Rapi-Note 03-037]

<sup>1</sup>These timelines documenting the history of changes at the National Water Quality Laboratory are not definitive. They were pieced together using disparate technical memos, reports, and Rapi-Notes. They may be missing one or more important changes.

