

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY CINCINNATI, OHIO 45268

Office of Ground Water and Drinking Water

November 4, 2022

MEMORANDUM

SUBJECT:	Satisfying the 16-hour Sample Hold Time for Acidified Metals Samples
FROM:	Daniel P. Hautman, Branch Supervisor Technical Support Branch (TSB) Standards and Risk Management Division
TO:	Heather Shoven, Deputy Director Laboratory Services and Applied Science Division Analytical Services Branch, U.S. EPA Region 5

This memo provides further clarification regarding the required sample holding time once an approved method or regulatory specified reagent/preservative is added to a collected drinking water compliance sample and the approved method or regulatory protocol requires the sample to be held for a specific amount of time prior to proceeding with the analysis. The defined time frame is considered the minimum amount of prescribed time the laboratory must wait prior to proceeding to the next processing step.

Analytical methods approved for compliance drinking water monitoring are listed and incorporated by reference in the Code of Federal Regulations (CFR). The requirements of these methods, along with other requirements specified within the CFR, must be followed. Within the CFR, there are two relevant citations:

- See the footnote to the preservation table in 141.23 (k)(2): ¹For cyanide determinations samples must be adjusted with sodium hydroxide to pH 12 at the time off collection. When chilling is indicated the sample must be shipped and stored at 4 °C or less. Acidification of nitrate or metals samples may be with a concentrated acid or a dilute (50% by volume) solution of the applicable concentrated acid. Acidification of samples for metals analysis is encouraged and allowed at the laboratory rather than at the time of sampling provided the shipping time and other instructions in Section 8.3 od EP Methods 200.7 or 200.8 or 200.9 are followed.
 - EPA Method 200.8, Section 8.3 specifies that "...for the determination of total recoverable elements in aqueous samples, samples are **not** filtered, but acidified with (1+1) nitric acid to pH <2 (normally, 3 mL of (1+1) acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible

contamination it is recommended that the samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for 16 hours, and then verified to be pH<2 just prior to withdrawing an aliquot for processing or "direct analysis". If for some reason such as high alkalinity the sample pH is verified to be >2, more acid must be added and the sample held for 16 hours until verified to be pH <2. See Section 8.1."

- 2. At 141.23 there is a reference to Technical Notes: 141.23 (k)(1) Analysis for the following contaminants shall be conducted in accordance with the methods in the following table, or the alternative methods listed in appendix A to subpart C of this part, or their equivalent as determined by EPA. Criteria for analyzing arsenic, barium, beryllium, cadmium, calcium, chromium, copper, lead, nickel, selenium, sodium, and thallium with digestion or directly without digestion, and other analytical test procedures are contained in Technical Notes on Drinking Water Methods, EPA-600/R-94-173, October 1994.
 - Within Technical Notes in the section dedicated to <u>Sample Digestion for</u> <u>Determination of Metal Contaminants</u> it states that, "preservation is complete after the acidified sample has been held for 16 hours."

Feel free to contact me if you wish to further discuss.