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U.S. GEOLOGICAL SURVEY
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NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 2017.01

March 28, 2017

Subject: Modification to the reporting of elemental results for whole-water recoverable (WWR) sample analyses with old and new laboratory and method codes

Effective: March 28, 2017

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Revision: Supersedes: TM0215.01; May 1, 2015; Modification to the reporting of elemental results for whole-water recoverable (WWR) sample analyses

PURPOSE

This technical memorandum describes the implementation of a correction to account for dilution during digestion of whole-water recoverable (unfiltered, WWR) samples analyzed at the National Water Quality Laboratory (NWQL), using inductively coupled plasma-optical emission spectrometry (ICP–OES) and inductively coupled plasma-mass spectrometry (ICP–MS). It also describes the procedure used to apply the dilution factor to elemental results.

BACKGROUND

The in-bottle digestion (INBD) procedure (laboratory code 1735; Hoffman and others, 1996) replaced the hot-plate digestion procedure (Fishman and Friedman, 1989) at the NWQL in April 1992 to reduce the opportunity for trace-element contamination during the acid digestion of WWR samples. In the INBD procedure, an aliquot of concentrated hydrochloric acid equal to 2 percent of the weight of the sample is added to the sample. The acidified sample is then digested in an oven at 65 °C for 8 hours.

The NWQL has determined that the accuracy of elemental results for WWR samples analyzed by ICP–OES and ICP–MS can be improved by accounting for the sample dilution associated with the INBD. Historically, the sample dilution resulting from the addition of the acid has not been taken into account when reporting results. The error associated with this exclusion was thought to

be insignificant, considering the unknown contribution of the sediment mass present in the sample as well as other practices in the INBD procedure that contribute to the propagation of error. The 2 percent negative bias may be important, however, when comparing filtered and unfiltered sample results. This is especially critical as elemental concentrations increase and considering that approximately 80 percent of whole-water samples submitted to the laboratory contains less than 100 milligrams per liter (mg/L) of sediment (Rus and others, 2012).

SCOPE

For all analyses performed on or after May 1, 2015, all elemental results from WWR by ICP–OES and ICP–MS analyses will be adjusted prior to reporting to account for the 2 percent sample dilution resulting from the addition of the acid.

To adjust for the dilution introduced during the digestion of WWR samples, calibrator nominal concentrations will be adjusted up by 2 percent prior to quantitating WWR sample data. For example, for a calibrator made to 1.0 mg/L, 1.02 mg/L would be used as the concentration in the calibration calculations. This will be accomplished by multiplying calibrator concentrations by 1.02 and using the adjusted concentrations to calculate sample concentrations.

Elemental results acquired prior to May 1, 2015 will not be corrected and reloaded. The magnitude of the data correction is considered small enough not to outweigh the time and effort associated with a data reload for all data associated with the introduction of the INBD process. This is a large amount of data that has the potential to affect many projects. A reload may also lead to confusion among data users. A reload of this magnitude would create a cascade effect since all data that have been used in numerous project reports and other publications would also have to be corrected.

There will be approximately a 2 percent shift in data for laboratory codes listed in table 1 reported on or after May 1, 2015. Data users will need to consider this shift in data when comparing data from before and after the implementation of the 2 percent correction and identify it in interpretive reports. New laboratory and method codes were assigned to the affected analytes (table 1). Table 2 summarizes the necessary changes to the method descriptions.

EFFECT ON DATABASE

Effect on USGS National Water Information System (NWIS) database

1. For samples analyzed on or after May 1, 2015, all data reported to NWIS will have been adjusted to account for dilution during digestion procedure.

2. No change to result values in NWIS, only the laboratory and method codes are being updated.

REFERENCES

Fishman, M.J. and Friedman, L.C., eds., 1989, Extraction procedure, water-suspended sediment, Method I-3485-85, *in* Techniques of Water Resources Investigations of the United States Geological Survey, Methods for the Determination of Inorganic Substances in Water and Fluvial Sediments, Book 5, Chapter A1, p. 50.

Hoffman, G.L., Fishman, M.J., and Garbarino, J.R., 1996, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—In-bottle acid digestion of whole-water samples, U.S. Geological Survey Open-File Report 96-225, 28 p.

Rus, D.L., Patton, C.J., Mueller, D.K., and Crawford, C.G., 2012, Assessing total nitrogen in surface-water samples—Precision and bias of analytical and computational methods: U.S. Geological Survey Scientific Investigations Report 2012-5281, 38 p.

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/signed/
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Supersedes: Technical Memorandum 2015.01, Modification to the reporting of elemental results for whole-water recoverable (WWR) sample analyses (May 1, 2015)

Key words: ICP–MS, inductively coupled plasma–mass spectrometry, ICP–OES, inductively couple plasma–optical emission spectrometry, in-bottle digestion, INBD, whole water recoverable, WWR

Distribution: by Rapi-Note announcement
posted to http://wwwnwql.cr.usgs.gov/USGS (the NWQL USGS-visible intranet) and http://nwql.usgs.gov/Public (the NWQL public internet)

Table 1. Laboratory and method codes affected by the modification in reporting elemental concentrations in whole-water recoverable (unfiltered) sample results from inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spec-trometry (ICP–MS).

[ICP–OES, inductively coupled plasma–optical emission spectrometry; ICP–MS, inductively coupled plasma–mass spectrometry; not applicable, N/A]

Previous Laboratory Code	Previous Method Code	Affected Parmeter Code	New Laboratory Code	New Method Code	Analyte Name
2351	PLA15	01105	3506	PLO07	Aluminum, WU, ICP
2352	PLA15	01007	3507	PLO07	Barium, WU, ICP
2353	PLA15	01012	3508	PLO07	Beryllium, WU, ICP
2354	PLA15	01022	3509	PLO07	Boron, WU, ICP
2355	PLA15	01027	3510	PLO07	Cadmium, WU, ICP
2356	PLA15	00916	3501	PLO07	Calcium, WU, ICP
2357	PLA15	01034	3511	PLO07	Chromium, WU, ICP
2358	PLA15	01042	3513	PLO07	Copper, WU, ICP
2359	PLA15	01045	3514	PLO07	Iron, WU, ICP
2361	PLA15	01132	3515	PLO07	Lithium, WU, ICP
2362	PLA15	00927	3502	PLO07	Magnesium, WU, ICP
2363	PLA15	01055	3516	PLO07	Manganese, WU, ICP
2364	PLA15	01062	3517	PLO07	Molybdenum, WU, ICP
2365	PLA15	01067	3518	PLO07	Nickel, WU, ICP
2366	PLA15	00956	3504	PLO07	Silica, WU, ICP
2367	PLA15	01077	3519	PLO07	Silver, WU, ICP
2368	PLA15	00929	3505	PLO07	Sodium, WU, ICP
2369	PLA15	01082	3520	PLO07	Strontium, WU, ICP
2370	PLA15	01087	3521	PLO07	Vanadium, WU, ICP
2371	PLA15	01092	3522	PLO07	Zinc, WU, ICP
2391	PLA15	01037	3512	PLO07	Cobalt, WU, ICP
3123	PLM11	01002	3301	PLM77	Arsenic, WU, cICP-MS
3125	PLM11	01037	3303	PLM77	Cobalt, WU, cICP-MS
3127	PLM11	01034	3302	PLM77	Chromium, WU, cICPMS
3129	PLM11	01042	3304	PLM77	Copper, WU, cICP-MS
3131	PLM11	01067	3305	PLM77	Nickel, WU, cICP-MS
3133	PLM11	01147	3306	PLM77	Selenium, WU, cICPMS
3135	PLM11	01087	3308	PLM77	Vanadium, WU, cICPMS
3137	PLM11	01154	3307	PLM77	Tungsten, WU, cICPMS
3139	PLM11	01092	3309	PLM77	Zinc, WU, cICP-MS
2374	PLM47	01007	3413	PLM78	Barium, WU, ICP-MS
2375	PLM47	01012	3414	PLM78	Beryllium, WU, ICPMS
2376	PLM47	01027	3416	PLM78	Cadmium, WU, ICP-MS
2501	PLM47	01022	3415	PLM78	Boron, WU, ICP-MS
2372	PLM48	01105	3411	PLM78	Aluminum, WU, ICP-MS
2373	PLM48	01097	3412	PLM78	Antimony, WU, ICP-MS
2380	PLM48	01051	3417	PLM78	Lead, WU, ICP-MS
2381	PLM48	01132	3418	PLM78	Lithium, WU, ICP-MS
2382	PLM48	01055	3419	PLM78	Manganese, WU, ICPMS
2383	PLM48	01062	3420	PLM78	Molybdenum, WU,ICPMS

2386	PLM48	01077	3421	PLM78	Silver, WU, ICP-MS
2387	PLM48	01082	3422	PLM78	Strontium, WU, ICPMS
2388	PLM48	01059	3423	PLM78	Thallium, WU, ICP-MS
2389	PLM48	28011	3424	PLM78	Uranium, WU, ICP-MS
2775	PLO01	00937	3503	PLO07	Potassium, WWR ICP

Table 2. Changes to method descriptions.

Previous Method Code	Previous Method Description	New Method Code	New Method Description
PLA15	metals, unfiltered water, inductively coupled plasma-atomic emission spectrometry	PLO07	metals, unfiltered water, acid digest, corrected for 2 percent dilution, inductively coupled plasma-optical emission spectrometry, NWQL TM 2015.01 modification
PLM11	elements in unfiltered water using collision/reaction cell inductively coupled plasma-mass spectrometry	PLM77	metals in unfiltered water, acid digest, corrected for 2 percent dilution, using collision/reaction cell inductively coupled plasma-mass spectrometry, NWQL TM 2015.01 modification
PLM47	metals, unfiltered water, Inductively coupled plasma-mass spectrometry	PLM78	metals, unfiltered water, acid digest, corrected for 2 percent dilution, inductively coupled plasma-mass spectrometry, NWQL TM 2015.01 modification
PLM48	metals, unfiltered water, Inductively coupled plasma-mass spectrometry	PLM78	metals, unfiltered water, acid digest, corrected for 2 percent dilution, inductively coupled plasma-mass spectrometry, NWQL TM 2015.01 modification
PLO01	potassium recoverable from unfiltered water by ICP-OES	PLO07	metals, unfiltered water, acid digest, corrected for 2 percent dilution, inductively coupled plasma-optical emission spectrometry, NWQL TM 2015.01 modification