United States Department of the Interior

U.S. GEOLOGICAL SURVEY
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IN REPLY REFER TO:

NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 1999.05

January 7, 1999

Subject: Validation of U.S. Environmental Protection Agency (USEPA) method 365.1 to replace U.S. Geological Survey (USGS) TWRI methods I-2607-90 and I-4607-90 for determination of phosphorus in the concentration range from 0.004 to 0.200 mg-P/L.

Effective date of changes: January 1, 1999

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Revision: none

Supplemental Material: none

PURPOSE

This technical memorandum announces replacement of USGS low-level, persulfate-digestion methods for determining total and dissolved phosphorus in the concentration range from 0.004 to 0.200 mg-P/L with a more rugged USEPA persulfate-digestion method 365.1 (see table 3), effective January 1, 1999. Customers should request this method for samples they know or suspect to have phosphorus concentrations between 0.004 and 0.200 mg-P/L. Customers should continue to request the USGS Kjeldahl-phosphorus method for samples containing phosphorus concentrations greater than 0.200 mg-P/L. If the customer requests the EPA method and the sample concentration is determined to be greater than 0.200 mg-P/L, the NWQL will switch to the USGS Kjeldahl-phosphorus method and report values from that method. If samples requesting the USGS Kjeldahl-phosphorus method have phosphorus values less than 0.200 mg-P/L, the NWQL will not switch to the EPA method. The EPA method should not be used as a sample screening method on a routine basis.

SCOPE

USEPA method 365.1 is suitable for determining phosphorus in samples of water, wastewater, brines, and water-suspended sediment at concentrations less than or equal to 0.200 mg-P/L. Data

collected during validation experiments conducted in October and November 1998 at the NWQL resulted in a preliminary method detection limit (MDL) estimate of 0.002 mg-P/L for USEPA method 365.1. This MDL corresponds to an interim nondetection value (NDV-see Foreman and others, 1998) of about 0.004 mg-P/L. USEPA persulfate-digestion method 365.1 is applicable to determination of all forms of phosphorus in filtered-chilled (FCC), filtered-chilled-acidified (FCA), and whole-water-chilled-acidified (WCA) samples. In contrast to discontinued USGS methods I-2607-90 and I-4607-90 (OFR 93-125) that were limited to low-ionic strength samples (specific conductance less than 100 uS/cm), USEPA method 365.1 is suitable for samples with high concentrations of suspended solids and salts. Therefore, the NWQL recommends the USEPA method 365.1 not only to former users of the discontinued USGS methods I-2607-90 and I-4607-90, but also to customers who may require lower reporting levels than those afforded by NWQL Kjeldahl phosphorus methods (Patton and Truitt, 1992).

BACKGROUND

U.S. Geological Survey Office of Water Quality Technical Memorandum No. qw92.10, (1992), "Phosphorus Methods and the Quality of Phosphorus Data," provides a detailed chronology of USGS phosphorus methodologies prior to 1992. Customers should be aware that recent statistical analysis of Kjeldahl phosphorus (lab codes 1983, 1984, 1992, 1993) data produced at the NWQL in 1997 indicate that most reported dissolved and total phosphorus concentrations were less than or equal to 0.20 mg-P/L. Results are summarized in tables 1 and 2.

Table 1.

[mg-P/L, milligrams phosphorus per liter; s.d., standard deviation; n, number; %, percent; >, greater than]

1/97-2/98 Dissolved Phosphorus Concentration (mg-P/L)

Range	Mean	s.d.	n	% of Total
-0.05 to 0.200	0.023	0.043	9,760	89.6
0.201 to 2.000	0.625	0.209	1,028	9.4
2.001 to 10.00	3.385	0.825	107	1.0
>10	37.660	6.995	2	0.0
	Total number of samples:		10,897	100.0

Table 2.

[mg-P/L, milligrams phosphorus per liter; s.d., standard deviation; n, number; %, percent; >, greater than]

1/97-2/98 Total Phosphorus Concentration (mg-P/L)

Range	Mean	s.d.	n	% of Total
-0.05 to 0.200	0.04749	0.057	6,416	73.0
0.201 to 2.000	0.53913	0.377	2,237	25.4
2.001 to 10.00	3.39774	1.556	137	1.6
>10	21.4075	20.908	4	0.0
	Total number of points:		8,794	100.0

These findings, coupled with recent increases in MDL and NDV for Kjeldahl phosphorus methods (NWQL Tech Memo 98.07, 1998), presented potential difficulty to NWQL customers with low-

concentration phosphorus reporting-level requirements in standard sample matrices, because methods I-2607-90 and I-4607-90 are applicable only to low ionic strength samples (specific conductance < 100 uS/cm).

In response to this problem, the NWQL validated USEPA persulfate digestion method 365.1 for acidified filtered and whole water samples and chilled unacidified filtered samples. USEPA method 365.1 provides phosphorus reporting levels comparable to discontinued USGS methods I-2607-90 and I-4607-90 in a much wider variety of sample matrices. Colorimetric analysis is in accordance with the 2-reagent variant of the phosphoantimonylmolybdenum blue procedure (Murphy and Riley, 1962; Pai and others, 1990) specified in USEPA method 365.1. Details of the third-generation, air-segmented continuous flow analyzer used to automate the procedure are documented fully in the NWQL standard operating procedure (SOP IM 0317.0) for USEPA method 365.1.

SUMMARY OF CHANGES

Effective January 1, 1999, the NWQL will replace USGS methods I-2607-90 and I-4607-90 with the updated USEPA method 365.1 (see Table 3). The NWQL strongly recommends method 365.1 to customers whose samples typically contain phosphorus concentrations in the range from 0.004 to 0.200 mg-P/L. Any samples with test requests for method 365.1 that have concentrations greater than 0.200 mg-P/L will be analyzed by the more range-appropriate Kjeldahl phosphorus methods (NWQL lab codes 1983, 1984, 1992, 1993), which share a 0.05 to 2.0 mg-P/L reporting range.

Table 3. NWQL lab code, NWIS parameter and method codes for discontinued and replacement persulfate-digestion, low-level phosphorus methods and new acidified labcode.

[NWQL, National Water Quality Laboratory; NWIS, National Water Information System; USGS, U.S. Geological Survey; TWRI, Techniques of Water-Resources Investigations; USEPA, U.S. Environmental Protection Agency]

Before January 1, 1999			After December 31, 1998		
USGS TWRI method number	NWQL Lab code/NWIS Parameter and (method) codes	Bottle type	USEPA method number	NWQL Lab code/NWIS Parameter and (method) codes	Bottle type
I-2607-90	1981/666 (E)	FCC	365.1	2331/00666 (G)	FCC
I-2607-90		FCA	365.1	2332/00666 (H)	FCA
I-4607-90	1982/665 (F)	RCC	365.1	2333/00665 (G)	WCA

The NWQL will update all existing schedules that include these methods for phosphorus with the new lab codes and prices. Pricing information is available in the NWQL catalog USGS customer home page, http://wwwnwql.cr.usgs.gov-USGS. Please evaluate and choose the method that best meets your analytical needs when requesting phosphorus. The price for the new methods is substantially lower than the old methods. Pricing information for the updated method is listed in SPN (schedules and parameters network). Validation data are available and show that data variability for phosphorus using this replacement method is equivalent to or better than the existing low-level phosphorus method. Improved data quality is expected from this method change.

EFFECT ON DATA BASE

Since historical reporting levels are almost identical, for the discontinued and the replacement method, there will be no effect on the phosphorus data base.

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Key words: Replacement, Automated segmented flow, Total phosphorus, Persulfate digest, Validated

/Signed/
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