



IN REPLY REFER TO:

United States Department of the Interior

U.S. GEOLOGICAL SURVEY

Box 25046 M.S. 407

Denver Federal Center

Denver, Colorado 80225

NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 05.01

Distribution: E
Subject: Change in method for determination of potassium from flame atomic absorption (FAA) to inductively coupled plasma-optical emission spectrometry (ICP-OES)
Effective date of Change: June 1, 2003 for filtered samples
August 1, 2003 for whole water recoverable samples
Author: Jeff Pritt, Metals Section
303-236-3475, jwpritt@usgs.gov
Revision: N/A

PURPOSE

This technical memorandum documents replacement of USGS direct flame atomic absorption (FAA) spectrophotometric methods (Fishman and Friedman, 1989) for determining filtered and whole water recoverable potassium with inductively coupled plasma-optical emission spectrometry methods (ICP-OES) (Clesceri and others, 1998). To stay current with modern cost-saving technologies and improve data quality, the NWQL replaced aging FAA instruments with modern ICP-OES instruments. ICP-OES technology has changed substantially in recent years, thus expanding the capability of the instrument to determine potassium. The new lab codes and method codes are listed below. The sample bottle type and the nitric acid preservation requirements did not change. These new codes are available in the Laboratory Information Management System (LIMS) per the dates mentioned above. The low-level potassium is available for samples with specific conductance of 100 microsiemens or less and is generally appropriate for precipitation and other pristine samples. If the low-level lab code (2774) is requested and the specific conductance exceeds 100 microsiemens or the concentration exceeds 1 mg/L -- the upper range for reporting potassium with lab code 2774 -- then the laboratory will switch to analysis by the regular lab code (2773) and results will be reported with lab code 2773.

Parameters and Codes

Name	Lab Code	Parameter Code/ Method Code
Potassium, Filtered	2773	00935 / C
Potassium, Low Level, Filtered	2774	00935 / D
Potassium, Whole Water Recoverable	2775	00937 / C

BACKGROUND

Office of Water Quality technical memorandum 98.05 describes the policy for approval of analytical methods. Upon consultation with the OWQ chief chemist, approval was granted to use Standard Methods for the Analysis of Water and Wastewater for the determination of potassium by ICP-OES (Clesceri and others, 1998). The NWQL and the Office of Water Quality require a demonstration that the method setup by a USGS laboratory performs according to the method cited. The demonstration included analysis of standard reference water samples to determine bias and precision, determination of method detection limits, and comparison of results of environmental samples analyzed with the new ICP-OES instrument and the older flame direct atomic absorption instrument. This memorandum summarizes these studies.

SCOPE

Method Detection Limit

Method sensitivity is determined from method detection limit studies. The procedure adopted is described in Childress and others (1999). The LT-MDL and LRL results from the annual LT-MDL/LRL updates for October 1, 2004 (FY 2005) are summarized and compared to the FY2003 FAA LT-MDL/LRL in Table 1.

Table 1 - Potassium reporting levels for the ICP-OES method compared to flame atomic absorption method. K, Filtered, potassium filtered (Lab Code 2773); K, Low-Level, potassium, low-level, filtered (Lab Code 2774); K, Whole-Water, potassium, whole-water, recoverable (Lab Code 2775); FAA, flame atomic absorption; LT-MDL, long-term method detection level; LRL, laboratory reporting level; ND, no data.

<u>Constituent</u>	<u>New Lab Code</u>	<u>LT-MDL</u>	<u>LRL</u>	<u>FY 2003 LT-MDL (FAA)</u>	<u>FY 2003 LRL (FAA)</u>
K, Filtered	2773	0.08	0.16	0.06	0.11
K, Low Level, Filtered	2774	0.005	0.010	ND	0.01*
K, Whole Water	2775	0.08	0.16	ND	0.1*

*MRL; method reporting level, no LT-MDL/LRL determined for potassium low-level filtered or whole-water recoverable by FAA.

Bias and Precision

Initial bias and precision data for the determination of potassium by ICP-OES were compiled from five Standard Reference Water Samples and blanks. Bias is calculated as the percent difference between the mean result and the most probable value (MPV) divided by the MPV for the reference material. Precision is calculated as the percent relative standard deviation (RSD). Bias and RSD were not calculated for blank data. The results are listed in Table 2a. Since the initial studies, long-term bias and precision data have been collected and are listed in Table 2b. The long-term data are more representative of analytical performance under routine operational conditions in comparison to

the initial bias and precision data in Table 2a. The Branch of Quality Systems blind sample project provided data to compare the old FAA method to the new ICP method (see Table 2c).

Table 2a - Initial bias and precision data for Standard Reference Water Samples and blanks. SRWS, Standard Reference Water Sample; BQS MPV, Branch of Quality Systems Standard Reference Water Sample Project published Most Probable Value; BQS F-pseudosigma, Branch of Quality Systems Standard Reference Water Sample Project published variability; Count, The number of determinations; K, Fil; potassium, filtered (Lab Code 2773); K, LL; potassium, low-level, filtered (Lab Code 2774); K, WWR; potassium, whole-water, recoverable (Lab Code 2775); RSD, relative standard deviation; ND, not determined or not calculated.

<i>Constituent</i>	<i>SRWS</i>	<i>BQS MPV</i>	<i>BQS F-pseudo-sigma</i>	<i>Mean</i>	<i>Median</i>	<i>Standard Deviation</i>	<i>Count</i>	<i>Bias (percent)</i>	<i>RSD (percent)</i>
K, Fil	135	0.96	0.09	0.948	0.951	0.046	68	-1.25	4.85
K, Fil	143	2.5	0.21	2.56	2.57	0.066	49	2.4	2.58
K, Fil	169	2.59	0.11	2.55	2.55	0.06	60	-1.54	2.35
K, Fil	171	2.8	0.14	2.72	2.72	0.049	60	-2.86	1.80
K, Fil	Blank	ND	ND	0	0	0.023	63	ND	ND
K, WWR	167	4.76	0.222	4.5	4.53	0.121	30	-5.56	2.69

Table 2b - Bias and precision data from August 2003 - February 2004 for continuing calibration verification standards (CCV), third party checks (TPC), and blanks. Control Limits are based on +/- 3 standard deviations of the specified value. Blank limits are +/- the method detection level. QC Type, type of quality control; RSD, relative standard deviation; ND, not determined or not calculated.

<i>Constituent</i>	<i>QC Type</i>	<i>Specified Value</i>	<i>Mean</i>	<i>Median</i>	<i>Standard Deviation</i>	<i>Count</i>	<i>Bias (percent)</i>	<i>RDS (percent)</i>	<i>Control Limits</i>
K, Fil	CCV	2.5	2.46	2.46	0.071	150	-1.47	2.87	(2.29-2.71)
K, Fil	TPC	2.5	2.46	2.45	0.074	60	-1.48	2.99	(2.28-2.72)
K, Fil	Blank	0	-0.002	-0.001	0.034	351	ND	ND	(-0.08-0.08)
K, LL	CCV	0.50	0.478	0.469	0.028	10	-4.46	5.76	(0.4-0.6)
K, LL	TPC	0.25	0.26	0.26	0.010	6	2.01	4.06	(0.22-0.28)
K, LL	Blank	0	-0.004	-0.004	0.009	33	ND	ND	(-0.004-0.004)
K, WWR	CCV	2.5	2.40	2.40	0.075	72	-3.98	3.12	(2.28-2.72)
K, WWR	TPC	2.5	2.42	2.42	0.081	50	-3.11	3.35	(2.26-2.74)
K, WWR	Blank	0	-0.012	-0.012	0.032	70	ND	ND	(-0.06-0.06)

Table 2c - Bias and precision data for old atomic absorption instrument and new inductively coupled plasma instrument for Branch of Quality System blind samples. AA, atomic absorption; ICP, inductively coupled plasma; LL, low-level; Fil, filtered; Std Dev, standard deviation; RSD, relative standard deviation.

<i>Parameter</i>	<i>BQS Sample</i>	<i>Specified Value</i>	<i>Mean</i>	<i>Median</i>	<i>Std Dev</i>	<i>Count</i>	<i>Bias (percent)</i>	<i>RSD (percent)</i>
K, Fil AA	50160-50158	1.96	1.85	1.84	0.063	18	-5.42	3.42
K, Fil ICP	50160-50158	1.96	2.02	2.01	0.083	16	3.56	4.09
K, Fil AA	50160-50162	2.7	2.61	2.59	0.101	18	-3.33	3.87
K, Fil ICP	50160-50162	2.7	2.77	2.82	0.169	11	2.59	6.11
K, Fil AA	25162-75158	2.08	1.99	2.00	0.108	22	-4.4	5.40
K, Fil ICP	25162-75158	2.08	2.130	2.140	0.074	21	2.43	3.45
K, Fil AA (LL)	P-37	0.5	0.48	0.48	0.023	6	-4.33	4.87
K, Fil ICP (LL)	P-37	0.5	0.51	0.51	0.017	6	1.65	3.28
K, Fil AA (LL)	P-38	0.83	0.81	0.81	0.036	4	-1.93	4.43
K, Fil ICP (LL)	P-38	0.83	0.871	0.86	0.039	6	4.91	4.53

Method Comparison with Environmental Samples

Consistency of water-quality data is critical for long-term data collection for the USGS scientific mission. As part of meeting that goal, a random sample of environmental samples collected during 2002, representing a wide range of concentrations for potassium, was analyzed by the new ICP-OES instrument and compared to results obtained by flame atomic absorption methods. A regression analysis of the data shows that the two methods are comparable. The regression parameters are listed in Table 3. A slope close to one represents very good comparability between methods. The slopes are within about 5 percent of 1.0. The small number of data pairs for the whole-water comparison reflects the number of available samples that had not already been discarded. In 2002, there were 10,533 determinations for filtered potassium and only 102 determinations for whole water, from which the random sample of comparison samples was drawn.

Table 3 - Environmental results for inductively coupled plasma instrument and atomic absorption instrument. R^2 , coefficient of regression, which is an indicator of how well the linear fit models the data; 1.00 represents a perfect fit of a line to the data.

Constituent/Matrix	Number of data pairs for comparison	Slope	R^2
Potassium, Filtered	356	1.05	0.996
Potassium, Whole water recoverable	20	0.97	0.996

REFERENCES

Childress, Carolyn J. O., Foreman, W. T., Connor, B. F., and Maloney, T. J., 1999, New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U.S. Geological Survey National Water Quality Laboratory: U. S. Geological Survey Open-File Report 99-193, 19 p.

Clesceri, L. S., Greenburg, A. E., and Eaton, A. D., eds., 1998, Standard methods for the examination of water and wastewater (20th ed.): Washington D.C., American Public Health Association, p. 3-37 to 3-43.

Fishman, M. J., and Friedman, L. C., eds, 1989, Methods for the determination of inorganic substances in water and fluvial sediments: Techniques of Water-Resources Investigations of the United State Geological Survey, book 5, chap. A1, p. 393-394.

U. S. Geological Survey, 1998, Policy for the approval of U.S. Geological Survey (USGS) water-quality methods: U.S. Geological Survey Office of Water Quality Technical Memorandum 98.05, accessed March 25, 2003 at URL <http://water.usgs.gov/admin/memo/QW/qw98.05.html>.

Effect on Data Base: None

/signed/

Gregory B. Mohrman, Chief
National Water Quality Laboratory
Branch of Analytical Services

Key Words

Flame Atomic Absorption (FAA), Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), Potassium

Distribution: E and <http://wwwnwql.cr.usgs.gov/USGS>