



United States Department of the Interior

U.S. GEOLOGICAL SURVEY
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NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 2011.02

July 15, 2011

Subject: Removal of bisphenol A, pentachlorophenol, and bisphenol A-d3 surrogate from laboratory schedule (LS) 1433; removal of bisphenol A and bisphenol A-d3 surrogate from LS 2249; and removal of benzidine from LS 1383; suggested alternative analytical schedules; and data reload

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Revision: N/A

PURPOSE

Effective on or after July 18, 2011, the NWQL will no longer include the following four analytes in selected laboratory schedules:

LS 1433:

- Bisphenol A (parameter-method code 62069GCM37)
- Pentachlorophenol (parameter-method code 34459GCM37)
- Bisphenol A-d3 surrogate (parameter-method code 99583GCM37)

LS 2249:

- Bisphenol A (parameter-method code 62069GCM37)
- Bisphenol A-d3 surrogate (parameter-method code 99583GCM37)

LS 1383:

- Benzidine (parameter-method code 39120GCM55)

The NWQL recognizes the importance of these compounds, especially bisphenol A, in environmental monitoring. A summary of affected laboratory schedules, parameters names, and suggested alternative laboratory schedules is presented in table 1. As an alternative, LS 4433 is available for analysis of bisphenol A and pentachlorophenol. Schedule 4433 is the unfiltered water equivalent of LS 1433. Bisphenol A is available in the hormone analyses, currently a custom method for filtered water, whole water, or sediment. The Techniques and

Methods report for the hormones in waters methods is currently in the approval process. Pentachlorophenol is also available in LS 1383 (unfiltered water).

Currently, the NWQL does not have an alternative method for benzidine analysis.

The NWQL adds bisphenol A-d3 to samples as a surrogate to help monitor method performance; it has no environmental significance.

Table 1. Summary of affected laboratory schedule and parameter names and suggested alternative laboratory schedule for bisphenol A compounds, pentachlorophenol, and benzidine

Laboratory schedule	NWIS parameter-method codes	NWIS parameter name	Alternatives NWIS parameter-method codes; NWIS parameter name; and laboratory schedule
1433 2249	62069GCM37	bisphenol A, water, filtered, recoverable, micrograms per liter	62816GCM99; bisphenol A, water, unfiltered, recoverable, micrograms per liter; LS 4433
	99583GCM37	bisphenol A-d3, surrogate, water, filtered, percent recovery	not applicable
1433	34459GCM37	pentachlorophenol, water, filtered, recoverable, micrograms per liter	39032GCM99; pentachlorophenol, water, unfiltered, recoverable, micrograms per liter; LS 4433 or 39032GCM56; pentachlorophenol, water, unfiltered, recoverable, micrograms per liter; LS 1383
1383	39120GCM55	benzidine, water, unfiltered, recoverable, micrograms per liter	none available

BACKGROUND

In October 2010 the NWQL released Rapi-Note [10-024](#) to notify customers of the ongoing qualification and the planned removal of the compounds listed above from the appropriate laboratory schedule. The aforementioned Rapi-Note stated that the NWQL will not be initiating any updates to affected data values; however, that decision has been changed. As it is not possible in all cases for customers to differentiate NWQL-derived data from other sources, the NWQL will initiate a reload to NWIS of affected data (see section below for details).

As a result of a significant change in method performance in March 2005, the above mentioned LS 1433 and LS 2249 analytes have routinely been reported with a null value, and a null-value qualifier of ‘u’ which is indicative of the poor and/or highly variable method performance of the compounds. Laboratory reagent spikes frequently exhibited poor or no recovery for these analytes. The NWQL investigated, but was unable to determine the cause for the method performance shift. The NWQL continued to report null values and the ‘u’ null-value qualifier for these LS 1433 / LS 2249 compounds until they could be removed with publication of this technical memorandum.

Similarly, benzidine in LS 1383 has had very poor historical method performance. Laboratory reagent spikes usually exhibited no recovery for this analyte. Benzidine data were routinely reported in the National Water Information System (NWIS) with a null-value and a null-value qualifier of ‘u’ due to poor and unreliable method performance since about November 2004. The NWQL continued to use the null-value and null-value qualifier for benzidine reporting until the compound could be removed with publication of this technical memorandum.

SCOPE

The NWQL utilizes laboratory reagent spikes to monitor method performance. A laboratory reagent spike is included with every set of up to ten LS 1433, LS 2249, and LS 1383 samples and is prepared by spiking a known concentration of each analyte into organic-free water. “Accuracy of the (laboratory) reagent spike reflects the best results that can be expected at the time the samples were analyzed ...” (Sandstrom, 1994). Laboratory reagent spikes are processed and analyzed identically to environmental samples and are reported in units of percent recovery. In every instance where a null-value and a null-value qualifier of ‘u’ were reported in a laboratory reagent spike, the value was changed to zero, “0,” for the calculations used in this document.

LS 1433 / LS 2249

Bisphenol A

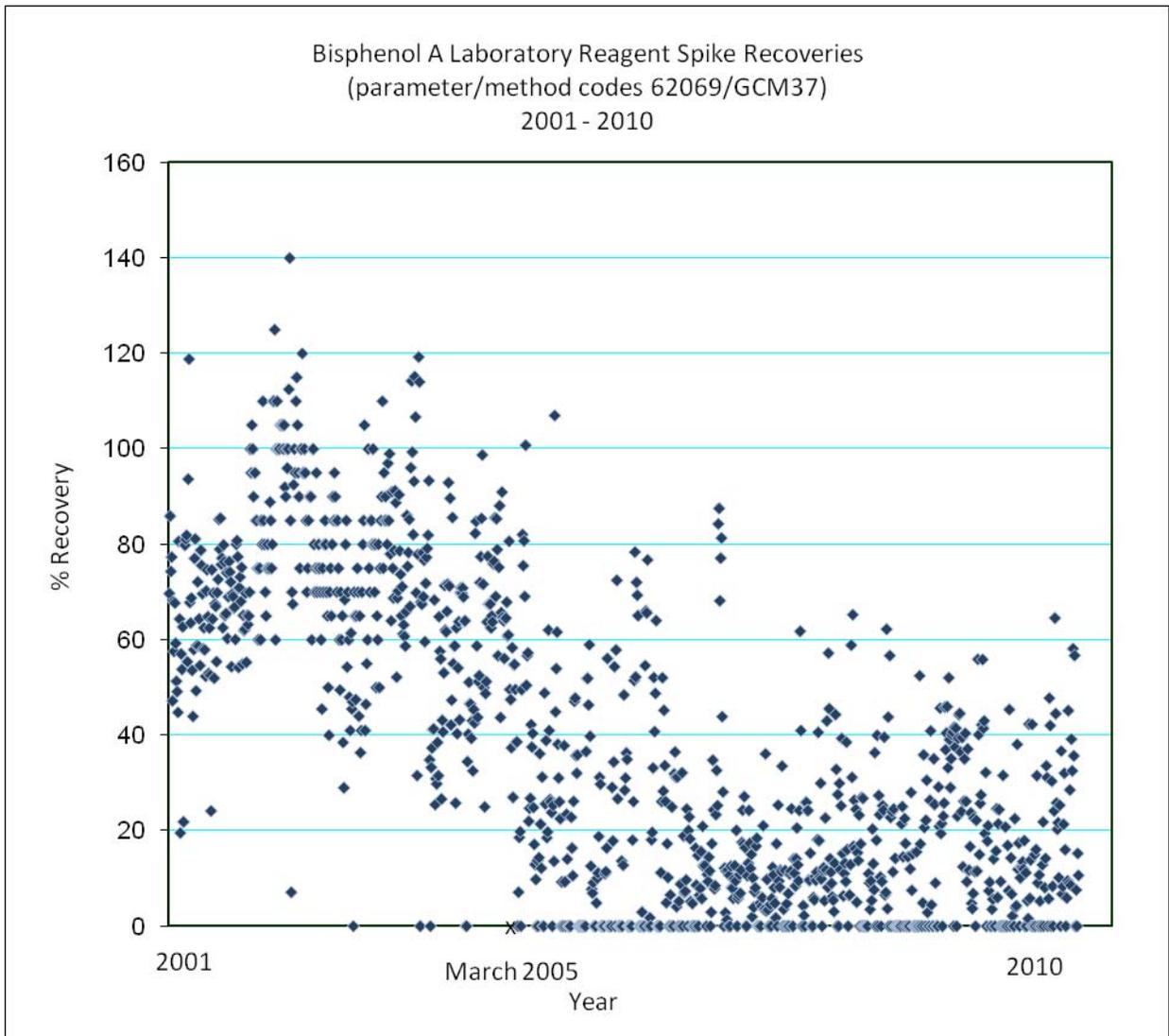
(parameter-method code 62069GCM37)

Table 2. Summary of LS 1433 / LS 2249 bisphenol A recoveries for samples extracted before and after March 1, 2005

Bisphenol A laboratory reagent spike performance data 2001 to 2010					
	Mean recovery (%)	Relative standard deviation (%)	0% recovery (%)	<10% recovery (%)	N
Before March 1, 2005	70	30	1.1	1.4	440
After March 1, 2005	17	108	27	45	710

In reviewing bisphenol A performance, results were compiled for 1,150 LS 1433 / LS 2249 laboratory reagent spikes analyzed during July 2001 through September 2010; 440 of the laboratory reagent spikes were extracted before and 710 were extracted after the March 1, 2005 apparent data shift (table 2). Prior to March 2005 the mean laboratory reagent spike recovery for bisphenol A was 70% with a relative standard deviation (RSD) of 30%. After March 2005 the mean laboratory reagent spike recovery was 17% with a RSD of 108%. Only 1% of the laboratory reagent spikes before March 2005 had recoveries below 10% compared to 45% of the laboratory reagent spikes after March 2005. A plot of recoveries for bisphenol A during this same timeframe displays the shift in performance starting March 1, 2005 (fig. 1).

Figure 1. Temporal pattern and apparent shift in laboratory reagent spike percent recovery for bisphenol A on LS 1433 / LS2249.

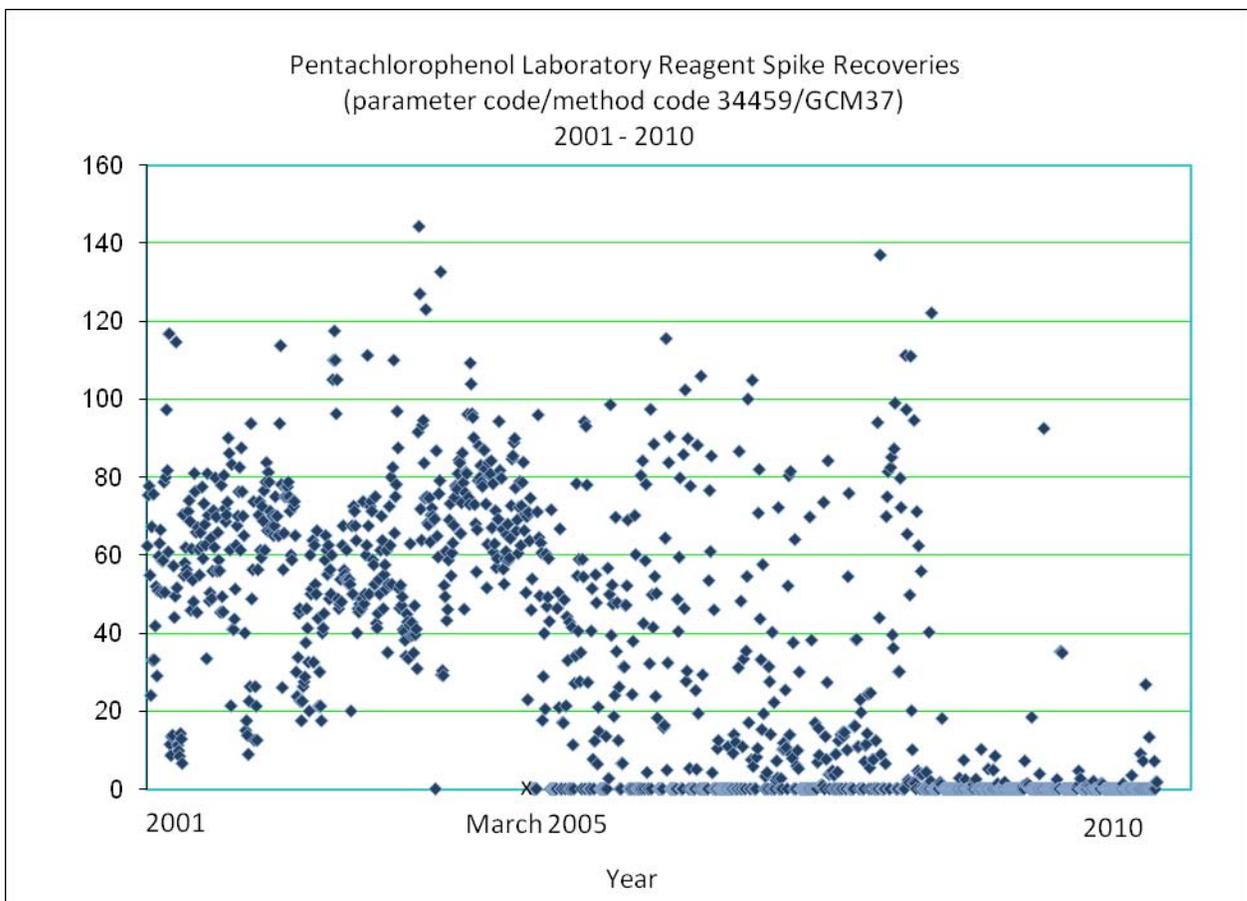


LS 1433
Pentachlorophenol
(parameter-method code 34459GCM37)

Table 3. Summary of LS 1433 pentachlorophenol recoveries for samples extracted before and after March 1, 2005

Pentachlorophenol laboratory reagent spike performance data 2001 to 2010					
	Mean recovery (%)	Relative standard deviation (%)	0% recovery (%)	<10% recovery (%)	N
Before March 1, 2005	61	36	0.22	1.4	443
After March 1, 2005	15	176	55	68	718

Figure 2. Temporal pattern and apparent shift in laboratory reagent spike percent recovery for pentachlorophenol on LS 1433.



A total of 1,161 LS 1433 laboratory reagent spikes was analyzed for pentachlorophenol during July 2001 through September 2010; 443 laboratory reagent spikes were extracted before and 718 were extracted after the March 1, 2005 apparent data shift (table 3). Prior to

March 2005 the mean laboratory reagent spike recovery for pentachlorophenol was 61% with a RSD of 36%. After March 2005 the mean laboratory reagent spike recovery was 15% with a RSD of 176%. Only 1% of the laboratory reagent spikes before March 2005 had recoveries below 10% compared to 68% of the laboratory reagent spikes after March 2005. A plot of recoveries for pentachlorophenol during this same timeframe displays the shift in data performance starting in March 1, 2005 (fig. 2).

LS 1433 / LS 2249
Bisphenol A-d3 Surrogate
(parameter-method code 99583GCM37)

Table 4. LS 1433 / LS 2249 bisphenol A-d3 surrogate recoveries for samples extracted before and after March 1, 2005

	Bisphenol A-d3 surrogate – Sample and quality control performance data 2001 to 2010				
	Mean recovery (%)	Relative standard deviation (%)	0% recovery (%)	<10% recovery (%)	N
Before March 1, 2005	64	60	8.8	11	5541
After March 1, 2005	21	143	41	54	7964

Surrogate compounds are added to all environmental and quality-control (QC) samples prior to sample preparation; they are not usually found in the environment and are chosen for their ability to behave similarly to the analytes of interest throughout the analytical process (Sandstrom, 1994). Surrogates monitor for matrix effects and gross sample-processing errors (Wershaw and others, 1987). In reviewing bisphenol A-d3 surrogate performance, a total of 13,505 LS 1433 / LS 2249 results (including environmental samples and laboratory reagent blanks and spikes) was analyzed during July 2001 through September 2010; prior to March 1, 2005 the mean recovery for bisphenol A-d3 surrogate was 64% with a RSD of 60%. After March 1, 2005 the mean recovery was 21% with a RSD of 143%. Only 11% of the data points before March 2005 had recoveries below 10% compared to 54% of the points after March 2005 (table 4). The bisphenol A-d3 surrogate behaves similarly to bisphenol A, providing additional documentation for the removal of bisphenol A from LS 1433 and LS 2249.

A review of 397 LS 1383 laboratory reagent spikes analyzed during June 2001 through September 2010 demonstrates the overall poor performance of benzidine throughout the history of the method (table 5). The mean laboratory reagent spike recovery over this approximate 9-year period of time was 2.3% with a RSD of 462%. Ninety-six percent of the

laboratory reagent spikes exhibited little (<10%) to no (0%) recovery. With a few exceptions in 2001–02 (fig. 3), benzidine has rarely performed well in the method.

LS 1383

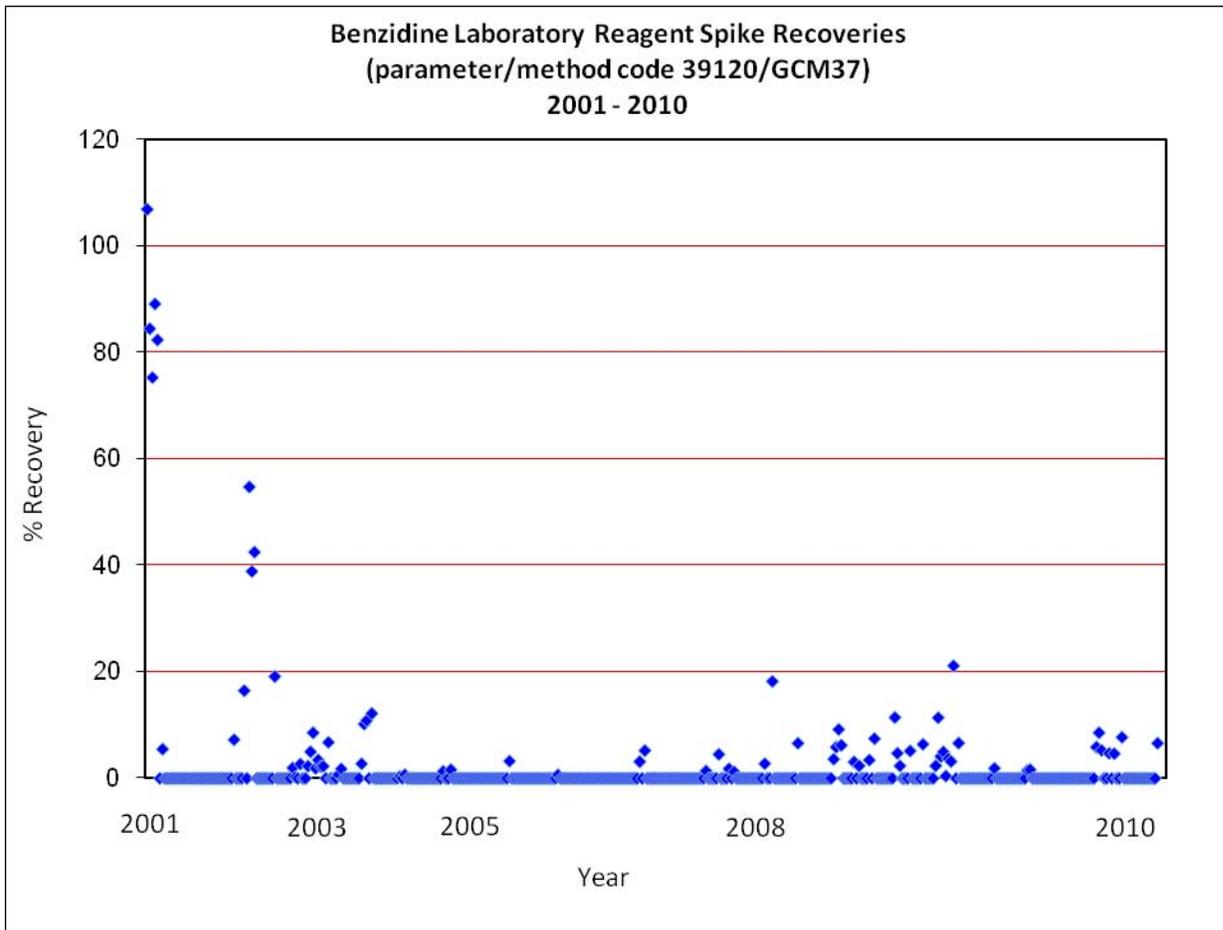
Benzidine

(parameter-method code 39120GCM55)

Table 5. LS 1383 benzidine performance from 2001 to 2010

LS 1383 benzidine laboratory reagent spike performance data 2001 to 2010				
Mean recovery (%)	Relative standard deviation (%)	0% recovery (%)	<10% recovery (%)	N
2.3	462	81	96	397

Figure 3. Historical data performance of benzidine on LS 1383.



DISCUSSION AND CONCLUSIONS

Due to a marked change in method performance for samples extracted starting March 1, 2005, bisphenol A and bisphenol A-d3 are being removed from LS 1433 and LS 2249; pentachlorophenol is also being removed from LS 1433. Analytical results for these samples will be reloaded as described below.

Benzidine is being removed from LS 1383; it has rarely performed well during the entire history of the method. Analytical results from Julian Date (JD) 1992010 to present will be reloaded as described below; data prior to JD 1992010 are also likely affected, but cannot be reloaded.

The NWQL will provide updates to the NWIS database for all affected data. Details of the effects on the database are described below. Publications that have included these compounds may require a revision notification from the authors. The decision to send revisions or interpretations of data should be determined on a case by case basis based on the magnitude of the error. Bisphenol A, in particular, has been identified and publicized as a

concern relative to human health, so scientists who have reported detections of this compound are encouraged to review and revise their findings.

EFFECTS ON DATABASE

Existing analytical results from the NWQL for the parameter-method codes described by this memorandum will require modification within the NWIS database. The results previously transmitted will be converted to null values and the 'n' null-value code qualifier will be added. To assist customer's management of their stored results within NWIS, the NWQL will reload these results. Some additional metadata fields that did not exist in previous versions of NWIS will be populated to further describe these affected data.

For each affected result, the reload will include the following updates:

- Analyzing entity field will be populated with the NWQL's code "USGSNWQL." This metadata field was not available prior to NWIS version 4.6
- The result Value will be set to 'null' or missing, and will be further qualified with the null-value qualifier code of 'n,' which has the following description: "non-performing compound, reasons unknown."
- A result comment stating "Please refer to NWQL Technical Memorandum 2011.02" will be inserted.

The null-value qualifier 'n' is newly available in the October 2010 NWIS Reference List update; therefore, that reference list is required to be installed prior to processing the reload (see <http://nwis.usgs.gov/communications/2010news/101028Oct-Reflist.html>).

A Rapi-Note will precede the release of data, notifying customers when data will be available. The NWQL will transmit updated result files to affected customers. These results will be sent to the Water-Quality Data Transfer (QWDX) System as a reloaded data set. This designation will necessitate manual processing at the local NWIS-host installation by a QWDX Local-DBA (please refer to Water Quality Information Note 2011.02 for the latest information about the QWDX program).

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bisphenol A, bisphenol A-d3, benzidine, LS 1433, LS 2249, LS 1383, pentachlorophenol

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