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A smarter way to take a temperature

A Northern California lab automates data-gathering and hands the tracking responsibility over to a computer

François Rodigari and Kenneth E. Osborn

One of many things that environmental laboratories must do is to track and document the temperatures of the laboratory's incubators and refrigerators. This means that the thermometers used to monitor these appliances must be read once or twice a day.

The East Bay Municipal Utility District (EBMUD) in Oakland, Calif., operates a full-service environmental laboratory with a staff of 37. The laboratory is made of a biology, inorganic chemistry, and organic chemistry section.

The lab has 28 appliances that must be checked on a daily basis. This is a lot of work, and it's not always something staffers can put on a chart recorder and forget about. Previously at EBMUD, a lab worker from each section would record temperatures onto a chart for each

thermometer. Then, twice a year, the charts would be collected and analyzed to ensure they were up-to-date, which they rarely were. There were always gaps in data.

If a temperature reading was outside limits, the assigned lab worker who recorded the temperature was supposed to notify the supervisor or quality assurance (QA) officer. Of course, if the person in charge wasn't available at the time, or if the lab worker became occupied with a more pressing matter, the discrepancy was likely to be forgotten.

A few years ago, EBMUD's organic chemistry supervisor devised a method that would eliminate a lot of the manual "handholding" in ensuring temperature readings were within acceptable ranges. Instead of recording temperatures on a piece of paper,

they would be recorded onto a personal digital assistant (PDA) and then uploaded into a laboratory information management system (LIMS).

Daily routine

Since then, the task of recording temperatures from thermometers is assigned to one staff person instead of four. The assigned staff person goes to each instrument and scans a bar code label on the instrument to be monitored. He or she then reads the temperature on the thermometer and enters it into the PDA. When finished entering the temperature for each instrument, the staffer synchronizes the PDA with a computer, and the data are uploaded automatically into LIMS. It takes one person half an hour to do all the readings for all the laboratory's appliances.

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Handbook to help small labs achieve NELAC certification

For some small laboratories that want to become certified in accordance with the National Environmental Laboratory Accreditation Conference (NELAC) standard, the costs associated with doing so may seem to outweigh the benefits. To counteract this perception, a group within the organization responsible for the standard is developing a document to help small labs become NELAC-certified. Currently under development, the document is expected to be published this summer, when the updated version of the current standard takes effect.

Time, cost pose obstacles to certification

For small labs, becoming NELAC-certified may seem daunting, espe-

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A smarter way to take a temperature

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Figure. Example temperature data from a freezer

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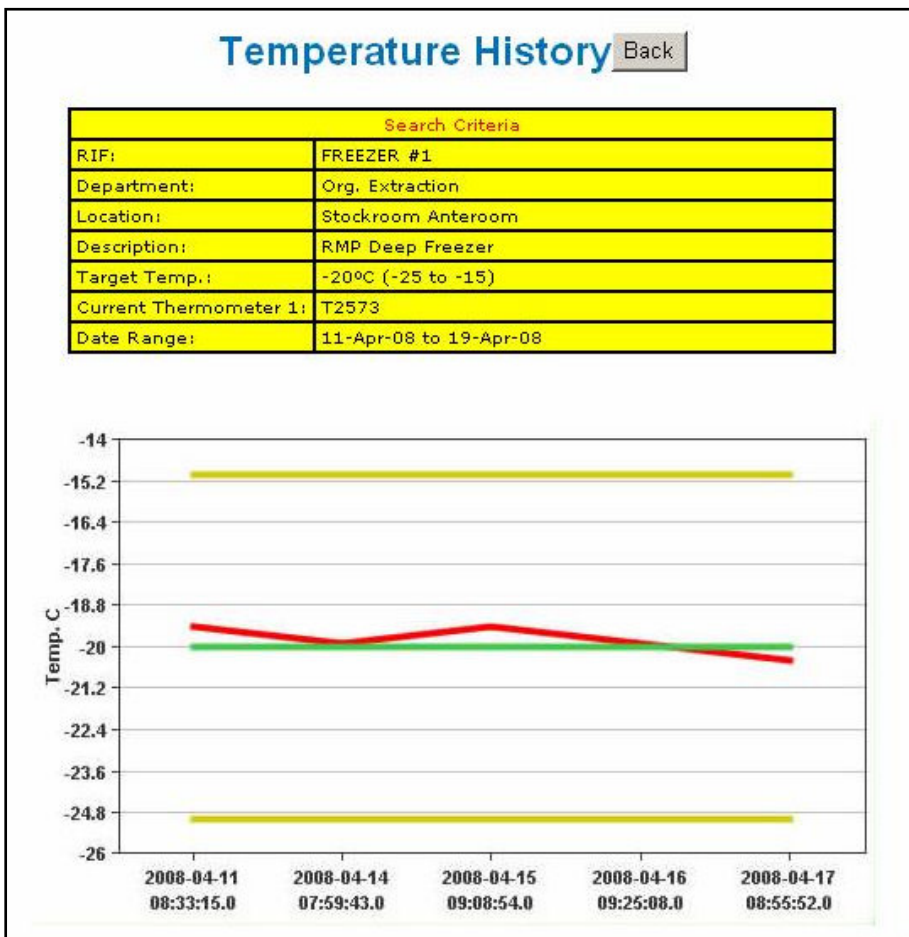
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In addition, limiting the data-gathering to one person not only reduces inconsistency between readings, but it also allows the manager to have one point person, instead of multiple people, to ask questions if something is wrong.

Data processing

Upon upload, the temperatures are adjusted by LIMS with the appropriate correction factor. Along with the correction factors, the last and next calibration dates are stored in LIMS for each thermometer. In addition, the data after correction are assessed for compliance with the acceptable temperature range established for each appliance. If the temperature for an appliance does not fall within range, the supervisor for the appliance as well as the QA officer are sent an

e-mail with the specifics of the outlier. Lastly, if monitoring data are missing for an appliance, the QA officer is e-mailed at the end of the day.

For EBMUD, something is usually out of line once a week, although it typically is not serious. For example, prior to the thermometer reading, a particular refrigerator might have been in high use and the door was opened more than usual. Or perhaps a freezer was undergoing an automated defrost cycle when measured. The supervisor can confirm this condition and make a note to compare temperatures from the next reading.

Repeated e-mails indicating that a temperature for an appliance is “out of control” will require an investigation by the QA officer. The repeated outliers typically indicate that a temperature adjustment may be required

or that the refrigerant in the unit may need to be recharged.

Data management

Web pages were developed to allow on-demand control charts for each of the monitored appliances. The Web also is used to allow select users to correct temperatures when a data entry error is made, to generate bar codes for new thermometers/appliances, to query missed temperature recordings, and to generate control charts for each thermometer/

appliance. See the figure (p. 2) for an example chart.

The output for the temperature data can be specified by the user to be in the form of a Web table, Web chart, or a spreadsheet after being exported to Microsoft Excel.

Cost

The system was developed using PDAs equipped with bar-code scanners. These PDAs were already in use in the laboratory to scan samples for batch creation and automated record-

ing of analysis times. It took the laboratory's part-time programmer about 3 weeks to develop the Web pages needed to monitor the temperatures and to write the parsing code for the data stored in the PDAs.

*Written with assistance from **Cathy Vidito. François Rodigari** is the laboratory supervisor of the organic chemistry section and **Kenneth E. Osborn** formerly was QA officer of East Bay Municipal Utility District (Oakland, Calif.).*

Handbook to help small labs achieve NELAC certification Continued from page 1

cially if lab staff are "starting from scratch," said Keith Chapman, laboratory program manager for the Willow Lake Treatment Plant (Salem, Ore.) and the current small lab advocate within The NELAC Institute (TNI; Weatherford, Texas). Formed in 2006 by the merger of NELAC and the Institute for National Environmental Laboratory Accreditation, TNI has developed the 2009 TNI standard, which upon implementation on July 1, 2011, will replace the 2003 NELAC standard currently in effect.

Achieving certification entails a significant amount of time and effort, Chapman said. "It takes time to do this and to understand what the TNI standard requires," he said. "In order to set yourself up to do these things, it's a lot of work." For many small labs, making time available for staff to pursue such tasks can be difficult.

Cost is another major issue, particularly for labs serving small communities, said Gerald Dechant, an independent consultant with Laboratory Quality Systems LLC (Grand Junction, Colo.). For labs associated with small utilities that have limited budgets, "there's a lot of concern as to how this whole process [of certification] is going to impact small communities," Dechant said.

Simplifying the process

In some respects, the format of the standard itself may hamper attempts by small labs to become certified. For example, the standard in certain cases is "prescriptive but not very explanatory," Chapman said, complicating efforts by small labs to comply with its requirements.

Another difficulty faced by small labs seeking NELAC certification is that the standard was "designed on a graded approach" that applies to large and small labs alike, Dechant said. As a result, the standard includes "some generic requirements" that large laboratories can meet by implementing sophisticated procedures, whereas small operations may not know how to comply with the requirements in a cost-effective manner, Dechant said. "Nobody's really explained to drinking water and wastewater folks and the small commercial laboratories how to apply this standard that is supposed to cover everybody," he said.

To remedy these problems, members of an entity within TNI known as the Small Laboratory Advocacy Group developed the handbook, which has the working title *Small Laboratory Guidance Handbook*. Organized to correspond to the format of the 2009 TNI standard, the handbook is intended to simplify the process of understanding the

requirements of the standard and the steps necessary to meet them.

Certification on a budget

The goal of the handbook is to suggest ways for small labs to become certified without having to incur significant costs or hardship, Dechant said. For example, the standard includes requirements having to do with tracking quality control data. Although large labs may have the resources to implement a sophisticated, and often expensive, system for managing such information, small labs typically do not. However, small labs may be able to track quality control data simply using something as basic as a Microsoft Excel spreadsheet, Dechant said. Therefore, the manual outlines such steps that small labs may take in order to simplify compliance with the various requirements of the standard.

Ultimately, the goal of the handbook is to enable small labs to generate defensible, reliable data cost-effectively and in keeping with the NELAC standard, Dechant said. "You can improve what you do without necessarily spending a whole lot of money," he said.

Summer release planned

With the new TNI standards scheduled to take effect on July 1, the

goal is to make the manual available around the same time, said Jerry Parr, executive director of TNI. Although the

exact cost of the manual has yet to be determined, the price will be “reasonable,” Parr said, so as to make it

affordable for small labs.

— *Jay Landers, Solutions*

Faster hormone results

Automated extractor shrinks hormone analysis time without compromising results

Michael Ebitson

Analysts monitoring low levels of hormones in drinking water and wastewater now can use an automated solid-phase extraction (SPE) method to help streamline the process. Traditionally, hormone extractions have been done with SPE cartridges at flow rates of 10 mL/min. These cartridges require slow flow rates or else the chances of hormone channeling and breakthrough increase, leading to low recoveries.

The new process uses an automated extractor; 47-mm, hydrophilic-lipophilic-balanced (HLB) SPE disks; and an automated drying and concentrator instrument to prepare samples for high-performance liquid chromatography (HPLC) and mass spectrometry (MS). It processes samples 10 times faster than the traditional method and improves the quality and consistency of results. Research demonstrated that this sample-preparation method provided recoveries between 79% and 96% when flow rates exceeded 100 mL/min.

Streamlining desired

Researchers used the following when developing the new method:

- an automated extractor system (SPE-DEX[®] 4790),
- a Web-based controller,

Table 1. Hormone method

Step	Solvent	Soak time	Dry time
Prewet #1	MTBE	1:00 min	30 sec
Prewet #2	Methanol	1:00 min	2 sec
Prewet #3	Reagent water	1:00 min	0 min
Prewet #4	Reagent water	1:00 min	0 min
Sample process			
Air dry 10:00 min			
Rinse #1	MTBE	1:30 min	30 sec
Rinse #2	MTBE	1:30 min	30 sec
Rinse #3	MTBE	1:30 min	1:30 min
Rinse #4	MTBE	1:30 min	2:00 min

MTBE = methyl tertiary butyl ether.

- 47-mm HLB SPE disks,
- an automated drying and concentrator system (DryVap[®]; Horizon Technology, Salem, N.H.),
- water-solvent separation membranes,
- a solvent-recovery system,
- a high-performance liquid chromatograph,
- a mass spectrometer,
- methyl tert butyl ether (MTBE),
- methanol, and
- reagent water.

Researchers had two SPE options: a disk or a cartridge. Both SPE options can be done manually or automatically via instruments, and

both typically result in small solvent volumes being used. However, cartridges cannot run particulate-laden samples while maintaining a fast sample-processing time without sacrificing results. Researchers chose an SPE disk because it provides faster extraction and processes 1 L of particulate-laden samples quickly and efficiently.

Extraction. Researchers collected a 500-mL sample of drinking water and adjusted its pH to between 5 and 7. They then added 25 mg of ascorbic acid (a preservative) to the sample and agitated it until the acid dissolved. Then, they

Table 2. Concentrator conditions

Parameter	Setting
Dry volume	20
Heat power	5
Auto rinse mode	1
Heat timer	Off

Table 3. Concentration results

Compound	Spiked amount, ppb	Average recovery, %
Estradiol	50	97
Ethyl estradiol	50	94
Progesterone	50	95
Estrone	50	97
Testosterone	50	100

Table 4. Analytical results

Compound	Flow rate, mL/min	Sample process time, min	Average extraction time, min	Average recovery, %
Alpha estradiol	10	50:00	78:01	103
Alpha estradiol	60	8:33	37:03	94
Alpha estradiol	125	4:00	27:43	93
Ethyl estradiol	10	50:00	78:01	78
Ethyl estradiol	60	8:33	37:03	83
Ethyl estradiol	125	4:00	27:43	79
Progesterone	10	50:00	78:01	94
Progesterone	60	8:33	37:03	83
Progesterone	125	4:00	27:43	92
Estrone	10	50:00	78:01	100
Estrone	60	8:33	37:03	82
Estrone	125	4:00	27:43	96
Testosterone	10	50:00	78:01	91
Testosterone	60	8:33	37:03	85
Testosterone	125	4:00	27:43	88

spiked the sample with 25 µg of hormone mix (7- α -estradiol, estrone, ethynyl, estradiol, progesterone, and testosterone).

Before placing a sample in the automated extractor, researchers placed a small piece of aluminum foil over the opening of the sample bottle and then screwed on a cap adaptor to seal the bottle. They put an SPE disk into the disk holder and placed it on the automated extractor platform. They attached a 40-mL volatile organic acids vial to the collection adaptor to collect the extract. Then, they loaded the sample into the automated extractor and started the hormone method (see Table 1, p. 4).

Researchers processed each sample through the SPE disk at three flow rates — 10, 60, and 125 mL/min — to determine whether recoveries would change. The final extract volume was 20 mL of MTBE.

Concentration. Researchers dried and concentrated the extracts via an automated drying and concentrator system. They assembled a

reservoir with a separation membrane to remove residual water from the solvent extract, loaded it onto the concentrator, and set the concentrator to the conditions shown in Table 2 (p. 4). They placed a 0.5-mL-tip concentration tube into the cradle and sealed it with the cover. Then, they poured the extract into the reservoir. This creates a vacuum that pulls the extract from the reservoir into the concentrator tube.

Once the extract filtered through the concentrator, researchers manually rinsed the reservoir with 15 mL of MTBE. As the MTBE filtered into the concentration tube, the concentrator automatically concentrated it to 0.5 mL. Once the extract reached the 0.5-mL mark, the concentrator rinsed 2 mL of methanol into the concentrator tube to solvent-exchange extract and then continued concentrating the sample to a final volume of 0.5 mL. To ensure that the concentrator would not affect recoveries, researchers ran several hormone spikes with 20 mL of MTBE.

Analysis. Researchers analyzed the sample using an HPLC and MS/MS in the APCI positive mode. The calibration curve consisted of six points: 1, 5, 10, 50, and 100 ppb. All five hormone calibration curves had regression coefficients of more than 0.99.

Results. The concentrator did not negatively affect recoveries for the five hormones (see Table 3, p. 4, and Table 4, left). It had a comparable recovery range for each compound at various flow rates. Results consisted of an average of six replicates. The SPE disk retained the hormones at a sample processing time of up to 125 mL/min.

Extractions in less than 30 minutes

The automated extractor extracted samples in less than 30 minutes. When examined individually, the various flow rates (from 10 to 125 mL/min) exhibited excellent recoveries and minimal recovery loss even though flow was increased by a factor of 10.

Disk extractions were done at 10 mL/min and showed excellent recoveries, but the sample-processing times were 50 minutes or more per sample. The automated drying and concentrator system proved to be reliable with both direct spikes and six replicate samples. It also was easy to load, set up the parameters for, and then start and walk away from. With the optical endpoint detection feature, the automated drying and concentrator system automatically shuts down; it has the extract sealed and ready to be vialled at the analyst's convenience.

Effective alternative

This research demonstrated that the automated extractor and SPE disk can fully automate the extraction of hormone compounds from water. Together, the automated extractor and automated drying and concentrator system reduce analyst labor, solvent use, and turnaround time, as well

as improve accuracy and precision. Automating the extraction and concentration procedure made it possible to obtain excellent results faster than using conventional SPE cartridge man-

ifolds and water bath concentrators.

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reached at mebitson@horizontechinc.com. The author thanks **Ali Haghani** at Montgomery Watson Labs (Monrovia, Calif.) for his time and assistance with this study.

Test drive required

Testing reveals which on-line analyzers work best in a given application

Stephanie Vermande, Rong Liu, and Alex Ekster

There is growing interest in using on-line meters to monitor and control wastewater treatment processes. Using on-line meters reduces the number of analytical tests, increases knowledge of both water quality and process performance, and enables real-time control of the process. This saves energy by reducing air consumption by 5.5% to 40%, reduces chemical costs by up to 50%, and cuts laboratory costs.

However, as noted in the 2007 Water Environment Research Foundation report, *On-Line Nitrogen Monitoring and Control Strategies* (03-CST-8), so many on-line sensor technologies are available and wastewaters vary so greatly that selecting the best equipment is difficult. So, wastewater treatment professionals should test the equipment to confirm that it is applicable before permanently installing it. This

is what the San Jose/Santa Clara (Calif.) Water Pollution Control Plant did when selecting total suspended solids (TSS) and ammonia meters.

Real-time monitoring wanted

The San Jose/Santa Clara plant is a tertiary treatment facility that treats domestic, industrial, and commercial wastewater. Its design flow capacity is 632,000 m³/d (167 mgd), with a peak hourly flow of 1.03 million m³/d (271 mgd). Its major treatment processes include grit removal, primary settling, biological nutrient removal (BNR), filtration, and disinfection. Waste activated sludge (WAS) is mixed with pressurized, air-saturated screened primary effluent, thickened in dissolved air flotation (DAF) tanks, and then pumped to anaerobic digesters for stabilization, volatile solids reduction, and methane gas generation.

The project team tested two types of on-line analyzers to measure TSS and ammonia at different locations in the plant. The sensors were tested in the following streams:

- raw wastewater after grit removal,
- primary effluent,
- mixed liquor,
- activated sludge effluent,
- filtered chlorinated effluent,
- DAF subnatant, and
- thickened WAS.

The project team tested three TSS meters from two vendors in five locations (see Table 1, below). The meters measured TSS based either on an absorption infrared light or a 60° back-scattered infrared light.

The team also tested three ammonia meters: two in mixed liquor and one in activated sludge and filtered chlorinated effluent (see Table 1). The meters tested in mixed liquor were *in situ* sensors whose measuring

Table 1. Meter characteristics

Meter	Parameter	Measuring principle	Measurement type	Cleaning system	Range	Location(s) tested
A	TSS	Absorption light, based on four-beam alternating light	<i>In situ</i>	None by default	0–12 g/L	Raw wastewater channel
B	TSS	60-degree backscattered infrared light, based on one source and one detector	<i>In situ</i>	Ultrasound cleaning	0–400 mg/L, 0–1000 g/L	Primary effluent channel Activated sludge effluent well DAF subnatant well Thickened WAS well
C	TSS	Absorption light, based on four-beam alternating light	<i>In situ</i>	None by default	0–50 g/L	Thickened WAS well
D	Ammonia	ISE	<i>In situ</i>	Compressed air	0.1–100 mg/L to 1–1000 mg/L	Mixed liquor
E	Ammonia	ISE	<i>In situ</i>	Compressed air	0.2–1000 mg/L	Mixed liquor
F	Ammonia	Amperometric	<i>Ex situ</i> Wet chemistry with two reagents ¹	N/A	0–2.00 mg/L	Activated sludge effluent Filter chlorinated effluent

DAF = dissolved air flotation. ISE = ion-selective electrode. TSS = total suspended solids. WAS = waste activated sludge. N/A = not applicable.

¹Reagent A is sodium hypochlorite with buffer and stabilizer. Reagent B is hydrogen peroxide.

principle was based on ion-selective electrode. The vendors claimed an accuracy of $\pm 5\%$ (± 0.2 mg/L in standard solution).

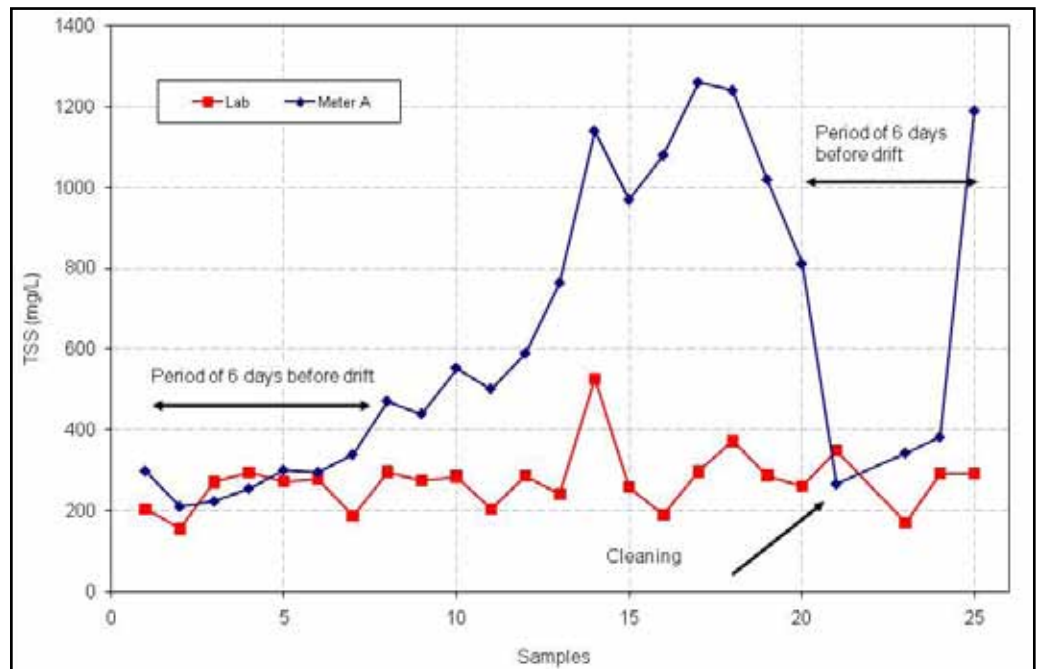
The meter tested in activated sludge effluent and filtered chlorinated effluent was an *ex situ* wet chemistry analyzer that consists of two amperometric sensors: one analyzes monochloramine in the raw sample, while the other analyzes monochloramine in the sample after the addition of a reagent that converts ammonia into monochloramine. The difference in monochloramine concentrations corresponds to the ammonia concentration in the raw sample. A filter upstream of the sensors removed any excessive particles from the sample. The vendor claimed an accuracy of ± 0.1 mg/L.

All of the on-line meters were installed in a temporary setup. The controllers were connected to data-loggers, which recorded meter readings every minute.

To evaluate the meters' accuracy, the project team took grab samples and immediately took them to the plant laboratory for analyses in triplicate. Analyses were done in accordance with the 21st edition of *Standard Methods for Examination of Water and Wastewater*. The team averaged the lab results and compared the averages to meter readings.

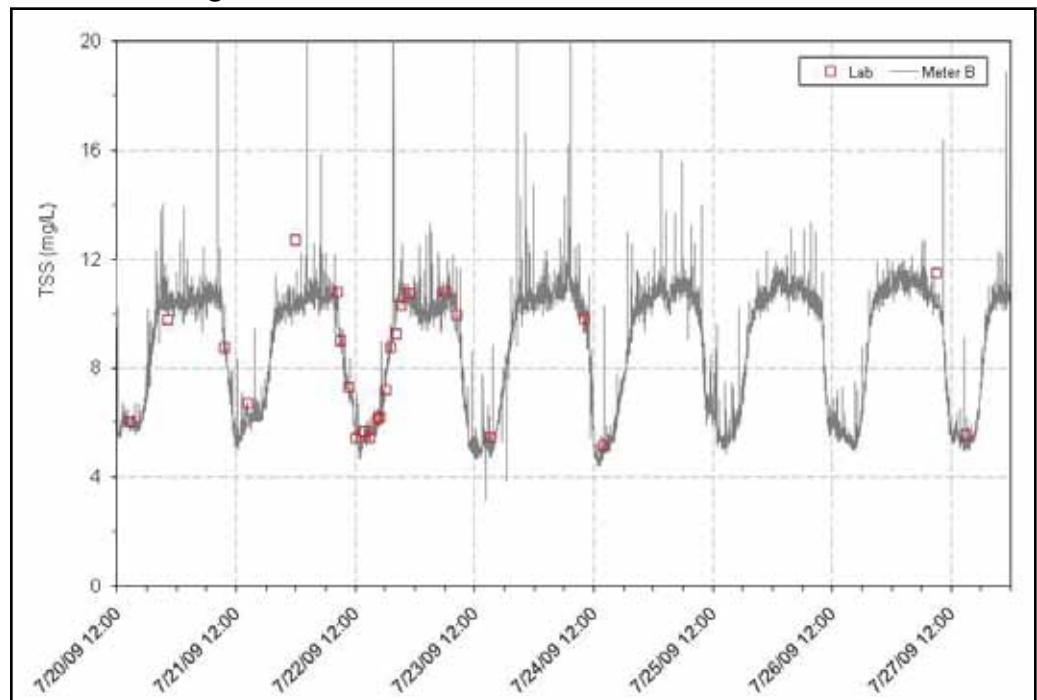
The project team also performed a simple cost analysis that included equipment cost, a weekly analysis for meter validation, and a daily analysis before meter installation. Installation and maintenance costs were not considered.

Figure 1. Comparison of TSS meter (Meter A) and laboratory results for untreated wastewater



TSS = total suspended solids.

Figure 2. Comparison of TSS meter (Meter B) and laboratory results for activated sludge effluent



TSS = total suspended solids.

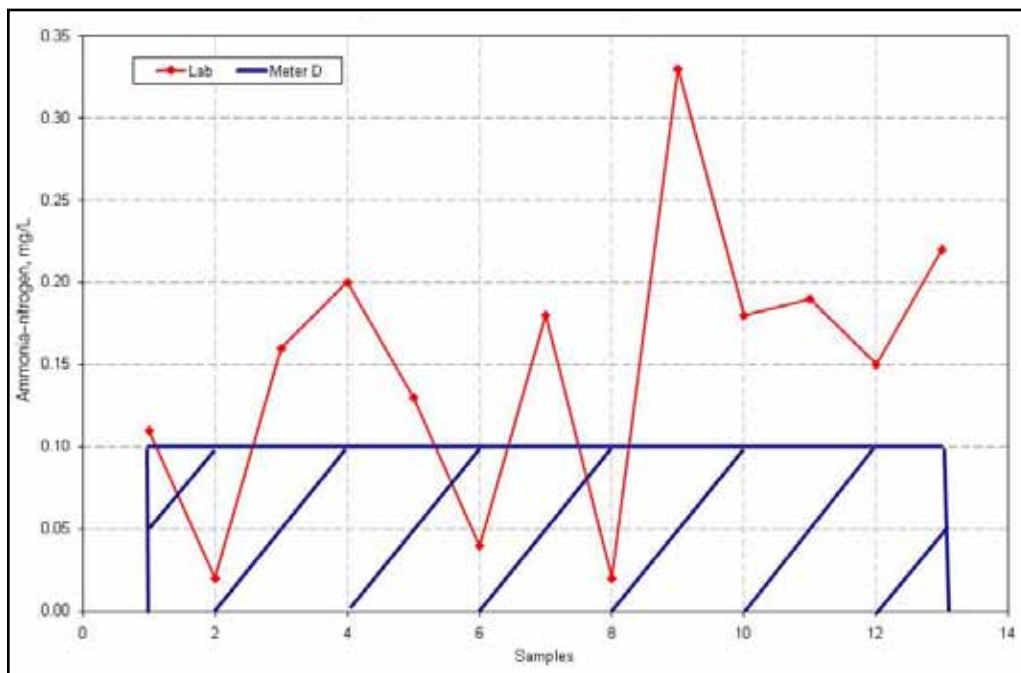
TSS meters

Raw wastewater. Real-time primary clarifier performance could be monitored by coupling two on-line TSS meters: one in raw wastewater and one in primary effluent. With this

in mind, the project team installed Meter A in the raw wastewater channel.

The lab's TSS measurements averaged 273 (± 76) mg/L; Meter A's values averaged 623 (± 368) mg/L.

Figure 3. Comparison of the ammonia meter (Meter D) and laboratory results for activated sludge effluent



The average difference — 350 mg/L (130%) — was clearly unacceptable. Also, the meter signal rapidly drifted after only 6 days in the stream (see Figure 1, p. 7), not to mention signal loss and rag accumulation around the probe.

Meter A did not include a default cleaning system, so the team added an external pneumatic cleaning system to reduce rag accumulation and improve accuracy. Unfortunately, this modification did not resolve the problems.

Primary effluent. The project team did not test Meter B in raw wastewater because it already performed poorly in primary effluent. When the team tested Meter B in the primary effluent channel, its TSS measurements averaged 94 mg/L, which was 125% higher than average lab results (178 ± 42 mg/L versus 84 ± 26 mg/L). Moreover, the TSS profiles obtained via lab and via meter did not agree; the meter did not reflect TSS variations properly.

The vendors hypothesized that the dark color of the raw wastewater and primary effluent absorbed most of the sensors' infrared light, caus-

ing inaccurate readings. Another hypothesis was that the streams' continuously changing particle distribution probably affected the sensors' optical properties.

Activated sludge effluent. The project team also tested Meter B in activated sludge effluent. Real-time monitoring of TSS in this stream would let operators adjust BNR clarifiers or downstream gravity filters more rapidly in response to TSS increases. After calibration, the difference between meter and laboratory results was 0.2 mg/L (1.6%), on average, for a TSS ranging from 4 to 12 mg/L. TSS profiles demonstrated that Meter B accurately captured TSS variations in activated sludge effluent, showing that TSS increased during the evening and night (from 5 to 10 mg/L; see Figure 2, p. 7). At press time, the origin of this fluctuation was still under investigation.

DAF subnatant. When the project team tested Meter B in DAF subnatant, there was a large discrepancy between meter and lab results under regular operating conditions (<100 to 120 mg/L of TSS). Lab results averaged 59 ± 20 mg/L, while meter

results averaged 40 ± 11 mg/L — a difference of 28% (19 mg/L). The DAF tanks receive WAS mixed with air-saturated primary effluent, so DAF subnatant mostly consists of primary effluent. However, when WAS solids migrated to DAF subnatant, the difference between laboratory and meter averages shrunk to within 7% (an acceptable value for this application).

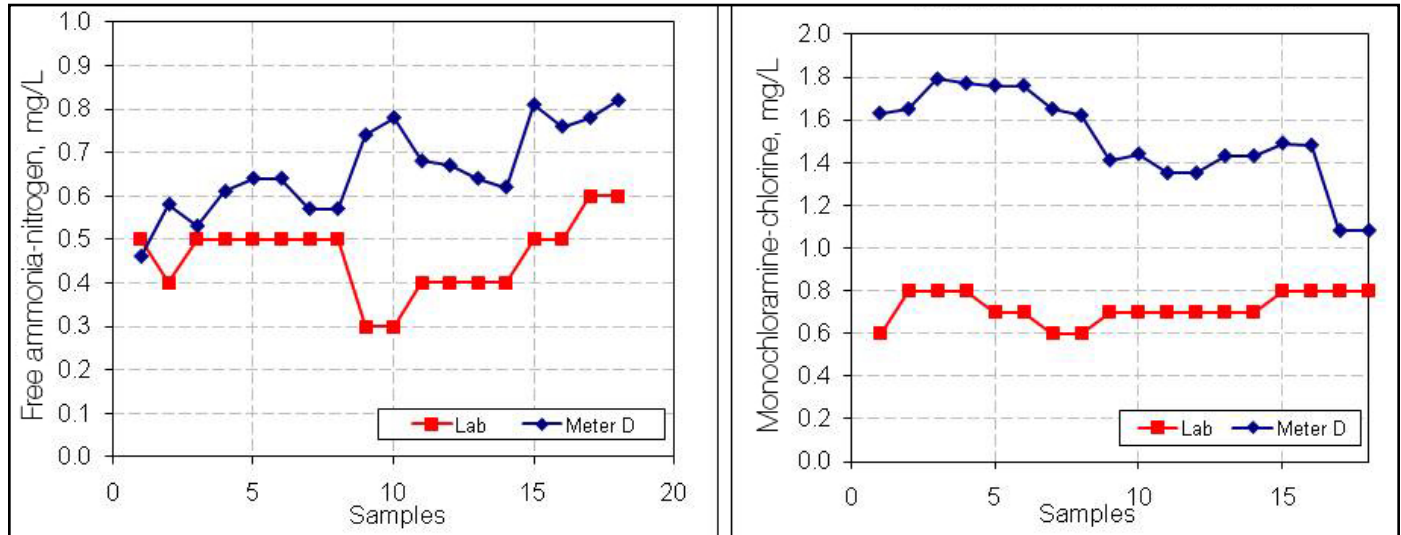
Thickened WAS. The project team tested both Meter B and Meter C in the well where thickened WAS was discharged from the DAF tank before being pumped to the anaerobic digester. The goal was to better characterize anaerobic digester feed.

According to laboratory analyses, the total solids concentration ranged from 20,900 to 46,900 mg/L and averaged 40,500 (± 5500) mg/L. Total dissolved solids were only about 770 mg/L, so TSS could be approximated by total solids. Unfortunately, Meter C's signal was lost, which made calibration impossible. Adding an air cleaning system did not improve results.

On average, the difference between Meter B and laboratory results was only 2%, but this did not reflect the fluctuations observed. Lab and meter values differed by up to 23,700 mg/L of total solids, and recalibrating the meter did not improve accuracy. The source of the problem may have been either the setup or an inefficient cleaning system. (Very little turbulence occurred in the thickened WAS well, and solids tended to adhere to the probe despite ultrasonic cleaning.) To confirm these hypotheses, two tests should be scheduled:

- one in which the probe remains where it is but a different cleaning system (e.g., pneumatic air) is used; and
- one in which the probe is installed

Figure 4. Comparison of Meter D and laboratory results for filtered chlorinated effluent



directly in digester feed line, where solids flow continuously. At press time, neither test had been performed.

Ammonia meters

Mixed liquor testing. The project team tested two on-line ammonia meters — Meter D and Meter E, which were based on the same measuring principle — in the aerated basins' mixed liquor. The goal was to control aeration in the BNR process to avoid ammonia breakthrough and reduce air consumption. Meter D was tested in four locations in the basin:

- at Location 1, the average concentration was 7.0 (± 1.5) mg/L of ammonia-nitrogen;
- at Location 2, the average concentration was 4.7 (± 1.5) mg/L of ammonia-nitrogen;
- at Location 3, the average concentration was 1.9 (± 0.8) mg/L of ammonia-nitrogen; and
- at Location 4, the average concentration was 0.2 (± 0.1) mg/L of ammonia-nitrogen.

This meter provided accurate readings within 5% when the ammonia concentration was more than 2 mg/L of ammonia-nitrogen; the difference was in the precision range claimed by the vendor. Meter values closely followed laboratory measurements.

When the concentration was less than 1.9 (± 0.8) mg/L of ammonia-nitrogen, the discrepancy between lab and meter results was 53% (0.23 mg/L). In other words, Meter D was not accurate enough to detect such low levels precisely. So, the team only recommended it for use when the mixed liquor's ammonia concentration is more than 2 mg/L.

Meter E was tested in two locations in the basin:

- at Location 5, the average concentration was 20.2 (± 2.7) mg/L of ammonia-nitrogen;
- at Location 6, the average concentration was 5.9 (± 2.0) mg/L of ammonia-nitrogen.

The average difference between lab and meter results for Location 5 was less than 2.4% (0.65 mg/L); however, most of the meter's ammonia readings were more than 10% different from lab results.

The average difference between lab and meter results for Location 6 was 56% (1.7 mg/L). Moreover, when the probe was immersed in laboratory standard solutions, the ammonia concentration drifted over time. The team made several attempts to improve accuracy (e.g., recalibration, changing cartridge, and troubleshooting with the vendor's R&D center) but none of these solved the problem. The vendor took the system back and reim-

bursed the plant.

Activated sludge effluent and filtered chlorinated effluent.

Because Meter D could not measure low ammonia concentrations, the team evaluated Meter F — an *ex situ* ammonia analyzer based on amperometric probes. The goal was to continuously monitor ammonia to capture breakthrough that could violate the plant's National Pollutant Discharge Elimination System permit. The team tested Meter F in both activated sludge effluent and filter chlorinated effluent for ammonia and monochloramine concentrations.

The activated sludge effluent did not contain monochloramine. Its ammonia concentration ranged from 0.02 to 0.33 mg/L of ammonia-nitrogen, and averaged 0.15 (± 0.09) mg/L (see Figure 3, p. 8). However, Meter F consistently indicated that the concentration was below 0.1 mg/L of ammonia-nitrogen, which appears to be its detection limit. The team made several attempts to recalibrate the sensor, and changed parts and reagents, but nothing improved accuracy.

The filter chlorinated effluent's free ammonia concentration averaged 0.46 (± 0.08) mg/L of ammonia-nitrogen and its monochloramine concentration averaged 0.72 (± 0.04) mg/L of ammonia-nitrogen. The difference between meter and lab

Table 2. Cost analysis

Meter	Location	Equipment cost	Laboratory cost	Payback period
B	Activated sludge effluent	~\$6000	\$27	9 months
B	DAF subnatant	~\$6000	\$27	9 months
D	Mixed liquor	~\$9000	\$37	9 months

DAF = dissolved air flotation.

results was 49% and 112%, respectively, for free ammonia and monochloramine (see Figure 4, p. 9).

The vendor hypothesized that the filtered chlorinated effluent contained dichloramine, which might be interfering with the meter readings. Laboratory analyses confirmed that the effluent contained equal amounts of dichloramine and monochloramine. Other meter issues included signal variations while pumping one sample, signal drift over time, and slow response.

Three successes

Based on testing results, the project team only recommended three on-line meters for permanent installation:

- Meter B for activated sludge effluent,
- Meter B for DAF subnatant, and
- Meter D in mixed liquor.

These meters have a short payback period (less than 1 year; see Table 2, above). This quick return on investment (ROI) makes these on-line sensors attractive. Moreover, if an aeration control strategy is developed, the ammonia meter's ROI could be even shorter. ROI on purchase of recommended on-line meters is less than a year when only the reduction of laboratory analyzes is considered. The ROI could be even shorter for the ammonia meter if aeration control strategies are developed.

Meanwhile, research and testing will continue to find on-line TSS and ammonia meters that perform correctly in raw wastewater, primary effluent, thickened WAS, and activated sludge effluent at the San Jose/Santa Clara plant.

As this article illustrates, on-line meter results are often site-specific due to wastewater characteristics and treatment train details. Before investing money and time in on-line meters and related control strategies, test several models to maximize the chance of success.

Stephanie Vermande is an associate engineer, Rong Liu is a sanitary engineer, and Alex Ekster is a senior engineer at the City of San Jose, Calif.'s San Jose/Santa Clara Water Pollution Control Plant.

The authors thank the San Jose/Santa Clara plant's Operation, Instrumentation, and Laboratory staff for their support during this project. They also thank Issayas Lemma and the process engineering interns.

The periodic table gets a makeover

The atomic weights of 10 elements are about to change

It may not spark the same level of public outrage as when scientists declared that Pluto was not a planet, or the widespread confusion wrought by the elimination of fats and oils from the food pyramid.

But in this, the International Year of Chemistry, is news that is likely to exasperate at least a few high school chemistry students.

The news: the Periodic Table of the Elements is, well, sort of wrong.

Yes, the chart on the walls of chemistry classrooms around the world will be coming down and replaced with a new version. On this one, the atomic weights of 10 elements will be expressed as a range with a lower and upper boundary,

rather than as a single standard value, according to Ty Coplen, a research chemist for the U.S. Geological Survey (USGS).

The new weight ranges, said Coplen, more accurately reflect how these elements — including hydrogen, oxygen, carbon, and nitrogen — are found in nature. Coplen is one of a number of experts who participate in the International Union of Pure and Applied Chemistry's Commission on Isotopic Abundances and Atomic Weights (Research Triangle Park, N.C.), which meets annually to study and update atomic weights, and with the support of USGS and other scientific organizations, is responsible for publishing the new table.

"For more than 150 years, standard atomic weights were thought to be constants," Coplen said. "But it's now possible to measure the atomic weight of many elements more precisely."

The atomic weight of an element depends upon how many stable isotopes it has and the relative amount of each stable isotope. Variations in atomic weight occur when an element has two or more naturally occurring stable isotopes that vary in abundance.

Take hydrogen, for example. The Periodic Table currently lists its atomic weight as 1.00794. In reality, its weight can range from 1.00784 to 1.00811.

The changes do more than make

chemistry class more challenging for students, who will have to select a single value out of many when doing chemistry calculations.

“Precise measurements of atomic weights can tell us many things and have many practical applications,” said Coplen.

Water investigations are one. “Let’s suppose you are drawing water out of a well,” Coplen continued. “By measuring the atomic weight of the hydrogen and oxygen in the water, it is possible to tell if the water is local groundwater, or if it is coming from another source.” Isotopic measurements of nitrogen, chlorine, and other elements can be used for tracing pollutants in streams and groundwater as well. That’s what the field of isotope hydrology is all about, he said.

And that’s just the tip of the iceberg. The variation in isotopes can be useful in checking the purity and sources of food, such as vanilla and honey. In investigations of athletic events, pre-

cise measurements of the abundances of carbon isotopes will enable scientists to identify performance-enhancing testosterone in athletes; the atomic weight of carbon in natural human testosterone is higher than that in pharmaceutical testosterone.

More to come

Other elements receiving an atomic weight makeover include lithium, boron, silicon, sulfur, chlorine, and thallium. But the Commission on Isotopic Abundances and Atomic Weights is not finished yet. Weight variations in an additional six elements will be discussed at its next meeting in Calgary in July.

But not all elements will ultimately be affected. “Elements with only one stable isotope do not exhibit variations in their atomic weights,” said Coplen. That means fluorine, aluminum, sodium, and gold, for example, are safe.

Coplen acknowledged that the updated Periodic Table has made

chemistry more complicated, but he thinks that’s a good thing.

“The updated chart really provides educators with a new teaching tool,” he said. “It gives them a way to teach about stable isotopes in hydrogen, oxygen, and other elements, and why their atomic weights vary.”

But don’t expect to see curriculum changes taking place overnight. When it comes to updating the Periodic Table, the wheels of progress move slowly and meticulously. After all, the commission has been debating how to represent the atomic weight variations since 1985, and first published a 98-page report with its recommendations in late 2010.

It may be years, in other words, before the new atomic weights are reflected on the classroom walls and chemistry textbooks. “Textbook publishers don’t work that fast, either,” Coplen said.

— Mary Bufe, *Solutions*

Twin time bombs

Potential pitfalls in U.S. EPA’s Methods Update Rule

William Ray

Last September, the U.S. Environmental Protection Agency (EPA) proposed its Methods Update Rule, which, like the 2007 version, adds new and updated methods to the long list of EPA analytical methods in Tables IA to IH. However, there are two significant changes that will give lab workers a headache for some time.

New citation protocol

The first is the change in the citation of methods from *Standard Methods for the Examination of Water and Wastewater*. In all past versions, *Standard Methods* was referenced by its print edition. Over the years, EPA has cited at least one edition up to the current version, with three print editions and the online edition. Now, EPA proposes to cite all methods by their

year of approval by the appropriate Standard Methods joint task group (JTG). For example, a citation for an *Escherichia coli* method might look like it does in the figure (below).

“9223 B” is the method number provided by *Standard Methods*, while “2004” is the year the method was approved by the JTG. The approval year can be found by examining the “A” section of a method. For example, the proposed method from *Standard Methods* for biochemical oxygen demand is 5210B-2001. At the bottom of the first page of Section 5210A is the following:

* Approved by Standard Methods Committee, 2001.

Joint Task Group: James C. Young (chair), George T. Bowman, Sabry M. Kamhawy, Terry G. Mills, Marlene Patillo, Ray C. Whittemore.

So which print edition does this method appear in? Not the 20th edition, as it was printed in 1998, but in the 21st edition, which was printed in 2005. But other methods are not in any print edition, as they have approval dates of 2009, such as the Inductively Coupled Plasma – Mass Spectrometry (ICP–MS) Method 3125-2009. The most likely source of methods from *Standard Methods* will be those available from the *Standard Methods* Web site (www.standard-methods.org), sometimes referred to as “*Standard Methods* online.”

Figure. Example of a *Standard Methods* citation

5. E. coli, number per 100 mL.	MPN multiple tube/multiple well	9223 B-2004
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But, as some lab managers know, the cost of a single method is as much as \$69 (the price per checkout page as of January) if you are not a subscriber to the online *Standard Methods*. And although the cost is waived for subscribers, a single-person site license for 1 year is \$295. For a nonsubscriber, purchasing a few methods could exceed the cost of the print version, and the cost of renewing a license every year is the same as purchasing the print edition every year. A useful strategy when more than three methods are needed would be to purchase a subscription for 1 year and then download every possible method needed. The good news is that all “_020” sections (e.g., 3020 or 9020) are free.

Quality assurance requirements

The second headache labs face is the proposed section on uniform quality assurance (40 *CFR* 136.7). EPA states in the preamble that it is “proposing to specify ‘essential’ quality control at Sec. 136.7 for use in conducting an analysis with an approved method and when insufficient instructions are contained in an approved method.” Sec. 136.7 contains a list of 12 essential elements (see sidebar, right) with the requirement that each “must be clearly documented in the written method along with a performance specification or description for each of the twelve quality control checks.”

Many have agreed that quality assurance varies greatly among methods. For example, *Standard Method* 9221B (multiple-tube fermentation for total coliforms) references 9020B as the source of its quality assurance requirements. Contrast this with the single requirement to check media lots against positive and negative cultures, as found in the approved Collert® method (IDEXX Laboratories Inc.; Westport, Maine). Many have also pointed out the total lack of any quality assurance requirements in

EPA’s own methods created in the 1970s and 1980s. The approved EPA Method 351.2 for semiautomated Kjeldahl nitrogen testing does not even have a quality assurance section.

Although there is a need to add missing quality assurance elements, EPA’s proposed rectification lacks on two fronts. First, it is geared for methods using sophisticated analytical devices, such as inductively coupled plasma or gas chromatography–mass spectroscopy. Second, there are no suggested resources for information to complete any element; how to present any found information in the method; how information should be selected, especially if there are two or more conflicting information sources; and how to defend eliminating any of the 12 elements.

The most commonly used methods do not fit the 12 elements. Method detection limits (MDLs; No. 2), reagent and fortified blanks (nos. 3 and 4), matrix spikes, internal standards, and calibration (nos. 5, 6, and 7) do not fit into any microbiology method. MDLs are not practical for any gravimetric or titrimetric method. In order to complete the requirements, some “creative fitting” will be needed. Does calibrating the balance cover the requirements of calibration (No. 7)?

The second headache is more important, as the writers of these revised methods will need sources to refer back to, especially if they need to justify dropping one of the 12 elements. The simplest situation is when the base method is from *Standard Methods*. The source is not only what is in the base method but also the associated _020 section, since each method references a _020 section. But even this situation is not conflict-free. *Standard Methods* Sec. 9020B calls for the reading of incubators twice a day — morning and afternoon. However EPA’s *Manual for the Certification of Laboratories Analyzing Drinking Water* calls for readings twice a day

Short list of the 12 quality assurance/quality control elements

- Demonstration of capability
- Method detection limit
- Laboratory reagent blank
- Laboratory fortified blank
- Matrix spike, matrix spike duplicate
- Internal standards, surrogate standards
- Calibration
- Control charts
- Corrective action
- Quality control acceptance criteria
- Definitions of a batch
- Minimum frequency

but no closer than 4 hours apart. In some states, including the author’s state of California, laboratory certification auditors have been demanding compliance with the EPA manual even though it is intended for drinking water laboratories and is not a requirement of state or federal regulations. Is the laboratory wrong in simply citing Sec. 9020B, or should it incorporate EPA’s manual requirements? EPA in its proposed rule is silent on this case and in all other choices a laboratory might make in describing one of the 12 elements.

Simplify if possible

So what is a hard-working lab to do? Fortunately, the proposed methods in the method update rule that are from *Standard Methods* are mostly older than the publish date for the 21st edition. Lab managers, however, will need the online versions of the methods for total and fecal coliforms by multiple-tube fermentation (approved in 2006; strangely, the method for *E. coli*

can be taken from the 21st edition, as it was approved in 2004). They also would need the online versions for ICP/MS for metals (2009), ion-chromatographic and colorimetric methods for hexavalent chromium, manual cold vapor for mercury, and gaseous hydride for selenium. The oldest method and, therefore, the only “oddball” is the dithizone colorimetric method for cadmium, which is from the 19th edition (1990) of *Standard Methods*.

Adding the 12 elements will be simpler if a method from *Standard Methods* is being used, as with few exceptions, the approved method references the appropriate _020 section. Just as easy to use are newer EPA methods, especially those numbered in the 1600s, and EPA’s methods 300.x, 200.6, 200.7, 200.8, and 200.9, as these contain

information covering most of the 12 elements. The element with sources that are most difficult to find and elements least likely to be covered within the method description or even in *Standard Methods’* _020 sections is No. 8, which deals with control charting and other trend analyses.

In contrast, methods from various manufacturers, older EPA methods, or the use of field-test kits will be the easiest to find quality assurance elements for. The best advice in these cases is to use the appropriate _020 section from *Standard Methods*. This works well for field-test kit work, as the test kit, if not directly approved by EPA, must follow the procedures found in an approved method — usually from *Standard Methods*.

Although the September

Methods Update Rule is not final, there is no reason to wait before beginning rewriting method procedures to incorporate the 12 elements. As EPA states in the preamble to the proposed rule, it “is proposing to specify ‘essential’ quality control.” These are essential elements and should be in your method procedures.

The comment period for the proposed rule ended in December. EPA has not indicated a date for the final rule. Informal guesses place publication of the final rule anywhere from the coming months to 2 years hence. But the time to plan is now. Will you be ready?

William Ray is a quality assurance program manager for the California State Water Resources Control Board.

Editor's note: According to *Standard Methods* editor Steve Posavec, the next edition of *Standard Methods*, expected for release next year, will include QA/QC information for each part.

LABWISE

Editor's Note: Due to the popularity, simplicity, and sheer utility of Labwise, a long-running department in *Laboratory Solutions* that disappeared for a few years, a decision was made to reintroduce it. For a bit of historical fun, and to ease readers back into the Labwise habit, editorial advisory board member Charles Lytle has created this quiz using an ancient copy of *Standard Methods*. Enjoy!

It's 1920. The 18th and 19th amendments to the U.S. Constitution are passed, and the League of Nations and the National Football League are formed. The Roaring Twenties are just a moment away, and the American Public Health Association publishes the 4th edition of *Standard Methods*. Test your knowledge of classic analyses with this quiz.

1. What do these apparatuses measure?

- The thermophone.
- The Lovibond tintometer.
- Platinum wire rod.

2. What were these reagents/materials used for?

- Pear's precipitated fuller's earth.
- Tolidin.
- Castile soap.
- Liebig's meat extract.

3. What would you be doing when you determined “the reaction” of sludge?

4. “One grain per U.S. gallon” equals how many parts per million?

5. What analysis used Clark's scale?

6. What concentration is an N/20 solution?

7. What is *B. coli*?

Answers on page 16.

WEBNOTES

Editor's Note: Questions and replies are taken from the technical discussion groups on the Water Environment Federation's Web site. Solutions assumes no responsibility for claims or comments.

High GGAs

Q: I have been doing carbonaceous oxygen demand (cBOD) for over 20 years, and this is a first! Have had high glucose-glutamic acid (GGAs) in BOD and cBOD for the past 3 months. Blanks and seed blanks all look good. There is no change to procedure, reagents, dilution water, or glassware. Normally, my cBOD GGA is around 172 [mg/L]. I have had 220 [mg/L], 188 [mg/L], 178 [mg/L], [and an] additional 5 [mg/L] in the 180s [mg/L]. [The] last time it was 215 [mg/L]. I'm just not sure what to change or check at this point. Please help!

Name withheld

A: I suspect your nitrification inhibitor is losing potency. We are in a humid environment, and it will occasionally degrade due to (we suspect) the humidity. Try changing that out and see if your performance improves. You mentioned getting high results in the BOD as well. Are you getting the high results on each on the same day? Are the seed and dilution water the same between the batches, or are you doing BOD and cBOD independent of each other?

Name withheld

A: I do not see that you have a problem. All your values are between 178 mg/L and 220 mg/L cBOD. This is well within the 198 mg/L \pm 30 mg/L [range] that *Standard Methods* requires for the analysis. I understand that they may

be higher than the 172 mg/L you were getting, but 172 mg/L is on the low end of the known value.

Our range is 195 mg/L to 212 mg/L total biochemical oxygen demand (TBOD) and 183 mg/L to 204 mg/L cBOD on GGA and a range of 189 mg/L to 218 mg/L TBOD for a 200-mg/L standard of potassium hydrogen phthalate (KHP). The KHP value is using a 0.70 factor for BOD/chemical oxygen demand (COD), making a BOD standard of the COD standard. This helps evaluate any nitrification interference with the GGA standard.

James Royer

*Chief chemist
Urbana (Ill.) Champaign Sanitary
District*

A: I can certainly try that, but that would not explain the high BOD values as well. BOD standard should be about 198 ppm. cBOD standard should be about 172 ppm. That is my understanding.

Name withheld

A: The BOD test is a bioassay rather than a chemical analysis. Thus, the expected value will be a certain percentage of the total oxidation value of the organic compounds in the sample. The BOD test is a wet oxidation and will follow the same chemical reaction as COD, just not to completion during the 5-day incubation period. The average published data for the 12th edition was 218 mg/L \pm 11 using fresh settled sewage. We now have an assigned

value of 198 mg/L, which is an average of many different laboratory results where purchased seed material is used, ensuring no nitrification interference.

The cBOD should have the same value as BOD, as the sample has the same organic content at the same oxidation rate utilized for both tests. The reason that cBOD has a lower value is that many laboratories get lower values than was averaged. Based on case studies published in *Third Century of BOD*, by Baird and Smith, 2002, trichloromethyl pyridine is not toxic to cBOD, and lower results are most likely due to improper test setup and insufficient seed amounts.

In our lab, we see no difference between BOD and cBOD results for GGA using purchased seed.

James Royer

A: How does one know if the seed has nitrifiers in it at all? Unless one is using commercial seed that is guaranteed to contain these, one should expect seasonal variation when using natural sources.

If your cBOD GGA is the same or more as the BOD GGA, then there are no nitrifiers in your seed, but your samples, particularly raw sewage samples, normally will contain nitrifiers.

Luis E. Manriquez

*Chemist 1
City of Phoenix Water Services
Department*

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Disinfection 2011

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Disinfection 2011 will provide a meeting ground for those water quality professionals concerned with disinfection needs and technologies, including the disinfection of water and wastewater, reuse water, and biosolids.

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This conference is held by the Water Environment Federation in cooperation with the U. S. Environmental Protection Agency, the Ohio Water Environment Association, and the Centers for Disease Control and Prevention.

www.wef.org/Disinfection

Follow WEF on:



A: The effects of nitrification are the most perplexing thing about the BOD analysis. I think this is the cause of the most variation of results that we see from lab to lab.

We do not want any nitrification in our BOD test as we want to evaluate the organics in the sample. This has been the case since the 9th edition of *Standard Methods* in 1946 when ammonium ion was added to the dilution water to standardize it. The thought then was that there are few nitrifiers in the samples, so there will be no problem. But after more treatment, nitrifiers are a problem.

So we want seed material with no nitrifiers or at least as few as possible.

James Royer

A: I know, and I'm sure that Luis and many others know, that scientifically it is better not to have nitrifiers in the seed. But from a practical standpoint, there is no problem with them being there when doing BOD. If the regulator (*i.e.*, a permit writer for a wastewater treatment plant) doesn't want nitrifiers to be a part of the test, the permit would be written for the plant to run cBOD rather than BOD.

When a WWTP (wastewater treatment plant) lab runs an effluent BOD sample, their objective is to make sure the plant is meeting its discharge permit limit. If they can do that with seed containing nitrifiers, they and their regulator are happy. When they run a GGA sample, their objective is to get results in the 198-mg/L range, so they can keep their

regulator/accreditor off their backs. The lab is more likely to do that with a seed containing nitrifiers, because if there are no nitrifiers in the seed, they are in effect doing a cBOD, and the cBOD test is known to give considerably lower GGA results than BOD.

Perhaps the fight to be fought is to get all regulatory agencies to require cBOD rather than BOD run on plant samples. However, because the vast majority of historical data for WWTP plants is BOD and not cBOD data, that change is probably not going to happen soon.

Perry Brake

*Lab accreditation section manager
Washington Department of Ecology
Manchester, Wash.*

Share your ideas!

Water Environment Laboratory Solutions is looking for two new editorial advisory board (EAB) members. Volunteer EAB members perform an extremely valuable service to WEF, lending their professional expertise to WEF periodicals and serving as our "eyes and ears" in the field. EABs are not peer review boards, nor do they approve editorial content. Rather, EAB members serve in an *advisory* capacity to the newsletter editor, providing news story ideas, feedback on features, and other suggestions.

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Interested? Send a resume and letter explaining your experience in laboratory analysis to *Solutions* editor Cathy Vidito at cvidito@wef.org.

Answers to LABWISE

- a. Water temperature at depth.
b. Color.
c. Turbidity.
- a. Turbidity.
b. Chlorine.
c. Hardness.
d. Coliforms.
- The alkalinity/acidity of a sludge/water suspension.
- 17.1.
- Hardness.
- 0.05 N.
- B.* stands for bacilli, and the term "*B. coli*" has been supplanted by the general term "coliform group."