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Laboratory to celebrate 30th anniversary

The U.S. Geological Survey (USGS) National Water Quality Laboratory, formerly referred to as the Denver Central Laboratory, was dedicated November 12, 1976, in a special ceremony at 5293 Ward Road in Arvada, Colorado, west of Denver. The Laboratory celebrates its 30th anniversary this year.

Guests at the dedication were introduced by Al Letey, Acting Assistant Director, Central Region. The speakers included Michael J. Norton, Regional Administrator, General Services Administration (GSA); William L. Rogers, Special Assistant to the Secretary of the Interior; Vincent E. McKelvey, Director, U.S. Geological Survey; and Joseph S. Cragwall, Jr., Chief Hydrologist, Water Resources.

Immediately after the program, platform guests were invited to tour the

building and dine at a buffet luncheon hosted by Survey employees.

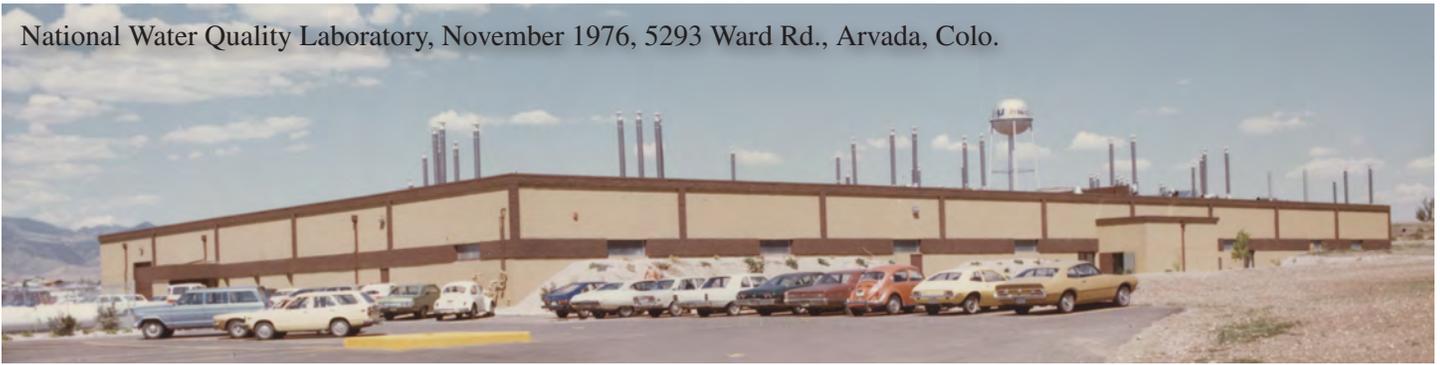
The new building was designed by Hornbein and White Architects/Planners, Inc., of Aurora. Construction was started in October 1975 and was completed by April 1976. The building was occupied by the USGS in April 1976. It was leased from Lea Company, Aurora, by the GSA.

After 23 years on Ward Road, the NWQL dedicated its new “world-class laboratory for 21st century science” June 9, 1999, in building 95 at the Denver Federal Center.

The following pages include related photos and articles by USGS employees—retired or still working—who reminisce about those early days in the life of the Central Lab.



Central Laboratory employees and platform guests at dedication ceremony, November 12, 1976, in the “Blue Carpet Area”



Harold Ardourel recalls dedication of NWQL in 1976

I was hired at the Denver Central Laboratory in early November 1976. There were only about 75 people working in the lab at that time. The lab was moved from Salt Lake City in May–June of that year, and it had a huge backlog of uncompleted samples after the relocation. Trays of samples were piled throughout the analytical lab.

To complicate matters, the lab was having a 2-day open house to dedicate the new building. Within a week after I started, all work had to stop to clean up the lab, move the sample trays to the warehouse, and set up demonstrations for the public and other USGS staff. Sample trays were cleverly hidden behind large orange fabric curtains. No one could start to train me on processing samples during this time, so I spent the first 2 weeks working in the washroom cleaning up glassware.

I remember a large number of officials attending the ceremonies and a lot of speeches. Russell McAvoy was the Lab Chief at the time and Doug Manigold was the Assistant Lab Chief. Of particular interest to the public attending the open house was a set of distillation flasks with red- and green-colored water circulating through the cooling coils to simulate a chemical analysis in progress, but actually it was meaningless. After the lab was dedicated, the sample analysis resumed but the summer backlog was not caught up until February–March 1977.

It was rumored that the public was invited to the open house so that it

could see what we were doing at the lab. Many local people living around the laboratory reportedly thought that we were involved in some way with the plutonium operations at nearby Rocky Flats and were suspicious of our work.

The original lab was a one-story building, and it had numerous vent pipes for the hoods sticking up off the roof. When I first went to find the lab for my interview with Doug Manigold, I was not familiar with what a lab looked like from the outside, and I actually thought the building was a meat-processing plant. A school close by looked more like a typical government facility, and I looked at it first before returning to the only other building in the area. The lab did not have a sign at the street for many years, and it was only when I noticed a number of cars in the parking lot

with government license plates that I realized that I was at the right place. The lack of an official sign may have fueled speculation that the lab was up to some kind of covert activity.

Unlike the computer-controlled operations of today, analysts at that time had to use the daily “big brother” list of samples to compile individual run sheets by hand. Results were circled or crossed off as they were printed from the instruments, and the unprocessed data and analytical curve data for analyses were submitted nightly to the keypunch area for data processing. You didn’t actually know if quality control (QC) passed or failed until the next day because you never got to do real-time data crunches, as we do today. Analysts set up their QC limits based on experience that if these limits were met, they would rarely fail the actual QC limits. Almost every-

thing was handwritten or graphed because calculators were about the only tool available for routine work.

- HAROLD ARDOUREL
[Ardourel is supervisory chemist of the NWQL Nutrients Unit]



TOURING THE OLD LAB—Russell McAvoy (right), Chief of the old Central Lab in 1976, led distinguished guests on a tour of the Laboratory following the dedication ceremony. Next to McAvoy is Vincent E. McKelvey, Director, USGS.

Recollections of 30th anniversary of NWQL

Hundreds of square feet of blue carpet in a laboratory work area where technicians and chemists used strong acids, bases, organic solvent, and other chemicals didn't turn out to be very practical. A few years after the dedication ceremony and a patchwork of carpet repairs, floor tile soon replaced the sea of blue that was affectionately called the "Blue Carpet Area."

In 1976, inorganic analyses provided much of the workload at the NWQL. Row after row of atomic absorption spectrometers (AAS) and continuous-flow colorimetric analyzers were used to analyze thousands of samples for elemental and nutrient concentrations, respectively. Computerization was nonexistent. Most analytical instruments lacked automatic sampler

changes, and so results were recorded by hand or traced out on a pen recorder. Substantial numbers of calculations were performed manually. Method detection limits ranged from 1 to 100 parts-per-billion, roughly 100 times higher than current limits. Organic analytical methods were just starting to be developed to determine pesticides and other organic contaminants.

Chemists from the NWQL and the National Research Program developed methods for laboratory use. NWQL's Method Research and Development Program wasn't started until the mid-1980s.

● JOHN GARBARINO
[Garbarino is a research chemist in the Methods Development and Research Program]



"Blue Carpet Area" in the old Central Laboratory, the hub for analytical work.

Erdmann, Fishman first occupants of National Lab on Ward Road

I think that 30 years have pretty well blotted out of my mind most of the things that happened in the early stages of the NWQL.

Considerable enthusiasm accompanied the decision to build a National Water Quality Laboratory. As I remember, LeRoy Schroder had primary USGS responsibility for monitoring the progress of building construction. Russell McAvoy and Art Beetem also had considerable input in this area.

Marv Fishman and I were the first occupants of this laboratory thanks to a fire in building 25 on the Federal Center. As a result of the fire, our laboratory space in building 25 was uninhabitable, and so we moved to the NWQL in March 1976.

The building was far from finished. There was no mail delivery, and the telephones, although installed, did not ring. A light did flash on the phone set. One would answer

the phone only in the unlikely event the flashing light was noticed. Needless to say, it was very quiet in those early days unless construction activities were taking place nearby.

"....no mail delivery and the telephones did not ring...."

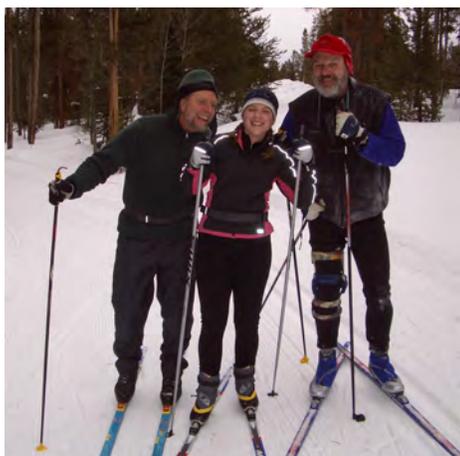
It was not unusual during the final construction phase to have Survey personnel assist in the unloading of large trucks containing laboratory furniture. The cooperation of everyone involved in these activities was excellent and was helpful in completing the laboratory.

The NWQL was pretty well occupied during the summer of 1976. Although probably tempered somewhat by the passage of time, the process of getting the laboratory operational seemed to go quite smoothly.

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There were, however, a couple of memorable exceptions. The fume hoods would funnel untempered air into the laboratory. Consequently, on cold days, reagent solutions in the hoods would freeze and working near them could be a bone-chilling experience. False fire alarms occurred frequently and with considerable disruption. In the overall scheme of things, these were relatively minor problems that were resolved over time.

• DAVID E. ERDMANN



STAYING IN SHAPE—Charles Patton and Edward Furlong, research chemists, serve as bookends for Sara, Patton’s daughter, at a December 30th outing at Snow Mountain Ranch, near Granby, Colorado. Actually, Sara, a high school senior, not only holds her own on the racing-style Nordic skis, but managed to outperform the two older men!

“The old Central Laboratory had come of age”

When I joined the USGS, the main management focus of the water-quality laboratories in Water Resources either was directed at district or project laboratories, whereas Geology had a group known as A-Labs (analytical laboratories) primarily in Denver and in Menlo Park.

I admired the Geology approach because my study areas encompassed parts of several states that allowed me to use a methods development laboratory in Denver but often required the use of a few smaller laboratories. As a result, our project staff frequently interpreted the results for the same analyte determined in different laboratories that might have used different techniques at different levels of quality control.

My complaints didn’t fall on deaf ears. I received a call informing me that I was to combine several district and project laboratories into a unit to be housed in Denver. Russell McAvoy, who was to become Chief of the new Central Laboratory, and I arranged to build a state-of-the-art laboratory in the Denver area that would house the new Denver unit and the Central Laboratory. The new laboratory would ultimately be known as the National Water Quality Laboratory.

Frankly, the physical structure that was built in 1975 and 1976 was obsolete compared to the laboratories built in the United States even a decade ago, but we were proud that preserved water samples were being sent to a single laboratory with defined quality control using modern analytical techniques. The old Central Laboratory had come of age.

Instrumental chemists and technicians were operating the analytical instruments on a full-time basis without having project responsibility. Instruments, such as inductively coupled plasma spectrometers and mass spectrometers coupled to gas chromatographs, were no longer available only for research purposes but were supplying the Water Resources projects with quality information and timely data at a fair price. Our goals had been reached.

The National Water Quality Laboratory is now 30 years young and is housed in a modern facility. Instrumental chemists and technicians are still providing quality determinations at a fair price using state-of-the-art analytical instruments and increasing the Nation’s knowledge of water quality.

• LEROY J. SCHRODER

“Time to send those separatory funnels to the dumpster”

I came to the Central Laboratory in March 1977, so I missed out on the new lab festivities, but there was still a substantial backlog of samples in the organics analytical lab resulting from the relocation to the new building, and the sample income was starting to pick up for the season.

The new Central Laboratory came about from the consolidation of USGS labs in Salt Lake City, Utah, Austin, Tex., Albany, N.Y., and probably oth-

ers; in fact, people were still arriving from the closure of the Albany lab after I arrived. I was surprised to be assigned to gas chromatographic (GC) analyses as soon as I hit the door. I had expected to be washing the dishes or preparing samples for a while; I had no idea what was actually going on at the lab.

I was very impressed with the level of computerization at the time, probably because I had very little prior

exposure to computers. There was a central Hewlett-Packard computer for processing GC data — no personal computers — they didn’t come around until the late 1980s. The operating system software was loaded using a paper tape reader, and home-grown BASIC programs were used for some of the data processing.

Reports came out on thermal line printers, and results were transcribed

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to paper reports, which were manually entered into the data system. We did manual injections on packed-column GCs and watched the GC signals come out on analog strip-chart recorders. The first autoinjector-equipped GCs and hard drive-based computers (with a 10 megabyte removable platter as big as a dinner plate) came around in the early 1980s. Some of the staffers said they were concerned they might lose their jobs to all that automation.

I installed the first fused silica capillary column in a GC/MS in 1981. Water samples were extracted using separatory funnels, which required quite a bit of labor relative to the current solid-phase extraction methods. Note, however, that 30 years later, we are still doing the same old separatory funnel methods for some analyses, albeit in substantially reduced quantities. It's time to get out of the stone age and send the separatory funnels to the dumpster!

Quality control (QC) was rudimentary—just a 2-point calibration curve and a blank were analyzed with each set of 10 samples. Reporting levels were a figment of someone's imagination (some would say they still are, but it's a much better figment), and control limits were nonexistent because there were no spikes, surrogates, continuing calibration verification solutions, and internal standards.

I recall now that there were also no standard operating procedures, log-books, demonstration of capability, e-mail, Internet, National Environmental Laboratory Accreditation Conference (NELAC), word processors, and Quality Management System. Safety awareness and waste management also were very primitive relative to the present. Simpler but not necessarily better times.

● **MIKE SCHROEDER**

[Schroeder supervises the Liquid Chromatography/Sediments Unit]

DISTINGUISHED VISITOR—Marv Fishman visited the Laboratory in December to meet with friends and colleagues. The long-time USGS chemist, research chemist, and supervisory hydrologist retired in November 1990. Marv and his wife Florine spend a lot of time traveling to far-away places.



Marv Fishman recalls early years, excitement

I recall a few problems with equipment in those early years. Two that come to mind are the fire alarm system and the exhaust hoods.

I was working with LeRoy Schroder in one of the quality-control laboratories when Russell McAvoy, the Lab Chief, walked in and said he had been looking for us and asked why we didn't leave the building. A fire alarm had sounded. Of course, we heard no alarm because they simply didn't work throughout the laboratory.

Exhaust hoods were a problem, too. They drew in outside air. An incident in 1976–77 was memorable. We were in need of acetic acid and had stored a bottle in the hood. One of us picked up the bottle of acetic acid and before our eyes, the acid crystallized.

Unofficially, the Central Laboratory was occupied in April 1976, while it was still under construction, because of a fire in building 25 at the Denver Federal Center, which destroyed the methods development laboratory and Standard Reference Water Sample Program. The construction company working on the new Central Lab hurried to finish two laboratories and offices. Marv Fishman and Dave Erdmann took the remaining files and equipment a week after the fire and moved into the partially completed Central Laboratory.

Needless to say, it was difficult to operate in the new building because we had no telephones and mail service. Included in the early move was LeRoy Schroder, who was supervising the construction. The three of us made daily trips to the Federal Center to pick up mail, telephone messages, and other documents. By late May 1976, the methods development project and Reference Sample Program were back in operation with new equipment in the Central Laboratory.

● **MARV FISHMAN**



PHOTOS WORTH A THOUSAND

WORDS—Carmen Reed-Parker, chemist, helps to install prints for the latest NWQL photo exhibit. The March/April theme is “Around the Laboratory and the Denver Federal Center.” The photography club has been active for 3 years. Visitors are invited to check out the photo gallery just inside the front entrance, main corridor, in building 95. The photo club web site can be accessed at URL <http://www.lablens.net>.

News briefs

Environmental Science & Technology Online News reports that the most-accessed article from January–June 2005 was Kolpin, D.W., **Furlong, E.T.**, Meyer, M.T., Thurman, E.M., **Zaugg, S.D.**, Barber, L.B., and Buxton, H.T., 2002, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: A national reconnaissance: *Environmental Science & Technology*, v. 36, no. 6, p. 1202–1211.

* * *

The NWQL Reference Library in building 95 has been relocated to room 1407 (just across the hall from the former records office). Feel free to peruse the books, periodicals, and other publications and return them when finished.

* * *

Bob Eganhouse, research chemist in the Branch of Regional Research, will present an informal seminar at 11 a.m. Friday, April 7, in NWQL's main conference room. Topic: Progress with the gas chromatography by gas chromatography/time-of-flight mass spectrometry on the nonylphenols and the Hurricane Katrina Sediment Project.



LABORATORY CONTRACTOR—Julie Ray, laboratory technician, sets up distillation apparatus to prepare for analyzing phenol samples. Phenols are hydroxy (OH) benzenes. The NWQL phenols method measures the aggregate concentration of most substituted phenols.

New publications

(NWQL authors in **boldface**)

Reports

Garbarino, J.R., Kanagy, L.K., and Cree, M.E., 2006, Determination of elements in natural-water, biota, sediment, and soil samples using collision/reaction cell inductively coupled plasma—mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, section B, chap. 1, 88 p. Available online at URL <http://pubs.water.usgs.gov/tm5b1/>

Sando, S.K., **Furlong, E.T., Gray, J.L.**, Meyer, M.T., and Bartholomay, R.C., 2005, Occurrence of organic wastewater compounds in wastewater effluent and the Big Sioux River in the Upper Big Sioux River Basin, South Dakota, 2003–2004: U.S. Geological Survey Scientific Investigations Report 2005-5249, 108 p.

Journal Articles

Barber, L.B., Murphy, S.F., Verplanck, P.L., **Sandstrom, M.W.**, Taylor, H.E., and **Furlong, E.T.**, 2006, Chemical loading into surface water using a hydrological, biogeochemical, and land use gradient: A holistic watershed approach: *Environmental Science & Technology*, v. 40, p. 475–486.

Kolpin, D.W., Thurman, E.M., Lee, E.A., Meyer, M.T., **Furlong, E.T.**, and Glassmeyer, S.T., 2006, Urban contributions of glyphosate and its degradate AMPA to streams in the United States: *Science of the Total Environment*, v. 354, p. 191–197.

Patton, C.J., 2006, Autonomous environmental water quality monitoring—The future of continuous flow analysis: *Environmental Chemistry*, v. 3, p. 1 and 2.

Nutrients Unit replaces instruments for determining ammonium, nitrite, and orthophosphate

This month, instruments for standard- and low-level dissolved ammonium, nitrite, and orthophosphate in the NWQL Nutrients Unit will change from automated continuous flow (CF) analyzers to automated discrete analyzers (DA). Time-honored USGS colorimetric chemistries for these analytes are the same on CF and DA platforms, so USGS method numbers and National Water Information System (NWIS) parameter codes will not change.

As listed in table 1, new NWQL lab codes and NWIS method codes have been assigned as historical markers of this instrument change. When determinations of these analytes are changed over to the DA platform, their lab and method codes will be activated in the NWQL Laboratory Information Management System (LIMS) as direct replacements for the corresponding CF platform lab and method codes. Existing schedules will be updated automatically to reflect these changes.

A single DA analyzer is replacing two CF analyzer systems that are designated the '4-channel' and 'low-level 4-channel' analyzers in the Nutrients Unit. It is noteworthy that the higher level of automation inherent in DA technology eliminates the need for sample submitters to choose between standard- and low-level methods for these three analytes.

Here's why: Based on statistical analysis of NWQL analytical results in 2004, 95 percent of ammonium concentrations (> 16,000 standard- and low-level results), 99 percent of nitrite concentrations (> 14,000 standard- and low-level results), and 90 percent of orthophosphate concentrations (> 16,000 standard- and low-level

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results) had concentrations less than or equal to 0.8 mg-N/L, 0.2 mg-N/L, and 0.2 mg-P/L, respectively.

During method development, NWQL chemists selected analytical ranges for DA tests that were consistent with these concentration distributions (see table 2, 4th column). In table 2, the lower number in each range indicates current (2006) NWQL laboratory reporting levels for CF methods and lowest calibrant for DA methods. During operation, DA software automatically accepts test results that fall within initial calibration ranges and flags the small fraction that does not. All out-of-range samples are automatically diluted 1+4 and reanalyzed (table 2, 5th column). The same 2004 statistics predict that after automatic 1+4 dilution, no nitrite tests, and only 1 and 5 percent of ammonium and orthophosphate tests should be out of range. Thus the DA handles about 95 percent of the 4-channel and low-level 4-channel analyzer workload in a single pass without operator intervention.

If the 1+4 dilution fails to bring a test result into calibration range, then DA software again flags the sample

and prompts the operator to enter a larger dilution factor—up to 1+119. After the operator enters a new dilution factor, the out-of-range sample is diluted accordingly and reanalyzed automatically. Any sample requiring greater than 1+119 dilution ($\text{NH}_4^+\text{-N} > 96 \text{ mg/L}$, $\text{NO}_2^-\text{-N} > 24 \text{ mg/L}$, or $\text{PO}_4^{3-}\text{-P} > 24 \text{ mg/L}$ —rare for samples received at the NWQL) would require manual dilution.

The three graphs that follow (figs. 1–3) show operational efficiencies achieved by the dynamic-concentration-range DA and the fixed-concentration-range, 4-channel CF analyzer for each analyte during validation experiments last August at the NWQL. In each graph, analytical results obtained with the DA (y-axis) are plotted as a function of analytical results obtained with the 4-channel CF analyzer (x-axis). Note first that despite a few obvious outliers, analytical results obtained by the CF and DA instruments are statistically equivalent (see linear regression parameters on each graph). Shaded zones around regression lines in these graphs indicate samples requiring operator intervention to complete analyses.

Results obtained for these analytes by the DA and low-level, 4-channel CF analyzers (not provided here) also are statistically equivalent. Discussions that follow pertain to standard-level, 4-channel CF and DA results only.

In the case of ammonium (fig. 1), about 91 percent of results (1,645 out of 1,812 data pairs) were within the DA initial concentration range and therefore would have been reported at levels 4 times lower than 4-channel CF analyzer results. Of the remaining 167 data pairs, 122 came into range after automatic 1+4 dilution by the DA without operator intervention. Only 45 data pairs (less than 3 percent of all results) had concentrations greater than 4 mg-N/L, which required operator entry of larger dilution factors to complete analyses. None required manual dilution. About 5 percent of results exceeded the 1.5 mg-N/L analytical range of the CF analyzer, all of which required manual dilution and reanalysis, sometimes in a subsequent batch of samples.

In the case of nitrite (fig. 2), about 98 percent of results (1,932 out of 1,964 data pairs) were within the DA

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Table 1. New lab and method codes assigned for instrument change in Nutrients Unit.

| Analyte as N or P | NWIS parameter code | Method analytical range | USGS method number | Analyzer type | | | |
|--------------------|---------------------|-------------------------|--------------------|-----------------|------------------|---------------|------------------|
| | | | | Continuous flow | | Discrete | |
| | | | | NWQL lab code | NWIS method code | NWQL lab code | NWIS method code |
| NH_4^+ | 00608 | Standard | I-2522-90 | 1976 | F | 3116 | J |
| | | Low | I-2525-89 | 1980 | H | | |
| NO_2^- | 00613 | Standard | I-2540-90 | 1973 | F | 3117 | I |
| | | Low | I-2542-89 | 1977 | H | | |
| PO_4^{3-} | 00671 | Standard | I-2601-90 | 1974 | H | 3118 | L |
| | | Low | I-2606-89 | 1978 | I | | |

Table 2. Concentration ranges for the analytes for the old and new analyzer instruments.

| Analyte | Concentration range (mg-N/L or mg-P/L) | | | |
|-------------------------|--|----------------|-------------------|-------------------|
| | 4-Channel CF analyzer | | Discrete analyzer | |
| | Low-level | Standard-level | Initial | 1+4 Auto dilution |
| NH_4^+ as N | 0.010 – 0.300 | 0.04 – 1.50 | 0.010 – 0.800 | 0.05 - 4.00 |
| NO_2^- as N | 0.002 – 0.200 | 0.008 – 1.00 | 0.002 – 0.200 | 0.01 - 1.00 |
| PO_4^{3-} as P | 0.006 – 0.200 | 0.018 – 1.00 | 0.002 – 0.200 | 0.01 - 1.00 |

initial concentration range and therefore would have been reported at levels 5 times lower than 4-channel CF analyzer results. The amount of rework (only 2 samples) on the 4-channel CF analyzer was minimal, but clearly analysis on the low-level, 4-channel CF analyzer would have been more appropriate for these samples.

In the case of orthophosphate (fig. 3), about 89 percent of results (1,028 out of 1,154 data pairs) were within the DA initial concentration range and therefore would have been reported at levels 5 times lower than 4-channel CF analyzer results. About 4 percent of all results required operator entry of larger dilution factors or manual dilution to complete analyses on the DA and CF platforms, respectively.

For the next few months, the Nutrients Unit will continue to determine standard- and low-level nitrate + nitrite (lab codes 1975 and 1979) by the CF analyzer methods. Determining nitrate by DA requires new method approval because soluble nitrate reductase has replaced toxic, granular cadmium that is used to reduce nitrate to nitrite in currently (2006) approved USGS and U.S. Environmental Protection Agency CF methods. Colorimetric reagents for CF and DA nitrate methods are identical. Over the past several years, the NWQL has expended considerable resources characterizing nitrate reductases as nontoxic replacements for cadmium and validating two commercially available types, YNaR1 and AtNaR2, as effective replacements for cadmium in manual, CF, and DA nitrate determination methods.

Validation experiments are now finished and method reports are near completion. Contingent on positive reviews, Office of Water Quality (OWQ) approval for nitrate reductase CF and DA nitrate methods is anticipated in June, at which time the Nutrients Unit will begin using DA nitrate methods routinely. The NWIS parameter code for enzymatic nitrate determination is unchanged, but new NWIS method codes and NWQL lab codes have been assigned (table 3).

After this method change, the NWQL LIMS system will automatically convert any requests for standard- and low-level nitrate tests by former lab codes—individually or within existing schedules—into lab code requests for DA tests. Note that the statistical concentration distribution of samples received at the NWQL for nitrate analysis is not amenable to combining standard- and

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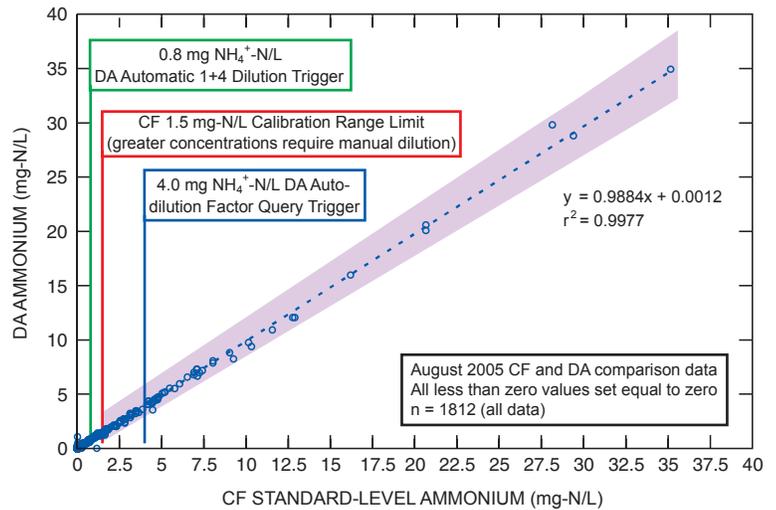


Figure 1.

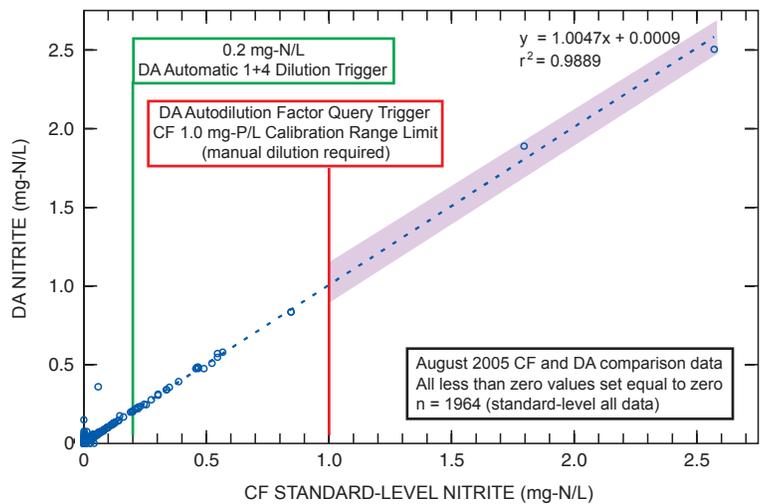


Figure 2.

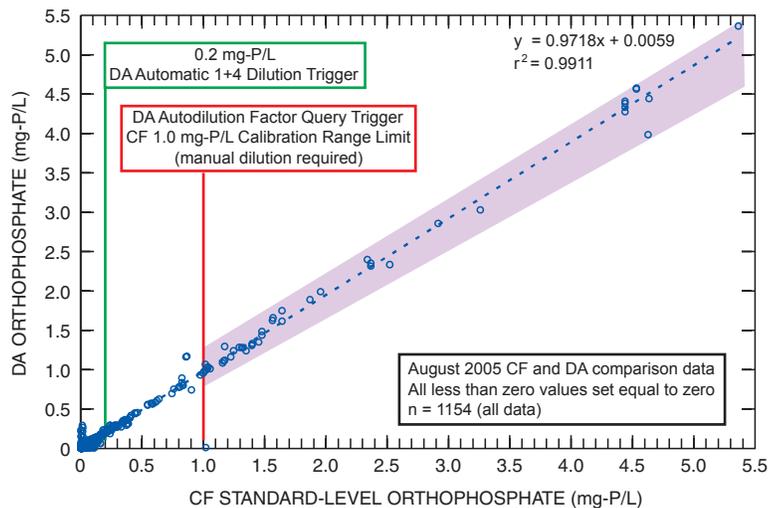


Figure 3.

low-level CF methods into a single DA method as was done with the other three 4-channel CF nutrient methods. Sample submitters, therefore, must continue to choose between the standard- and low-level nitrate methods.

As listed in table 4, DA software automatically accepts results that fall within the standard-level nitrate method initial concentration range and flags the small fraction that falls outside the range for automatic 1+4 dilution and reanalysis. Any low-level nitrate results that exceed the initial concentration range, however, are flagged by DA software and automatically reanalyzed by the standard-level method (*reflexing* in DA terminology). Interim method detection limits for the standard- and low-level methods correspond to the lower value of tabulated initial concentration ranges.

As was the case for nitrate determinations by the low-level, cadmium reduction CF method, the Nutrients Unit urges sample submitters to choose the low-level, enzymatic reduction DA method only for samples likely to contain less than 1 mg $\text{NO}_3^- + \text{NO}_2^-$ -N/L and then only when their data-quality objectives demand the lower reporting limit. Statistical analysis of results for about 5,000 samples submitted to the NWQL for low-level nitrate analysis in 2004 suggests that customers follow this guidance, because less than 2 percent of reported concentrations were out of range.

Basic operation and modular components of a discrete analyzer are shown in figure 4.

The total volume of nutrient tests—sample + reagents—on the NWQL’s DA is about 150 μL (3 drops!), 10 times less than the volume of the same test on a typical CF analyzer. Savings in reagent costs and decrease in analytical waste, therefore, will be substantial. The tiny amounts of sample required for DA analysis of dissolved nutrients would permit dissolved nutrient samples to be collected in 10-mL evacuated tubes (sample containers of

choice for clinical diagnostic testing for years). This possibility, which the OWQ and NWQL are currently investigating, would make dissolved nutrient sample collection faster, easier, and cleaner and also would reduce shipping costs and NWQL refrigerated storage space requirements by a factor of 10.

Nominal analysis rates of NWQL’s DA is 600 tests per hour, about a

third faster than the 4-channel CF analyzers. In addition, barcode readers and software built into most DAs that can link test requests resident in LIMS to barcode ID labels on sample containers provide levels of automation not found in previous generation environmental laboratory instruments. Potential efficiencies of operation for Water Science Centers and the NWQL made possible by DA technology are substantial.

• CHARLES PATTON

Table 3. New codes for enzymatic nitrate determination.

| Analyte | USGS method number | NWIS parameter code | NWIS method code | | NWQL lab code | |
|------------------------------------|--------------------|---------------------|------------------|-----------|----------------|-----------|
| | | | Standard-level | Low-level | Standard-level | Low-level |
| $\text{NO}_3^- + \text{NO}_2^-$ -N | Pending | 00631 | J | K | 3156 | 3157 |

Table 4. Standard- and low-level concentration ranges for nitrate.

| Analyte | Concentration range (mg-N/L) | |
|--|------------------------------|---|
| | Initial | Automatic dilution (1+4) |
| $\text{NO}_3^- + \text{NO}_2^-$ as N (standard) | 0.05 – 5.00 | 0.25 – 25.0 |
| $\text{NO}_3^- + \text{NO}_2^-$ as N (low-level) | 0.01 – 1.00 | (<i>reflex</i> to standard level test) |

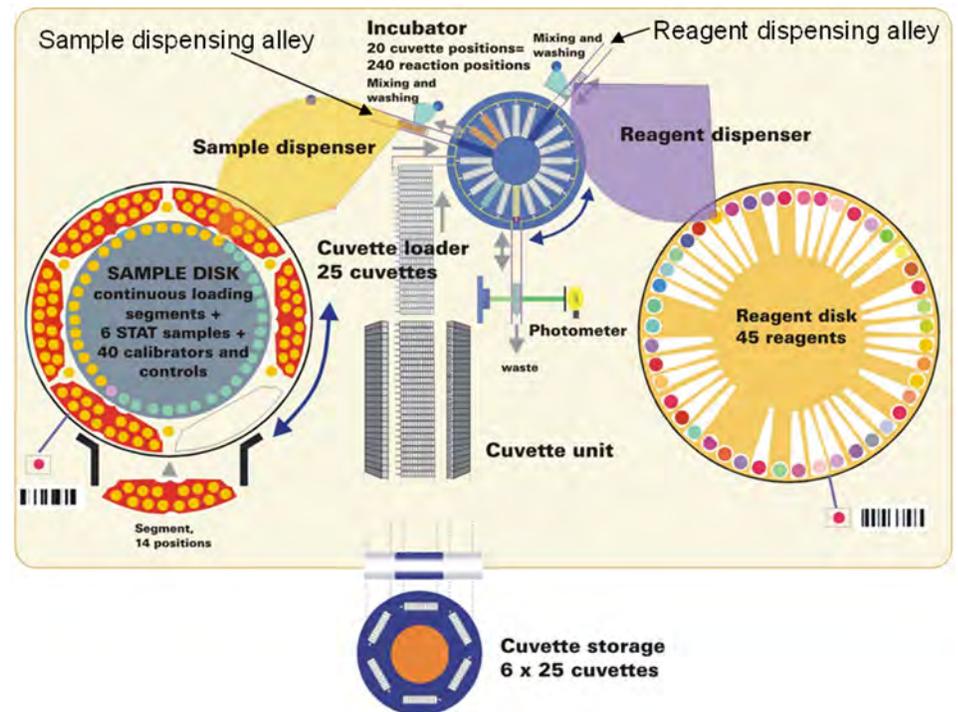


Figure 4. Basic operation and modular components of an automated discrete analyzer.

Note: see page 11 for photo of discrete analyzer team.

Frequently asked questions

New analytical method for elemental analysis using collision/reaction cell inductively coupled plasma–mass spectrometry reduces molecular ion interference

What does the new method offer?

The elements As, Co, Cr, Cu, Ni, Se, V, and Zn in filtered water and digestates of unfiltered water, biota, sediment, and soil are determined using collision/reaction cell inductively coupled plasma–mass spectrometry (cICP–MS). Other elements, such as Ca, Fe, K, Mg, Na, Si (as SiO₂), and W that were not determined routinely by earlier ICP–MS methods, have been added. In addition, arsenic species can be determined using high-performance liquid chromatography for separation and cICP–MS for detection.

Elements that were determined in earlier ICP–MS methods and are unaffected by molecular ion interference also are determined by cICP–MS by not introducing hydrogen or helium into the gas cell.

New laboratory and parameter codes are not required for Ag, Al, B, Ba, Be, Cd, Li, Mn, Mo, Pb, Sb, Sr, Tl, and U because the plasma conditions, acquisition characteristics, and analytical performance for these elements are not so different from earlier ICP–MS methods that did not use reaction/collision cell technology.

What are the features of the new method? Most method detection limits are lower or relatively unchanged compared to earlier methods except for Co, K, Mg, Ni, Si, and Tl, which are less than a factor of 2 higher.

Molecular ion interferences are greatly reduced or eliminated by using collision/reaction cell technology without the need of correction equations. He or H₂ is introduced into the cell during data acquisition for the elements that are affected by molecular ion interferences and purged from the cell for other elements.

How are data calculated and reported? The operating system calculates analyte concentrations automatically from linear regression equations, monitors results for samples for quality control and quality assurance in real time, and updates calibration whenever acceptance criteria fail. Sample carryover is minimized by automatically increasing the length of the rinse cycle until an analyte signal reaches an acceptable level.

Results for water samples are reported in either micrograms (µg) or milligrams (mg) per liter (L), depending on the element. Elemental results for biota, sediment, and soil digestates are reported in µg or mg per gram (g), dry weight, depending on the element. All arsenic species are reported in µg As/L.

What are the new method numbers, and laboratory and parameter codes? For elemental analyses, the U.S. Geological Survey (USGS) method number is I-2020-05 for filtered water, I-4020-05 for unfiltered water, I-9020-05 for biota, and I-5020-05 for sediment and soil. The method number for arsenic species is I-2197-05 by field separation, I-2196-05 by lab separation using malonate/acetate, I-2195-05 by lab separation using phosphate, and I-2193-05 by lab separation using nitric acid.

The lab and parameter codes, reporting limits, units, and sample containers are available on the NWQL USGS-visible web site at http://www.nwql.cr.usgs.gov/USGS/USGS_gen.html. Select LIMS Catalog in the upper right corner. Search by analyte name (for example, cobalt) to retrieve the above information. The determination of Ca, Fe, K, Mg, Na, or Si using cICP–MS is by special request.

What procedures are required for shipping samples to the NWQL?

Samples are collected and preserved using the protocols outlined in the

USGS national field manual for the collection of water-quality data (U.S. Geological Survey, variously dated).

Ship samples by overnight carrier to the NWQL as soon as possible after collection. Special handling is required for biological samples (must be shipped frozen on dry ice) and sediment and soil samples (must be shipped on ice).

May any Water Science Center use the new methods? Yes. The Office of Water Quality approved the new water quality analytical method for the determination of elements in filtered water, unfiltered water, biota, sediment, and soil by cICP–MS on 3 November 2005.

How do I obtain a copy of the new methods? A copy of the report by Garbarino and others (2006) may be downloaded from URL <http://pubs.water.usgs.gov/tm5b1/>, or requested by E-mail to the NWQL Technical Editor (jwraese@usgs.gov) or LabHelp@usgs.gov, or by calling 1-866-ASK-NWQL.

References

- Garbarino, J.R., Kanagy, L.K., and Cree, M.E., 2006, Determination of elements in natural-water, biota, sediment, and soil samples using collision/reaction cell inductively coupled plasma–mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, sec. B, chap. 1, 88 p.
- U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–5 and A5.6.4, accessed 6 September 2005, at URL <http://water.usgs.gov/owq/FieldManual>

• JOHN GARBARINO and
ALLISON BRIGHAM



FUN WITH MAGIC MARKERS—Hobbies are supposed to provide enjoyment and creativity. Such is the case with Brooke Connor, chemist in the Branch of Quality Systems, whose whimsical pen-and-ink drawings were on display at an open house last month at Reed Photo-Art Gallery and Imaging, in Denver. She is shown with a piece called “Fish in the Headlights.” Brooke mixes her imagination with pastels and colorful ink to create delightful images on archival watercolor paper. The technique is called *giclee* (zhee-CLAY), a high-resolution, high-fidelity reproduction on a special large format printer. Giclees are produced from digital scans of existing artwork.



DISCRETE ANALYZER TEAM—Team members (left to right) Jennifer Kryskalla, chemist; Colleen Gupta, chemist; Charles Patton, research chemist and team leader; Burt Johnson, information technology specialist; and Harold Ardourel, supervisor, Nutrients Unit, take a moment to pose next to the automated discrete analyzer with Robert Green, chief, Methods Research and Development Program and Greg Mohrman, chief, NWQL. The discrete analyzer is replacing automated continuous flow analyzers long used to determine dissolved ammonium, nitrite, and orthophosphate at the NWQL.

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