Title: Determination of Nitrogen by Flow Injection Analysis in Environmental and Wastewaters

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DETERMINATION OF NITROGEN BY FLOW INJECTION ANALYSIS IN ENVIRONMENTAL AND WASTEWATERS

1. Begin by describing where I work and the types of samples we analyze.

SLIDE 1 – LANL
1. Chemical analyst at LANL in North Central NM for 14 yrs.
2. The original mission of Los Alamos was development of nuclear weapons.
3. Recently work at the Lab is not just weapons work but is a mixture of research and development in many different fields including biochemistry, nuclear medicine, thermal fusion, lasers, industrial hygiene, geothermal energy, radioactive and hazardous waste treatment, and environmental science.
4. Lab occupies at least 50 tech and extends over 43 sq miles of terrain much of it mesas and canyons.
5. Chemical wastewater from the technical sites is collected and treated at a central radioactive liquid waste facility which is also the location of the lab in which I work.

SLIDE 2 LRW
6. Most of these scattered sites are connected to the chemical wastewater plant directly by a network of double-walled pipes (This wastewater is isolated from the sanitary sewage system because of its chemical and radioactive content). Valves and sensors are controlled and monitored by computer systems also located at our facility. The plant treats over 5 million gallons of wastewater a year. A typical working day might produce as much as 15,000 gals. of influent to be treated.
7. Member of the inorganic analytical team which (as part of our total capability) performs a variety of manual and automated wet chemistries.
8. A significant part of our workload is from plant operations - the influent samples (waste coming into the plant for treatment) - and effluent samples (outflow after the treatment processes).
9. Main stream of liquid rad waste is presently treated by a conventional coagulation process using Fe2(SO4)3 and lime Ca(OH)2 followed by filtration.
10. In the next 2 yrs several major upgrades are planned using tubular ultrafiltration & reverse osmosis.
11. Another major upgrade is in the works to reduce high levels of nitrate, which until now have not been adequately treated. We have seen on occasion effluent NO3-N levels at several hundred ppm which exceeds NM ground water standards of 10 ppm. The new process will be EDR –electrodialysis reversal an electrolytic process that reduces the NO3-N to N2 gas – which is released to atmosphere.
12. On-line analysis of waste has recently begun using Ion Chromatography, but off-line more comprehensive analysis at concentrations of < 1 ppm, are done routinely (for purposes of documentation and compliance) on composite samples – i.e. small samples that represent inflow and outflow to the facility.

13. Composite samples each day are made up by sampling aliquots of both the influent and the treated effluent which are proportional to the amount of waste measured flowing in and out for that day. Mixed together in the correct proportions, they are representative samples of the total waste treated. The composites are preserved, stored and analyzed in batches along with water samples we run from other outside processes and projects.

SLIDE 3 – TYPICAL SAMPLE TYPES

The treatment plant influent is dilute radioactive waste containing Pu, U, and Am typically in the nCi or pCi/l range.

OTHER SAMPLE TYPES ARE:

EFFLUENT - CENTRAL SANITARY WASTEWATER TREATMENT PLANT
ENVIRONMENTAL SURFACE WATERS - STREAMS, LAKES, SPRINGS, ARROYOS, etc

WELLS AND DRINKING WATERS – nearby communities including a number of neighboring Indian pueblos

SPILL IDENTIFICATION - spills occurring on lab sites

NPDES SAMPLES – PROGRAM OF TESTING MANDATED BY EPA PERMIT FOR OUTFALLS under CWA

Protocol for handling, analysis and reporting has to be closely followed.

SLIDE 4 N SPECIES AS POLLUTANTS

14. N in its various oxidation states is continually recycled in balanced ecosystems. Elemental N2 gas makes up 80% of the atmosphere and in several forms is a vital nutrient essential to all living things. But in excess, N compounds are major pollutants.

15. Here are listed the most common forms of nitrogen listed by increasing oxidation state, some major sources of pollution for each and the resulting environmental effects.
NH3-N and organic pollution from fertilizer, sewage and other biological waste can deplete oxygen in water resulting in overgrowth of microorganisms and stagnant conditions.

Nitrates and nitrates from fertilizer and industrial wastes are toxic or carcinogenic.

<table>
<thead>
<tr>
<th>N SPECIES</th>
<th>SOURCES</th>
<th>EFFECT</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH3-N &amp; organic N</td>
<td>Fertilizers, sewage</td>
<td>Overgrowth of algae, bacteria, etc.</td>
</tr>
<tr>
<td></td>
<td>Decayed organic matter</td>
<td>O2 depletion in water</td>
</tr>
<tr>
<td></td>
<td>Industrial wastes</td>
<td></td>
</tr>
<tr>
<td>NO2-N</td>
<td>Industrial corrosion inhibitor</td>
<td>Toxic, Carcinogenic, Methemoglobinemia</td>
</tr>
<tr>
<td>NO3-N</td>
<td>Fertilizers</td>
<td>Toxic, carcinogenic</td>
</tr>
<tr>
<td></td>
<td>Industrial waste</td>
<td></td>
</tr>
</tbody>
</table>

16. All samples for N are presently analyzed by FIA. Starting in 1985 we have used three different systems, all from Lachat Instruments. Presently we have the Quikchem AE system and for last 1 ½ yr the newer QuikChem 8000.

17. The methods for nitrogen we run now are listed here along with the EPA method number, the type of method, and our present detection limits.

<table>
<thead>
<tr>
<th>SLIDE 5-METHODS</th>
<th>ANALYTE</th>
<th>EPA #</th>
<th>METHOD</th>
<th>MIN DETECTION LIMITS (MG/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH3-N</td>
<td>350.1</td>
<td>Alkaline phenol</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>NO2-N</td>
<td>353.2</td>
<td>Diazo colorimetric</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>NO3-N</td>
<td>353.2</td>
<td>Diazocolorimetric with online</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cd reduction</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TKN</td>
<td>351.2</td>
<td>Salicylate-nitroprusside</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>(Total Kjeldahl N)</td>
<td></td>
<td>Block digestion</td>
<td></td>
</tr>
</tbody>
</table>
18. We have a great variety of sample loads and types, some of which we can anticipate, others with higher or lower levels of priority which we fit into the workload according to what the customer requires. So flexibility of flow injection instrumentation is important.

**FIA**

**SLIDE 6  FIA PHOTO**

19. This is the QuikChem 8000 system with a Cetac XYZ sampler at the left.

20. The 4 N methods we use are run individually (although the system can be run with up to 8 different channels each running a different method).

21. All are linear colorimetric chemistries measuring a colored species directly proportional to the analyte.

**SLIDE 7  FIA DIAGRAM**

22. The FIA process is based on the precise injection of a specific amount of liquid sample into a moving non-segmented carrier stream that matches the matrix of the sample (some other continuous-flow analyzers use carriers streams segmented by air or gas bubbles).

23. The injection of sample is followed by addition of reagents, mixing within coiled tubing, in some cases a heating step, and finally detection of color absorbance in a flow cell at a specific wavelength of light determined by the interference filter used.

24. Analysis time or the time to read results for each sample is typically < 60 sec.

25. In order to operate at this speed and put out results with the highest accuracy each std and sample has to be measured at the same relative point in the reaction (measuring at the completion of the reaction would require much longer analysis time).

26. Two factors are extremely important—

   precision of the volume of sample injected which is determined by the length of the fine-bore tubing of the sample loop

   and the precise time in the reaction at which the absorbance detection is made. (or the # of secs from injection to the start of the peak).

27. Timing parameters are setup by the analyst & are easily changed. It is easy, when method is first setup or changed, to time the flow of sample to key points in the system using dye (visible through the clear tubing) and a stop watch.
28. The two key components that have greatest effect on volume of sample and time of peak measurement are the injection valve and the proportioning pump.

SLIDE 8  VALVE
This shows a side view of the injection valve showing the 6 ports or connections where sample and carrier are directed to the system.

SLIDE 9  VALVE CONFIGS

29. The injection valve has two configurations resulting from the rotation of two grooved plates inside the valve.
In the load state slug of sample loaded into a sample loop. The length of loop varies with method and sensitivity required.
In the Inject state sample in the loop in redirected and injected onto the reaction manifold along with the carrier.

SLIDE 10  PUMP

30. The proportioning pump is the source of the continuous flow of liquid in the system and operates by the peristaltic action of rollers against compressed pump tubing.

31. The speed of the pump is adjustable and reproducible which is crucial for good results.

32. The pump moves the sample aspirated from the sampler, carrier solution, all the reagents, as well as the wash solution that cleans the sample probe between samples, and pushes out the waste out after reading in the flow cell.

33. The proportion of reagents is controlled by using flow-rated, color-coded pump tubing.

SLIDE 11  MANIFOLD

34. The reaction module or manifold is configured specifically for each method according to the reagents used, mixing steps, and in the case of NH3 and TKN heating step to accelerate the color reaction.

35. The heater is simply a heated metal core wrapped with the same tubing used throughout the system. The reaction mixture is heated at set temperature for the length of time it takes to flow through that particular length of tubing.
36. A single manifold is used for NO3-N and NO2-N methods. The color reaction involves only the reduced NO2-N form. So for the NO3-N method the NO3-N in the sample is first reduced by passing through a column containing Cd. The resulting NO2-N is then determined. So the NO3-N method always measures any pre-existing NO2-N as well. True NO3-N concentration then is the difference between the two methods. A virtual channel may be set up on the FIA 8000 to do the subtraction and report true NO3-N results.

SLIDE 13 - DETECTOR

37. The detector module consists of the light source, interference filter, flow cell and the photometric detector which converts the absorbance readings to units.

38. Peaks are displayed on the system monitor and within seconds integrated to give results as concentration in (mg/L).

39. Data from a set of 7 to 8 standards, of known concentration which have preceded the samples through the system, are used to calculate the calibration curve and its correlation coefficient.

SLIDE 14 PEAKS

40. The monitor shows peaks in real time and displays a runtime report. The analyst can print these out as well as customized reports of final results.

41. A useful feature is the ability to reanalyze the original data by changing integration parameters such as peak base width and peak threshold. The original data file is kept and may be retrieved later unchanged. This is important for keeping the integrity of the data.

42. There is also an option for exporting the data to a separate database or LIMS system interface.

SLIDE 15 ADVANTAGES OF FIA

III. **ADVANTAGES OF FIA – 8000**

To summarize some features of flow injection that have been important in our application---

43. Modular components do not require on site service. Each can be disconnected and shipped for repair.

44. Separate reaction manifolds for each analysis eliminate cross-contamination between chemistries.

45. Changeover times between methods are short - usually 10 to 20 min including washing out lines.
46. Small sample volume is required in most cases just several mL of filtered sample in sampler tube.

47. Results are done in 1-2 min from sampling.

48. High degree of sensitivity - ppb range.

49. QA performance has been good.
   QA samples such as blind qcs, duplicates, spike recoveries, and performance study results are routinely within prescribed limits.

50. Visually being able to follow flow through the system simplifies troubleshooting.

IV. RESEARCH WORK

51. FIA has been used extensively the last two years in research work into reducing the high levels of nitrates in chemical influent treated in the RLW facility - levels are high due to use of HN03 throughout the Lab.

52. An alternate process using bacteria to reduce nitrates has been studied, but implementing the bacterial process at a rad waste facility presents some problems - so an electrolytic process EDR to reduce nitrates has become the favored approach.

53. All 4 of FIA N methods have been useful in support of these projects. Besides accurate results, we need a quick analysis time, sometimes running 3 methods in a day on small amounts of sample at several different dilution levels.

IV. TKN

54. TKN has been needed on many of the high-NO3-N research samples tubes.

The TKN procedure using EPA method 351.2 is the most complex of the four procedures since it involves digestion prior to analysis. The new method using a new block digestor, also from Lachat, with the capacity to digest up to 46 samples, has been a big improvement over the old open tube digestion.

SLIDE 16 DIGESTOR SLIDE

55. A digestion solution of H2SO4 containing Hg as a catalyst, under controlled conditions of time and high temperature, breaks down proteins and other biological matter to ammonium ion.

20 mL sample, standard, or QC sample added to each tube

Digestion solution of H2SO4, K2SO4 to elevate the boiling point, and HgO, as a catalyst, is added with boiling chips to control bumping

The block is set to 160 deg C and held at that temperature automatically 1 hr to boil off water.
At 1 hr special tops called “cold fingers” are placed in each tube. The
temperature steps up to 380 deg C for 90 mins more. During this time the
organic N is slowly converted to ammonium ion.

Cold fingers act as cool condensing surfaces and act as a pressure release
keeping the system at a constant atmospheric pressure. This is much more
controlled than the old Nessler open tube digestion and has given much more
consistent results.

At 90 mins the block shuts off, tubes are removed and 20 mL MP H20 is added
to bring the the solution back to original volume. After mixing the digestes may
be analyzed by FIA or held for later analysis since the matrix is acidic.

TKN colorimetric reactions measure the total concentration of any free NH3-N
in addition to the (NH4)2SO4 converted by the digestion from organic N
compounds. For the true concentration of just organic N, we can subtract the
result of the NH3-N method from TKN result.

45. For the most part, we have good consistent results from the method.

The determination of TKN in 8 EPA certified qc samples over a period of
4 months with a true value of 3.75 mg/L had a mean of 3.77 mg/l and a std dev
of 0.12 mg/L at the 1 sigma level. 8 samples spiked with 2.50 mg/L over 4
months had an average recovery of 109% and ranged from 102 to 118%.

46. But we have seen negative interference when high NO3-N concentrations,
usually when the NO3-N level is > 10 times TKN.

We see this effect in some of our treatment plant samples where spike
recoveries are quite low.

SUMMARY

47. In summary, three generations of Lachat FIA systems have been used in
our laboratory over a period of 13 yrs, running, in addition to the 4 N methods,
CR+6, SIO2, Fluoride by ISE. Overall flow injection systems have been
versatile and reliable and a good choice in our lab for analyzing a wide variety
of samples quickly.