On-Line Monitoring of Wastewater Using Ion Chromatography

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Abstract

Ion Chromatography (IC) has been used for the on-line determination of anions and cations in a variety of process streams. On-line monitoring of process and wastewater streams optimizes the control of treatment methods by providing early indications of problems that could increase discharges of hazardous compounds to the environment. It is important for the immediate detection and remediation of process upsets in critical streams. The waste flow to the Radioactive Liquid Waste Treatment Facility at the Los Alamos National Laboratory (LANL) is processed before discharge and requires monitoring. Process chromatography is used to monitor the trends of contaminants in real time. The purpose of this study is to develop an automated on-line IC procedure for the simultaneous determination of anions in LANL wastewater.

Introduction

Waste-management programs are occasionally concerned with the various compounds of nitrogen because of the effects that nitrogenous compounds could have on the environment. Trace quantities of nitrates are found in surface water, but high quantities of nitrates may be found in some groundwater. At the Los Alamos National Laboratory (LANL), a 10-mg/L nitrate as nitrogen has been imposed on groundwater. The use of nitric acid throughout the LANL complex produces the nitrates in the plant influent that is discharged to Mortendad Canyon. The extensive use of fertilizers and improper disposal of wastewater is the primary cause of the nitrate problem in New Mexico.

The Radioactive Liquid Waste Treatment Facility (RLWTF) treats industrial and radioactive liquid wastes that are generated at multiple research and production facilities across the LANL (Figure 1). This facility processes approximately 28,000 gal/day of wastewater. Waste is collected and treated to reduce radioactive contamination to levels that meet the limits specified in the National Pollutant Discharge Elimination System permit and Department of Energy orders. The permit is administered by the New Mexico Environmental Department and requires LANL to meet the groundwater limit for nitrates. The RLWTF performs chemical and physical separation processes in order to concentrate radioactive constituents in a sludge that is dehydrated to 30% solids. The solidified sludge (depending on radionuclide concentration) is either disposed of as low-level waste or stored as transuranic waste.

Experimental

Ion chromatography (IC) has been shown on a laboratory scale to be a reliable method for the determination of inorganic anions and cations in water and waste samples (1). The determination of common anions (chloride, fluoride, nitrite, nitrate, and sulfate) in real time is desirable in order to characterize or assess the need for a specific wastewater treatment method. IC provides a single instrumental technique for rapid sequential measurement and also eliminates the use of any hazardous reagents.

A wastewater sample was injected and then pumped through a resin-packed column along with an eluent. The eluent facilitates the separation of the sample ions in the column. The anions of interest were separated on the basis of their relative affinities for the resin. The separated anions flowed through a suppressor that selectively enhanced detection of the sample ions while suppressing the conductivity of the eluent. The conductivity of the sample ions was measured and identified on the basis of retention time as compared with standards.

Grab sampling (followed by laboratory analysis) has provided valuable information. However, the lag time between sampling and results is often too long to permit rapid operational decisions and troubleshooting on a plant-wide level. This type of sampling was impractical because of the labor and time required for sampling, analysis, data reporting, and

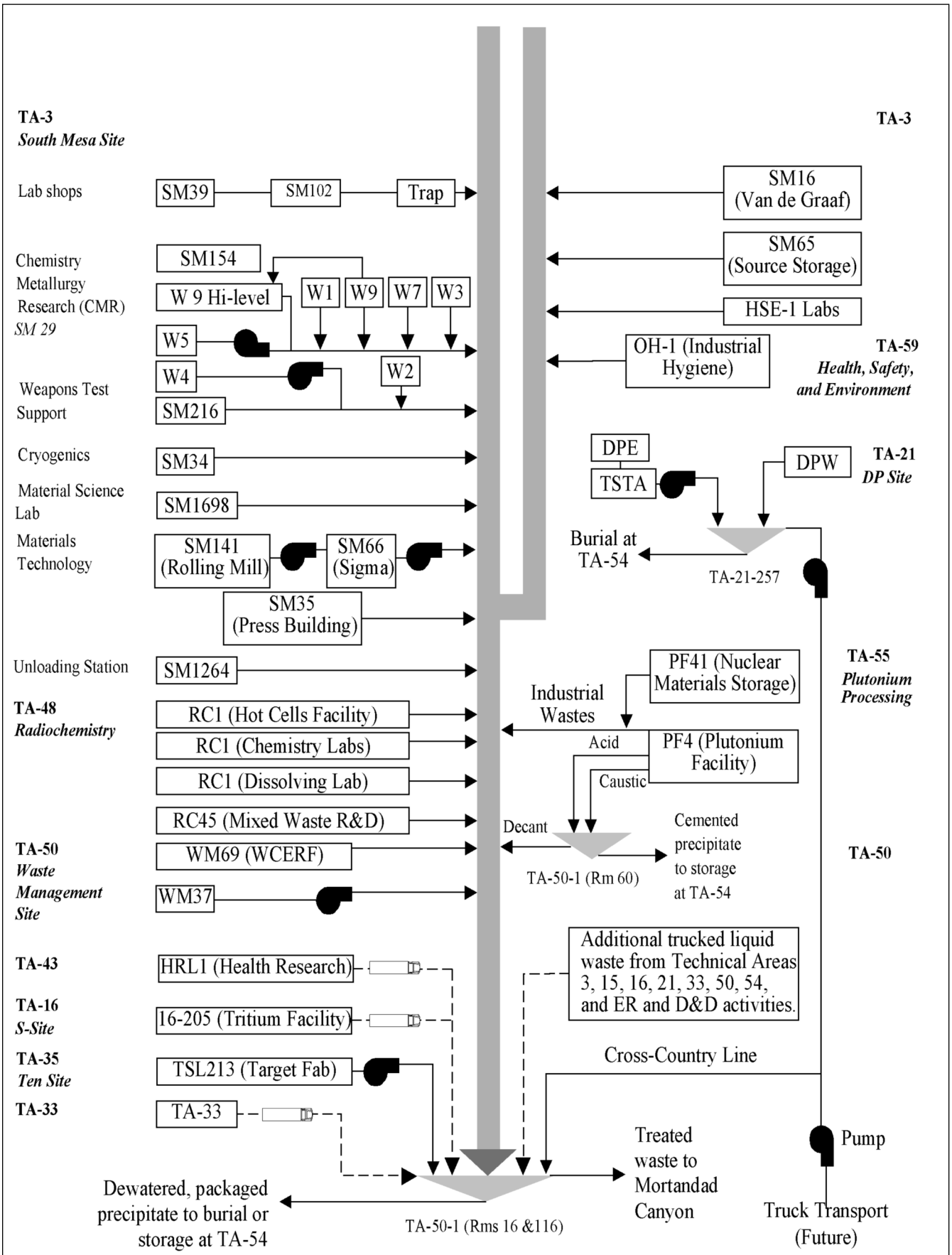

Figure 1. The LANL radioactive liquid-waste-collection systems.

interpretation. Automated on-line IC is a cost-effective way of determining the efficiency of a waste-treatment facility. It is capable of high throughput in routine day-to-day monitoring of wastewater. With an automated on-line method, sample lines were connected directly to the analyzer, eliminating the manual treatment of standards and samples. More information was obtained automatically and sample contamination eliminated.

Instrumentation

The RLWTF is the central waste-processing area for the radioactive liquid wastes generated throughout LANL. At the RLWTF, the pH of the influent waste was adjusted to 7 in a neutralization tank and the flow measured. The waste stream was then pumped through a bag filter that removed particles smaller than 10 µm. A 7.5-gal/h representative stream was pumped into a Dionex DX-800 on-line ion analyzer (Dionex, Sunnyvale, CA). The DX800 was housed in enclosures meeting the National Electrical Manufacturer's Association' regulation 12 for protection of the internal components from the environment. Figure 2 is a diagram of the on-line chromatograph. The SS80 sample selector of the analyzer selected the sample stream or calibration standard to be analyzed. The SS80 was mounted on a wall and allowed sampling from multiple sources. In the SS80, the sample select valves were configured to allow continuous flow of the sample through the manifold.

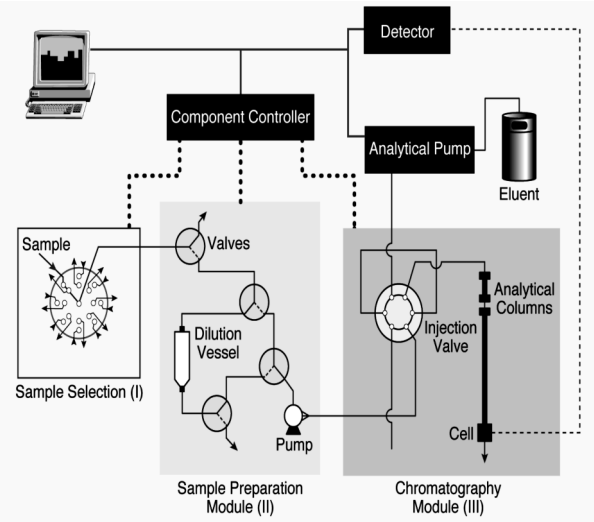

Figure 2. Block diagram of DX-800 process analyzer.

A sample preparation module automatically prepared multiple-level standards for calibration over the range of interest. There were electronically actuated valves and precision pumps that performed sample concentration, dilution, or reagent addition. The analytical portion of the analyzer provided analysis of the components of interest, and an analytical pump delivered a consistent stream of eluent and mobile phase to the analytical columns. The chromatography module contained the load/inject valve, columns, the conductivity detector cell, and the self-regenerating suppressor. In this module, the sample and calibration standards were loaded to the analytical columns with subsequent detection by a conductivity detector. The data output was controlled by the PeakNet-PA (Dionex) software. The software provided automated control of the DX-800. It allowed for instrument control, data acquisition, and data reporting. Data reports were obtained in the form of chromatograms or as numerical printouts of concentrations or graphical data trends. The software was combined with WonderWare's In Touch (WonderWare, Silver Spring, MD) in order to view analyzer status and results, handle alarms, and interface with the RLWTF computing and control systems.

Table I. Operating IC Conditions

Eluent	3.5mM $NaHCO_3$/1.0mM Na_2CO_3
Flow rate	0.30 mL/min
Column	Dionex AG14/AS14 (2-mm i.d.)
Detection	suppressed conductivity, ASRS 50 mA
Injection volume	10 µL

Procedure

The operating conditions for the determination of anions in the wastewater are shown in Table I. The calibration standard solutions were prepared from commercially available 10,000-mg/L stock standards of fluoride, chloride, sulfate, *N*-nitrite, and *N*-nitrate (SPEX CertiPrep, Metuchen, NJ). Commercially available 0.5M sodium carbonate and 0.5M sodium bicarbonate concentrates (Dionex) were used for eluent preparation. All standards and reagents were prepared in 18MΩ water produced by a Milli-Q system (Millipore, Bedford, MA) and stored in polyethylene containers. A dilution vessel in the sample preparation module was programmed to prepare several different concentrations of standards from a single parts-per-million standard (Table II) as well as to dilute samples.

Table II. Different Levels of Standard Concentration

	Stock concentration (mg/L)	Level 1 (mg/L)	Level 2 (mg/L)	Level 3 (mg/L)	Level 4 (mg/L)	Level 5 (mg/L)
F^-	100	1.19	2.38	5.94	9.50	11.90
Cl^-	300	3.52	6.96	17.80	28.50	35.60
NO_2–N	30	0.35	0.70	1.78	2.85	3.56
NO_3–N	100	1.19	2.38	5.94	9.50	11.90
SO_4^{2-}	300	3.52	6.96	17.80	28.50	35.60

Results and Discussion

The purpose of on-line analysis was to constantly monitor streams with precise analytical methods. The process analyzer was installed at the RLWTF so that the IC could operate continuously with minimal maintenance. The on-line chromatograph was calibrated using combined anions

standards. A linear least-squares best-fit regression analysis was used in the multilevel calibrations. Table III shows the method detection limits (defined as 3.14 times the standard deviation of 7 replicates). Figure 3 (a sample chromatogram of the wastewater stream) shows the separation of the anions. It depicts the simultaneous IC separation of fluoride, chloride, *N*-nitrite, *N*-nitrate, and sulfate. All the anions were separated with good resolution.

Table III. Method Detection Limit (mg/L)

Fluoride	0.05
Chloride	0.04
N-nitrite	0.04
N-nitrate	0.03
Sulfate	0.03

An example of trending information over a time period is shown in Figure 4. Component trending provides the ability to see upsets or shifts in the analyte results. This particular plot shows the number of nitrate upsets over time and trends of the given concentration. On this one occasion, a *N*-nitrate upset occurred and resulted in out-of-specification water for several hours. The *N*-nitrate observed was more than double the guidelines. The upset more than likely stemmed from one of the sites at LANL. Thus, if the instrumentation was placed upstream, this on-line real-time method would alert the RLWTF operator.

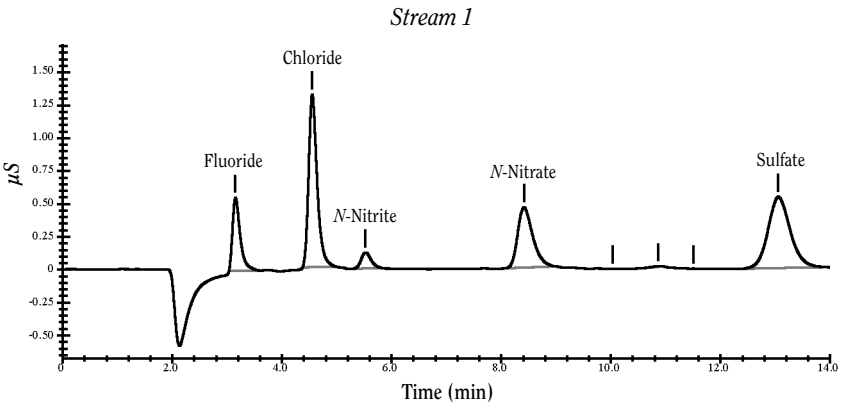

Figure 3. Chromatogram of a waste stream.

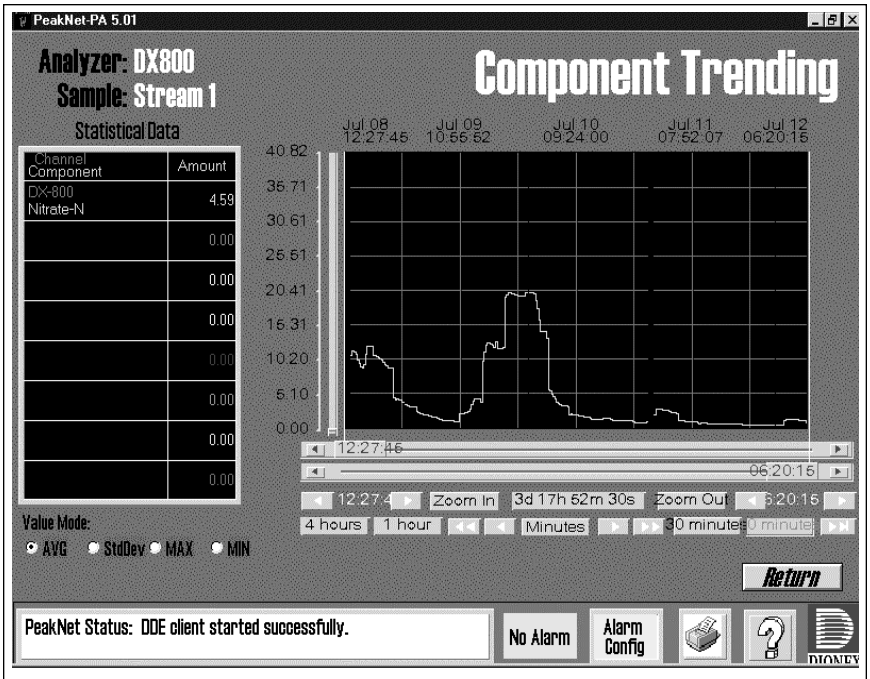

Figure 4. Trending of NO_3–N.

Conclusion

RLWTF is faced with nitrate discharge regulations and limits that have become stringent, along with high penalties for discharging concentrations above these limits. The state has requested a groundwater discharge plan to meet all groundwater standards, including one for nitrate standards. Additionally, environmental agencies verify the accurate reporting of discharges within the discharge limits required for optimum performance of the waste-treatment plant. On-line IC is an effective, reliable, and accurate analytical technique for the continuous monitoring of anions in wastewater. It provides real-time process information that can be used to optimize treatment and serve as an early indicator of waste-treatment problems prior to discharge. The present analysis was constructed so that the process analyzer could operate continuously with minimal maintenance, provide process information that can be useful to optimize treatment, and detect the occurrence of out-of-specification data.

Reference

1. J. Weiss. *Ion Chromatography*, 2nd ed. VCH, New York, 1995.

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