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ON-LINE PROCESS MONITORING IN A LIQUID WASTE TREATMENT FACILITY USING ION CHROMATOGRAPHY

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ABSTRACT

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. On-line monitoring is important for the immediate detection and remediation of process upsets in critical streams. The waste flow to the Radioactive Liquid Waste Treatment Facility (RLWTF) at the Los Alamos National Laboratory (LANL) is processed before discharge and requires monitoring. Process chromatography is used to monitor trends of contaminants in real time. The purpose of this study is to develop an automated on-line chromatography procedure for the simultaneous determination of anions in LANL wastewater.

INTRODUCTION

Waste management programs are occasionally concerned with the various compounds of nitrogen, due to the effects that nitrogeneous compounds can have on the environment. Trace quantities of nitrates are found in surface waters, but high quantities of nitrates maybe found in some groundwaters. At LANL, a 10 mg/L nitrate as nitrogen has been imposed on drinking water to prevent methemoglobinemia. The use of nitric acid throughout the LANL complex produces the nitrates in the plant influent discharged to Mortendad Canyon. The extensive use of fertilizers and improper disposal of wastewater are the primary cause of the nitrate problem in New Mexico.

The RLWTF treats industrial and radioactive liquid wastes generated at multiple research and production facilities across the LANL (Fig.1). This facility processes about 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 (NPDES) permit and the Department of Energy (DOE) orders. The permit is administered by the New Mexico Environmental Department (NMED) and requires LANL to meet the drinking water limit for nitrates. The RLWTF perform chemical and physical separation processes to concentrate radioactive constituents in a sludge that is dewatered to 30 percent solids. The solidified sludge, depending on radionuclide concentration, is either disposed of as LLW or stored as TRU wastes.

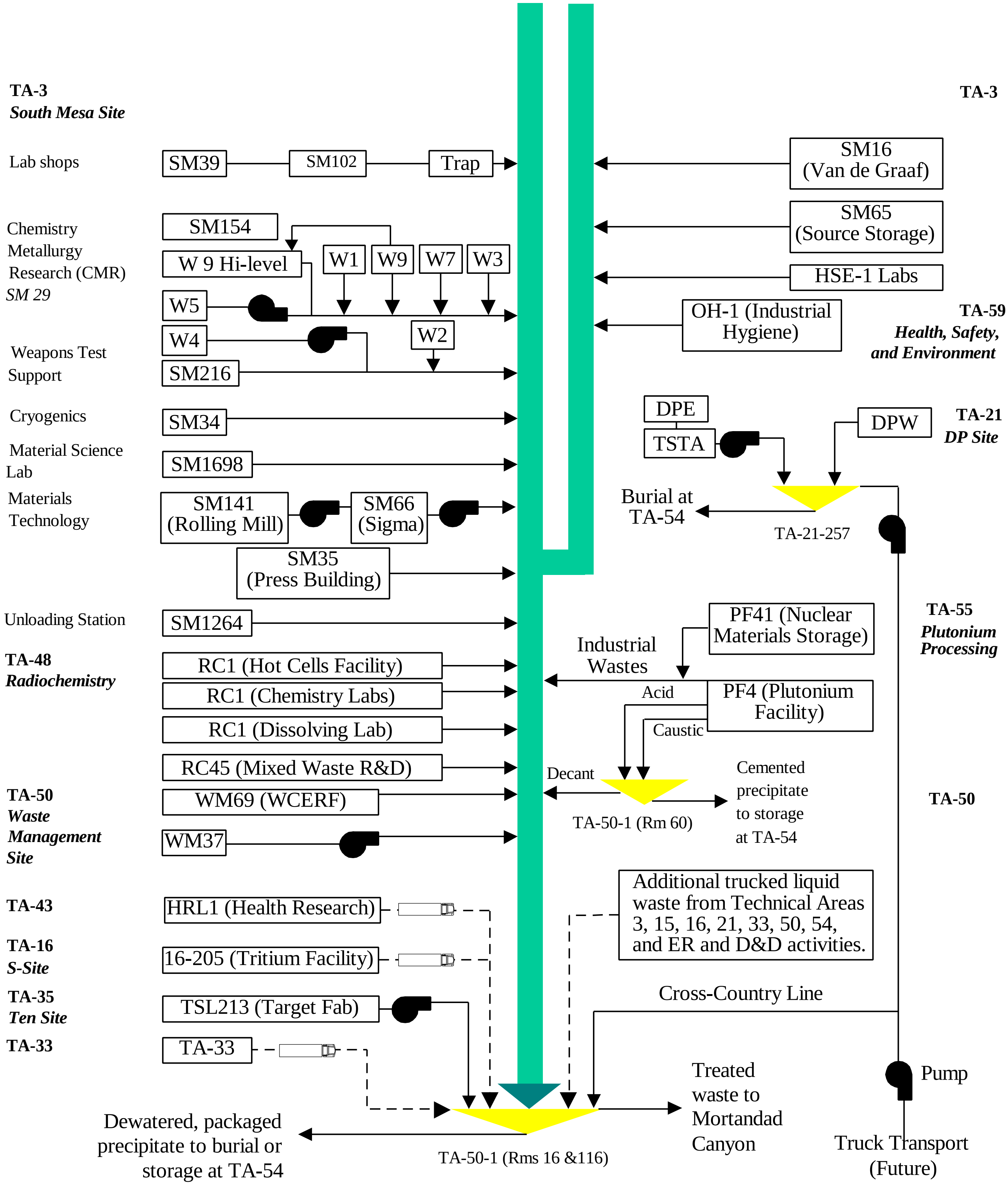

Fig.1. LANL Radioactive Liquid Waste Collection System (RLWCS)

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 (e.g., chloride, fluoride, nitrite, nitrate, and sulfate) in real time is desirable to characterize or assess the need for a specific wastewater treatment method. Ion chromatography provide a single, instrumental technique for rapid, sequential measurement, and also eliminates the use of any hazardous reagents.

A wastewater sample is 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 are separated on the basis of their relative affinities for the resin. The separated anions flow though a suppressor that selectively enhances detection of the sample ions while suppressing the conductivity of the eluent. The conductivity of the sample ions is measured and identified on the basis of retention time as compared to 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 is impractical due to the labor and time required for sampling, analysis, data reporting, and interpretation. Automated on-line ion chromatography 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 are connected directly to the analyzer, eliminating the manual treatment of standards and samples. More information is 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 is adjusted to 7 in a neutralization tank and the flow measured. The waste stream is then pumped through a bag filter that removes particles smaller than 10 micron size. A 7.5 gal/hr representative stream is pumped into a Dionex DX-800 on-line ion analyzer (Dionex, Sunnyvale, CA, USA). The DX800 is housed in enclosures meeting NEMA 12 for protection of the internal components from the environment. The SS80 Sample Selector (I) of the analyzer selects the sample stream or calibration standard to be analyzed. The SS80 is mounted on a wall and allows sampling from multiple sources. In the SS80, the sample select valves were configured to allow continuous flow of the sample through the manifold.

A Sample Preparation Module (II) automatically prepares multiple-level standards for calibration over the range of interest. There are electronically-actuated valves and precision pumps to perform sample concentration, dilution, or reagent addition. The analytical portion of the analyzer provides analysis of the components of interest and an analytical pump delivers a consistent stream of eluent and mobile phase to the analytical columns. The Chromatography Module (III) contains the load/inject valve, columns, the conductivity detector cell, and the self-regenerating suppressor. In the module, the sample and calibration standards are loaded to the analytical columns with subsequent detection by a conductivity detector. The data output is controlled by the PeakNet-PA software. The software provides automated control of the DX-800. It allows for instrument control, data acquisition, and data reporting. Data reports are obtained in the form of chromatograms, or as numerical printouts of concentrations or graphical data trends. The software is combined with Wonderware's In Touch in order to view analyzer status and results, handling alarms, and interface with the RLWTF computing and control systems. A diagram of the on-line chromatograph system, as described above, is shown in Fig. 2.

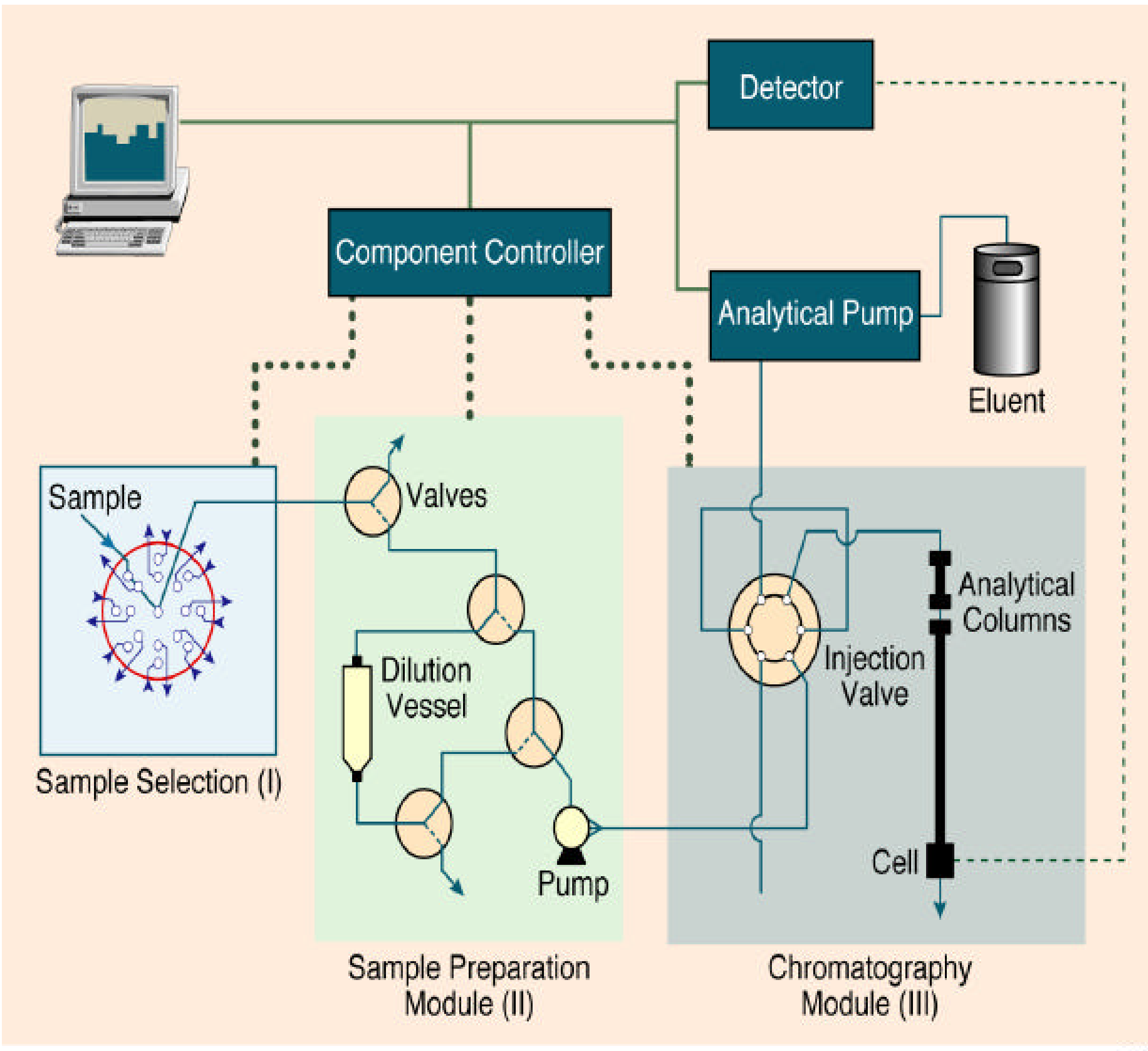

Fig 2. Block Diagram of DX-800 Process Analyzer

PROCEDURE

The operating conditions for the determination of anions in the wastewater are shown in Table 1. The calibration standard solutions were prepared from commercially available (SPEX) 10,000mg/L stock standards of fluoride, chloride, sulfate, nitrite-N and nitrate-N. Commercially available (Dionex) 0.5 M sodium carbonate and 0.5 M sodium bicarbonate concentrates were used for eluent preparation. All standards and reagents were prepared 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 ppm standard (Table 2), as well as to dilute samples.

Table 1. Operating IC Conditions

Eluent	3.5mM $NaHCO_3$/1.0mM Na_2CO_3
Flow Rate	0.30 mL/min
Column	AG14/AS14 (2mm I.D.)
Detection	Suppressed Conductivity, ASRS 50 mA
Injection Volume	10 μL
Sensitivity	10 μL

Table 2. Different Levels of Standard Concentration

	Stock Conc (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 is to constantly monitor streams with precise analytical methods. The process analyzer was installed at the RLWTF so that the ion chromatograph could operate continuously with minimal maintenance. The on-line chromatograph was calibrated using combined anions standards. Fig. 3, a sample chromatogram of the wastewater stream, shows the separation of the anions. It depicts the simultaneous ion chromatographic separation of fluoride, chloride, nitrite-N, nitrate-N and sulfate. All the anions were separated with good resolution.

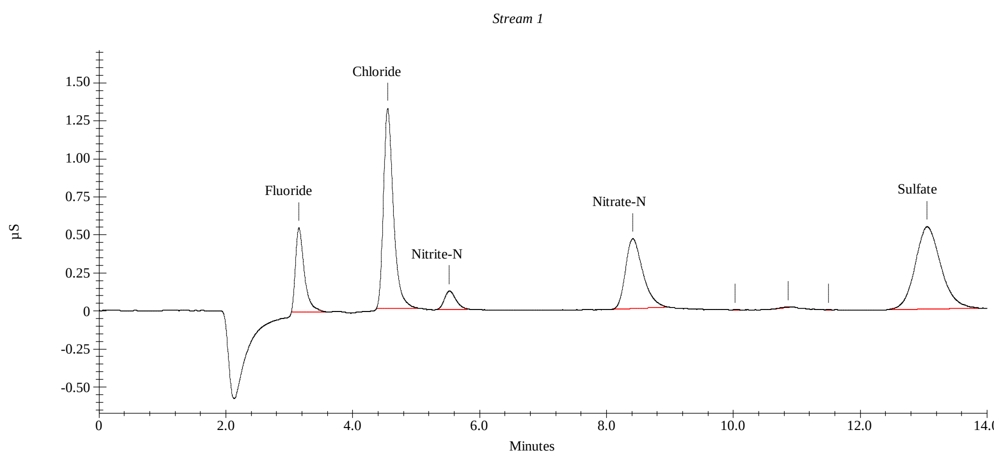

Figure 3. Chromatogram of a waste stream

An example of a trending information over a time period is shown in Fig 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 the given concentration. On this one occasion, a nitrate-N upset occurred and resulted in out-of-specification water for several hours. The nitrate-N observed was more than twice greater than the guidelines. The upset more than likely stemmed from one of the sites at LANL. Thus, if the instrumentation is placed upstream, this on-line real time method would alert the RLWTF operator.

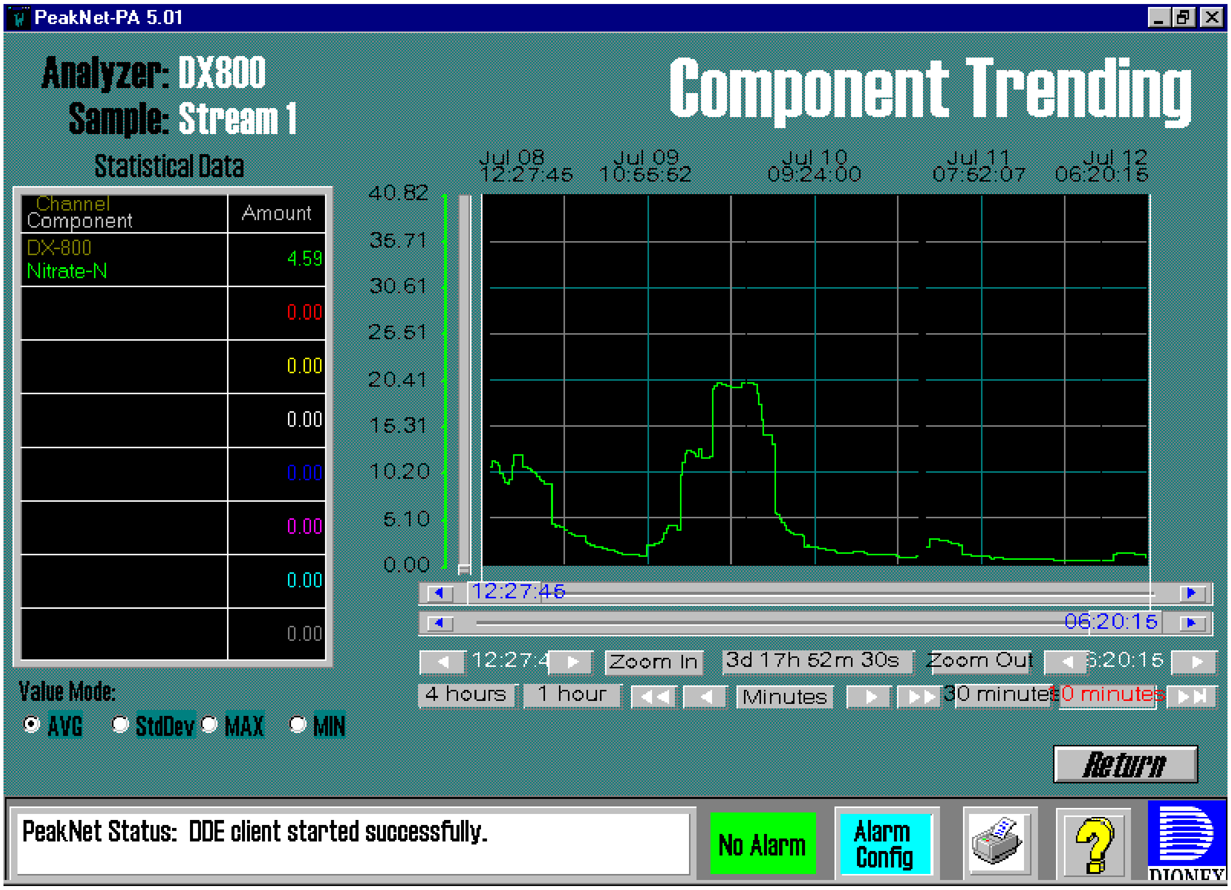

Figure 4. Trending of NO3-N

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 nitrates standard. Additionally, environmental agencies verify the accurate reporting of discharges within the discharge limits required for optimum performance of the waste treatment plant. On-line ion chromatography 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 set up so that the process analyzer could operate continuously with minimal maintenance, provide process information that can be useful to optimize treatment, and detect occurrence of out-of-specification data.

REFERENCES

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