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Short communication

Trace perchlorates in a radiological liquid-waste treatment facility

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Abstract

Waste management programs at the Radioactive Liquid Waste Treatment Facility (RLWTF) at the Los Alamos National Laboratory (LANL) are concerned with the levels of perchlorates due to the effects it can have on the environment and resultant regulations. The RLWTF treats industrial and radioactive wastes generated at multiple research and production facilities across the LANL. Perchloric acid is the major source of the perchlorate ion in the RLWTF used in the analytical chemistry laboratories and for metal dissolution. Perchlorate is present in the influent to the RLWTF at concentrations up to several thousands µg/l level. Ion chromatography is the method of choice to analyze the concentrations of perchlorate in the wastewater generated at the RLWTF. Perchlorate was separated by elution through a CS16/CG16 with an EG40 eluent generator. To minimize background conductivity and enhance analyte conductance, an anion self-regenerating suppressor was used. The method achieved a perchlorate method detection limit of 1 µg/l. The method is successfully being used to monitor the perchlorate levels at the RLWTF and provide data for the pilot tests to remove perchlorate from the RLWTF effluent.
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1. Introduction

The Radioactive Liquid Waste Treatment Facility (RLWTF) treats industrial and radioactive liquid wastes that are generated at multiple research and production facilities across the Los Alamos National Laboratory (LANL). Together with the US Department of Energy (DOE), the LANL is striving to achieve excellent water quality in the effluent from the RLWTF. Attention has been given recently to the development of an analytical procedure for perchlorates [1]. In 1997, the California Department of Public Health issued a health advisory limit of 18 µg/l of perchlorate in drinking water. In 2002, the State of California Department of Health Services reduced the perchlorate action level from 18 to 4 µg/l. The DOE advised that the RLWTF investigate a perchlorate removal technology that will limit perchlorate concentrations in the RLWTF effluent below 4 µg/l. Perchloric acid is the major source of the perchlorate ion in the RLWTF used in the analytical chemistry laboratories and for metal dissolution. The RLWTF investigated a removal technology using a perchlorate selective ion-exchange resin that will limit perchlorate concentrations to below 4 µg/l. Perchlorate concentrations in the RLWTF influent varied between 20 and 150 µg/l.

The purpose of this paper is to use ion chromatography (IC) as the method of analysis for perchlorates that can be applied to wastewater treatment. IC has been shown to be a simple and reliable method for the determination of trace concentrations of per-

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chlorates in drinking water [2]. A number of analytical techniques have been applied to perchlorate analysis but most were not suitable for analyzing trace concentrations of the perchlorate ion. Ion selective electrodes have a high detection limit; voltametry and flow injection analysis lacked the required sensitivity. IC was used for the determination and monitoring of perchlorate levels in the RLWTF effluent. AS16/AG16 columns were used for the analytical separation of the different anions and perchlorates in conjunction with an automated KOH eluent generator. The method detection limit for this method is 1 μg/l. This method follows the US Environmental Protection Agency (EPA) Method 314.0 which is specified for the perchlorate analysis in surface, ground and drinking waters and is the analytical method designated for monitoring perchlorate levels at large public water systems, as required by recent revisions to the Unregulated Contaminant Monitoring Rule [3].

2. Experimental

2.1. Instrumentation

A Dionex DX500 ion chromatographic system (Dionex, Sunnyvale, CA, USA) was used which consisted of a GP50 gradient pump with automated eluent degassing, an EG40 eluent generator which eliminates the manual preparation of eluents thereby increasing the level of automation of the system, an AS40 automated sampler and a CD20 conductivity detector. Sample vials (5 ml) with filter caps with no pre-treatment were used throughout the experiment. Separations were performed using an AS16 (250$\times$ 2.0 mm) analytical column with an AG16 (50$\times$ 2.0 mm) guard column. An anion self-generating suppressor (2 mm ASRS-ULTRA) was used to minimize background conductivity and enhance analyte conductance operated at 50 mA in the external water mode. Flow-rate was 0.38 ml/min with an eluent concentration of 65 mM potassium hydroxide. All the instrument control, data collection and data processing were performed with the PeakNet Chromatography station.

2.2. Reagents

All solutions were prepared from analytical-grade reagent-grade chemicals in 18 MΩ water, obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Dilute working solutions were prepared from commercially available (SPEX) 1000 mg/l stock standard of perchlorate. A KOH EluGen cartridge (Dionex) was used with the EG40 eluent generator to generate the 65 mM potassium hydroxide.

Fig. 1 shows a typical chromatogram of a 1 mg/l perchlorate standard with a 250 μl injection loop, a 65 mM hydroxide eluent operated at 0.38 ml/min, and suppressed conductivity detection. The perchlorate elutes within 10 min while the common inorganic anions elute near the column void volume. The method detection limit (MDL) for this method was calculated at 1 μg/l.

3. Results and discussion

Even though the RLWTF effluent is not a source of drinking water, a potential does exists for the contamination of the groundwater aquifer. Thus, a pilot testing was conducted for the best technology for perchlorate removal down to 4 μg/l. The analytical results obtained for the determination of perchlorates were used in the pilot test as well as the monitoring of perchlorates at RLWTF. It was shown that perchlorates are present in the influent to the RLWTF at concentrations up to the several thousands μg/l level [4]. Fig. 2 shows the concentration of perchlorate in the RLWTF influent and effluent. The influent ranges from 700 μg/l to less than 100 μg/l over the time period shown. The RLWTF effluent concentration also varied from 400 μg/l to less than 100 μg/l. Fig. 3 demonstrates that perchlorates exist in the treated radioactive liquid-waste effluent from the RLWTF above the 18 μg/l level advised by the California Department of Health Services. During the test, the perchlorate concentration the RLWTF water, upstream of the ion-exchange resins, varied between 20 μg/l and 150 μg/l. As shown by the different sampling events (SEs) in Fig. 4, the perchlorate concentrations after the ion-
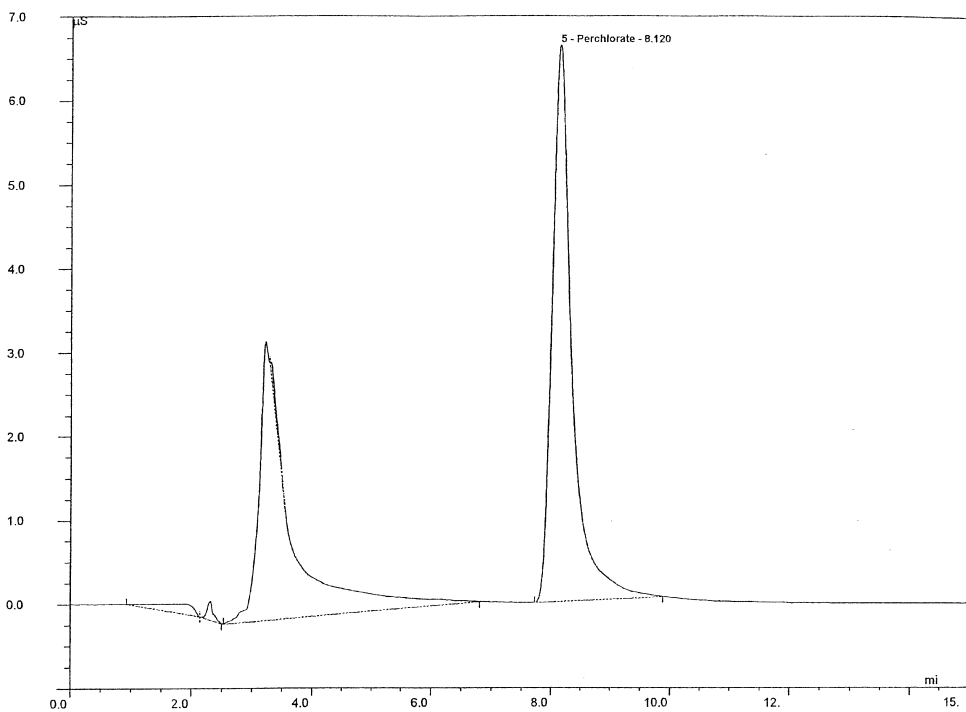
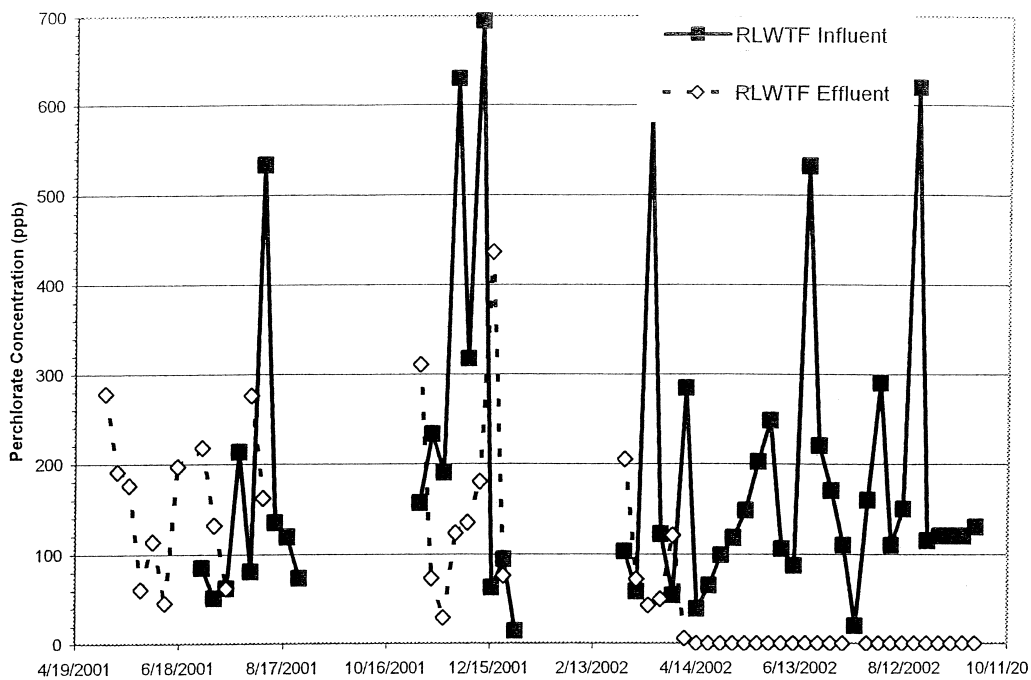Fig. 1. Perchlorate chromatogram.

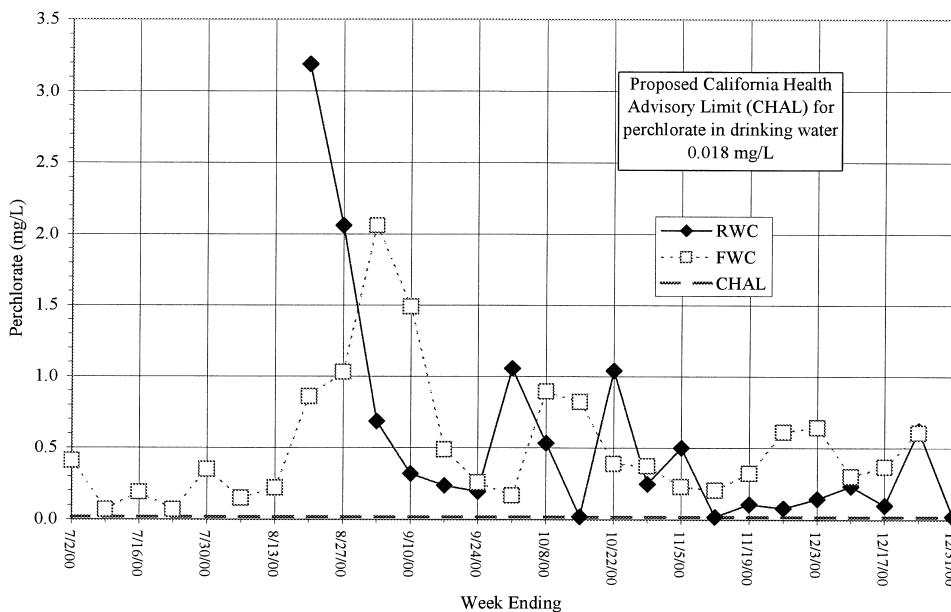Fig. 2. Perchlorate in influent and effluent samples.

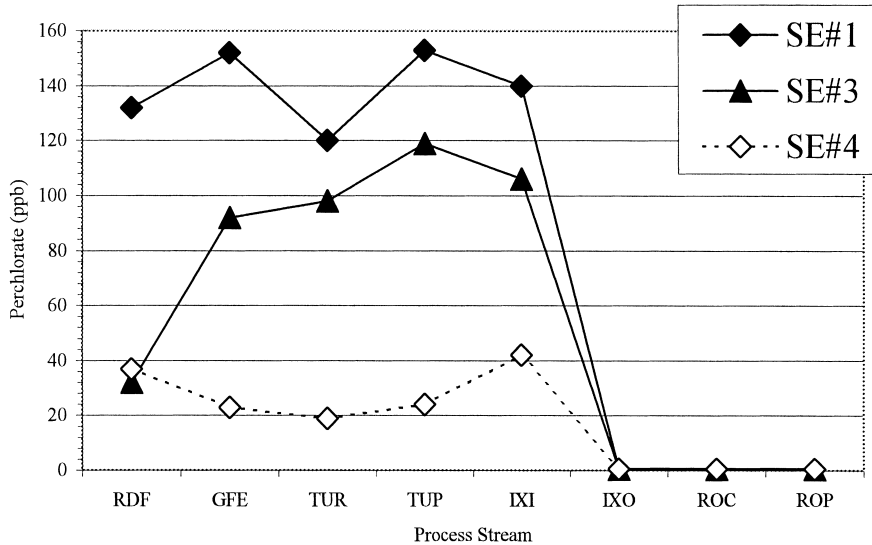Fig. 3. Perchlorate in raw weekly composite (RWC) and final weekly composite (FWC) samples at the RLWTF.

Fig. 4. Perchlorate in RLWTF process streams.

exchange resins are less than the method detection limit.

4. Conclusions

IC is a viable tool for the determination of perchlorates in wastewater. The method enabled accurate and reliable results of perchlorates used in the monitoring of the RLWTF influent and effluent. The data obtained by the pilot studies was instrumental in deciding which ion-exchange resin can remove perchlorate from wastewater to concentrations below 4 μg/l.

Acknowledgements

References

[1] P.E. Jackson, S. Gokhale, T. Streib, J.S. Rohrer, C.A. Pohl, J. Chromatogr. A 888 (2000) 151.
[2] J. Weiss, Ion Chromatography, 2nd ed., VCH, New York, 1995.
[3] US Environmental Protection Agency, Fed. Reg., 64 FR 50555, September 1999.
[4] V.P. Worland, Removal of Perchlorate from the Los Alamos National Laboratory RLWTF Effluent by Ion Exchange, LA-UR-01-6519, 2001.