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$^{37}Cl/^{35}Cl$ isotope ratio analysis in perchlorate by ion chromatography/multi collector -ICPMS: Analytical performance and implication for biodegradation studies

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HIGHLIGHTS

- Precise $^{37}Cl/^{35}Cl$ isotope ratio analysis in perchlorate by IC/MC-ICPMS is proposed.
- Satisfactory analytical performance of the proposed method was demonstrated.
- Tracing of perchlorate biodegradation in microcosm study resulted in $\varepsilon^{37}Cl = -13.3 \pm 1‰$.

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ABSTRACT

In the present study we propose a new analytical method for $^{37}Cl/^{35}Cl$ analysis in perchlorate by Ion Chromatography(IC) coupled to Multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS). The accuracy of the analytical method was validated by analysis of international perchlorate standard materials USGS-37 and USGS -38; analytical precision better than ±0.4‰ was achieved. $^{37}Cl/^{35}Cl$ isotope ratio analysis in perchlorate during laboratory biodegradation experiment with microbial cultures enriched from the contaminated soil in Israel resulted in isotope enrichment factor $\varepsilon^{37}Cl = -13.3 \pm 1‰$, which falls in the range reported previously for perchlorate biodegradation by pure microbial cultures. The proposed analytical method may significantly simplify the procedure for isotope analysis of perchlorate which is currently applied in environmental studies.

1. Introduction

During the last two decades, widespread contamination of soil and groundwater by perchlorate has been reported in many places in the world (Balakrishnan et al., 2014; Calderón et al., 2014; Kim et al., 2014; Nadaraja et al., 2015; Vigreux-Besret et al., 2015; Sijimol et al., 2016). The contamination is mostly of anthropogenic origin and usually associated with perchlorate production and use (Motzer, 2001). In Israel, significant concentrations of perchlorate in the vadose zone of coastal aquifer and groundwater (up to thousands mg/L) were detected near an ammonium perchlorate manufacturing plant north of Tel-Aviv (Nativ and Adar, 2005).

The toxicity of perchlorate for the human body is associated with the disruption of iodide uptake in the thyroid gland because of its similarity in ionic radius to iodide (Wolff, 1998; Leung et al., 2014). Due to a potential adverse effect of perchlorate on human health, proper treatment of the contaminated sites for perchlorate clean-up is of a high importance.

During the past several years it has been demonstrated that a group of perchlorate-reducing microorganisms present in soil, groundwater and surface water can degrade perchlorate under anaerobic conditions (Rikken et al., 1996; Logan, 1998; Hatzinger, 2005; Gal et al., 2008). These microbial communities use perchlorate as an electron acceptor for metabolism.

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Perchlorate biodegradation is an enzyme-catalyzed consecutive process involving perchlorate reduction to chlorate, and then to chlorite catalyzed by perchlorate reductase, following by chlorite transformation to chloride and molecular oxygen by chlorite dismutase (Rikken et al., 1996) as follows:.

ClO_4^- (perchlorate) → ClO_3^- (chlorate) → ClO_2^- (chlorite) → Cl^- (chloride) + O_2

The ability of microorganisms to degrade perchlorate can be utilized for remediation of perchlorate contaminated sites.

It has been suggested that applying compound-specific stable isotope analysis of perchlorate can be a helpful tool for detecting perchlorate biodegradation (Coleman et al., 2003; Sturchio et al., 2003, 2012). It was shown that biodegradation of perchlorate is associated with significant enrichment in chlorine and oxygen with heavy isotopes; the isotope enrichment factors $\varepsilon^{37}Cl$ and $\varepsilon^{18}O$ obtained from microcosm experiments with various bacterial strains fall in the range from −16.6 to −11.5‰ (Coleman et al., 2003; Sturchio et al., 2003; Ader et al., 2008) for chlorine and from −36.6‰ to 29‰ for oxygen (Sturchio et al., 2007); however, in the field experiment on perchlorate bioremediation the apparent in situ isotopic fractionation factors for both O and Cl in ClO_4 were only about 30–40% of the values reported for the pure culture (Hatzinger et al., 2009).

It has been observed that during isotopic fractionation, the ratio of enrichment factors $\varepsilon^{18}O/\varepsilon^{37}Cl$ ~2.5 remains nearly invariant for biodegradation by different types of microorganisms, in laboratory experiments as well as in the field study (Sturchio et al., 2007). However, the application of stable isotope analysis for monitoring perchlorate biodegradation is still. One of the possible reasons for that is the absence of robust analytical methods for accurate stable isotope analysis of chlorine in perchlorate.

Analytical methods used until now for $^{37}Cl/^{35}Cl$ and $^{18}O/^{16}O$ isotope ratio analysis in perchlorate were based on the off-line perchlorate extraction from aqueous solutions and its separation from the matrix. This procedure included perchlorate extraction from the solution using a bifunctional anion-exchange resin, followed by purification by cation exchange, oxidation and evaporation steps resulting in precipitation of $CsClO_4$ (Hatzinger et al., 2011; Böhlke et al., 2017). Whereas $^{18}O/^{16}O$ ratio analysis in perchlorate can be done by Elemental Analysis – Isotope Ratio Mass Spectrometry (EA-IRMS), $^{37}Cl/^{35}Cl$ ratio measurements require additional labor-intensive and time-consuming preparation steps, including $CsClO_4$ conversion into an alkali chloride, followed by its transformation to AgCl and, finally, to methyl chloride (CH_3Cl); $^{37}Cl/^{35}Cl$ ratio analysis in CH_3Cl is performed by Gas Source – Isotope Ratio Mass Spectrometry (IRMS) (Sturchio et al., 2012).

Since the complete conversion of each step is necessary for reliable isotope analysis, the efficiency of each step should be controlled during the procedure(Hatzinger et al., 2011). Approximately 20 μmol of ClO_4^- are needed to obtain duplicate stable isotope ratio measurements by IRMS for both O and Cl (Hatzinger et al., 2011).

In a recent study we reported on a possibility of precise $^{37}Cl/^{35}Cl$ ratio analysis in anionic species by Ion Chromatography coupled to MC-ICPMS (Zakon et al., 2014), and suggested that this technique could be suitable for $^{37}Cl/^{35}Cl$ ratio analysis in perchlorate. Although, IC/MC-ICPMS cannot be used for $^{18}O/^{16}O$ ratio analysis, this technique can significantly simplify $^{37}Cl/^{35}Cl$ ratio analysis of perchlorate, further advancing an implementation of perchlorate isotope analysis for environmental investigations.

Therefore, in the present study we intended to validate $^{37}Cl/^{35}Cl$ ratio analysis in perchlorate by IC/MC-ICPMS and investigate the possibility of using this analytical method for biodegradation monitoring. Method development for $^{37}Cl/^{35}Cl$ ratio analysis in perchlorate was based on our previous study of $^{37}Cl/^{35}Cl$ isotope ratio analysis in anionic species by IC/MC-ICPMS(Zakon et al., 2014). Analytical performance of the developed method was evaluated by analysis of the international standard materials USGS-37 and USGS-38 (Böhlke et al., 2017) and by analysis of commercially available perchlorate salts. In addition, the developed analytical method was tested for assessment of chlorine isotope enrichment factor, $\varepsilon^{37}Cl$, in laboratory study on perchlorate biodegradation by microbial cultures enriched from contaminated soil.

2. Experimental

2.1. Materials

High purity water with conductivity <0.05 S/cm (Milli-Q, Millipore) was used for the preparation of all the solutions. Perchlorate salts analyzed in the present work included: $NaClO_4 \cdot H_2O$ (purity 98%, Sigma-Aldrich), $NaClO_4 \cdot H_2O$ (purity 99%, Merck), $Mg(ClO_4)_2$ (anhydrous, purity 99.5%, Leco); $KClO_4$ (USGS-37 and USGS-38) were purchased from USGS (Reston Stable Isotope Laboratory).

2.2. Instrumental setup for $\delta^{37}Cl$ isotope analysis

Instrumental setup for on-line $\delta^{37}Cl$ analysis in perchlorate was based on the analytical technique for ion specific isotope analysis by IC/MC-ICPMS developed earlier by our group (Zakon et al., 2014). A schematic representation of the IC/MC-ICPMS system is shown in Fig. 1.

An ion chromatography system (ICS2100, Dionex) included an AS40 auto sampler, an eluent generator equipped with a KOH eluent cartridge Dionex EGC III, an inorganic anion column, self-regenerating suppressor and a conductivity detector. Samples were injected via a 500 μl loop, mixed with in-situ generated KOH eluent (90 mM), and further pushed through the guard column, following by the analytical ion chromatography column (AS19). After that, the sample passed through the suppressor, where exchange of cations with H^+ was accomplished. Passing the detector, the eluent (pH~5) was nebulized into the Apex Q desolvation unit and introduced into the MC-ICPMS. The suppressor unit was continuously rinsed with deionized water. The IC eluent flow of 0.45 ml/min was applied to fit the optimal flows of nebulizer and MC-ICPMS sample introduction system. Samples were analyzed for isotopic composition using a MC-ICPMS (Nu Plasma II, UK) equipped with 16 Faraday cups. The instrumental working parameters

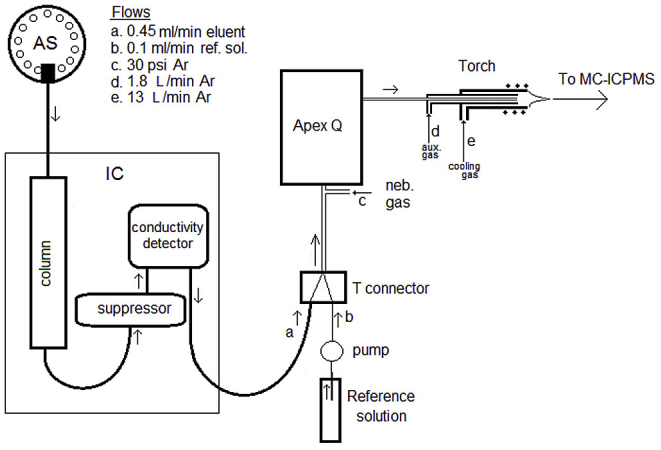

Fig. 1. Schematic representation of the IC/MC-ICPMS system.