Development of $\delta^{37}Cl$ isotope analysis by Ion Chromatography/MC-ICPMS and its application for studying biodegradation of perchlorate

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Purpose: Perchlorate is a widespread environmental contaminant. It is primarily associated with releases of ammonium perchlorate in military related sites. Although it is a strong oxidant, perchlorate anion is very persistent in the environment due to the high activation energy associated with its reduction. In concentrations above the permitted level (30 μg/L) perchlorate is toxic for humans since it can affect thyroid gland functions. Microbial biodegradation of perchlorate is one of the possible treatment technologies for perchlorate removing. During biodegradation perchlorate is reduced to chloride through chlorate and chlorite formation. $\delta^{37}Cl$ isotope analysis may serve a helpful tool to trace this process in the environment. Until now $d^{37}Cl$ analysis was performed mainly by Gas Sourse – Isotope ratio Mass spectrometry or by TIMS and required a complex sample preparation procedure.

The present work we present a new on-line $d^{37}Cl$ isotope analysis in perchlorate by Ion Chromatography (IC)–MC-ICPMS. This method was applied for evaluation of $^{37}Cl/^{35}Cl$ isotope enrichment factor (ε_{Cl}) during microbial degradation of perchlorate in laboratory experiments in field study.

Methods: The method is based on separation of individual anionic species by IC followed by their direct isotope analysis by MC-ICPMS. Generally, $\delta^{37}Cl$ analysis in all anionic species (Cl^-, ClO_2^-, ClO_3^-, ClO_4^-) containing Cl can be performed during the same analytical run. Major isobaric interferences were reduced by using "dry" plasma conditions and applying sufficient mass resolution power ($\Delta M/M$ ~10000). Sample-standard bracketing technique was used for mass bias correction. Precisions in the range 0.3-0.4‰ were attained for analytes containing 1 μmol of Cl.

Results: The developed method for $\delta^{37}Cl$ isotope analysis allowed to attained sufficient precision for tracing the changes in perchlorate isotope composition during biological transformations.
Laboratory experiments with microbial cultures from the contaminated site showed significant chlorine isotope fractionation (ε_{Cl} ~14) in perchlorate during biodegradation. These results are in a good agreement with the data previously published in the literature.

Conclusion: IC-MC-ICPMS method for the $\delta^{37}Cl$ analysis shows a good performance and can be applied routinely for analysis of perchlorate and other chlorine containing anionic species. This method can be applied for tracing degradation of perchlorate in the environment.