

³⁷Cl CHLORINE ISOTOPE ANALYSIS BY CONTINUOUS-FLOW ISOTOPE RATIO MASS SPECTROMETRY

Sample Preparation:

Chlorine stable isotope analysis is conducted on methyl chloride (CH₃Cl) gas after converting chloride ions (Cl⁻), in solution, to CH₃Cl gas through a multi step procedure. Briefly, inorganic chlorides are precipitated in the form of silver chloride in solution at fixed [Cl⁻] content, fixed ionic strength and fixed pH. Samples are diluted or evaporated to create the desired Cl-concentration, brought to a pH of 2 with ultra pure nitric acid, and heated to drive off CO₂. Potassium nitrate, sodium phosphate dibasic, and citric acid monohydrate are then added to solution to fix the ionic strength, buffer the pH, and remove sample contaminants. Silver nitrate is added in order to precipitate silver chloride, and samples are stored in the dark. When complete precipitation has occurred, samples are rinsed with nitric acid (5%) and dried. Silver chloride is then reacted with methyl iodide (CH₃I) to form CH₃Cl gas. For the reaction to proceed to completion, vials are placed in an oven for 48 h at 80°C. Typically, at least 2 mg of Cl⁻ is required for analysis, however, samples with concentrations as low as 0.1 of Cl⁻ can be analyzed using this method.

Sample Analysis:

The ratio of chlorine stable isotopes (³⁷Cl/³⁵Cl) is determined by a continuous-flow isotope ratio mass spectrometry. An IsoPrime, Micromass is used to measure ³⁷Cl, and an Agilent 6890 gas chromatograph (GC) equipped with a CTC Analytics CombiPAL autosampler is attached to the IRMS for CH₃Cl separation. Sample and standard measurements consist of measuring the separated CH₃Cl against a set of reference gas (CH₃Cl) pulses. Typically, the reference gas is measured 6-8 times and the isotopic ratio of the sample or standard peak is determined against the average readings of the reference gas. Each sample is measured 2-4 times. All results are corrected and reported against the Standard Mean Ocean Chloride (SMOC). A calibrated internal standard is used during every run.

The analytical precision for analysis is ± 0.2%.