DEVELOPMENT OF COMPOUND-SPECIFIC CHLORINE ISOTOPE ANALYSIS FOR SUB-MICROMOL QUANTITIES

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Introduction

Chlorinated hydrocarbons is a common class of substances known to be of high ecotoxicity largely due to their persistence and strongly lipophilic properties[1]. This group of chemicals include the semivolatile compounds dichloro-diphenyl-trichloroethane (DDT) and polychlorinated biphenyls (PCB), which, together with solvents like trichloroethylene (TCE) and perchloroethylene (PCE), are globally present at detectable levels in all natural environments. The volatile chlorofluorocarbons (CFCs), albeit relatively nontoxic, play key roles in global warming and ozone depletion in the stratosphere[2].

Shifts in the chlorine isotope composition due to degradation, or synthesis, of a compound are in the order of a few per mil of the initial isotope ratio (Fig. 1).
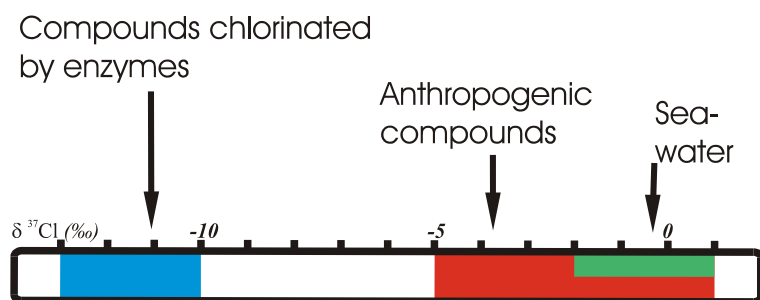

Figure 1. Stable chlorine isotopes can differentiate between different sources of a given organochlorine compound.

The cause of the kinetic isotope effect (KIE) arises from differences in preferential phase distribution of isotopic species[3]. The isotope ^{37}Cl will form bonds of greater stability than will the ^{35}Cl due to the relative reduction of the mass dependent bond vibrational energy. Hence a metabolite formed by C-Cl cleavage typically exhibits a depletion in ^{37}Cl compared to the initial substance, a prime example being DDE formed by dehydrochlorination of DDT[4]. Compound specific isotope analysis (CSIA) of stable chlorine should accordingly provide knowledge relevant to source apportionment, degradation rates, distribution patterns and reaction pathways for organochlorines.

Isotope analysis of chlorine, derived from chlorinated hydrocarbons, can be performed using thermal ionisation mass spectrometry (TIMS) with positive ions. This lowers the limit of determination from about 30 µmol Cl for conventional electron ionisation mass spectrometry (EIMS), to less than 0.3 µmol Cl with a precision of 0.25 ‰ (1s) for TIMS[5]. Such a decrease by a factor 100 in the requirements of sample size will enable CSIA of samples collected away from the immediate vicinity of strongly contaminated areas. The aim of this study is to develop a functioning sequence for i) combustion of solid phase chlorinated hydrocarbons equivalent to <0.7 µmol Cl, ii) conversion of formed chloride to CsCl by ion exchange chromatography and iii) analysis of chlorine isotopes in TIMS.

Material and Methods
Four major analytical stages are distinguished in the preparation of a chlorinated organic compound for TIMS (Figure 2).
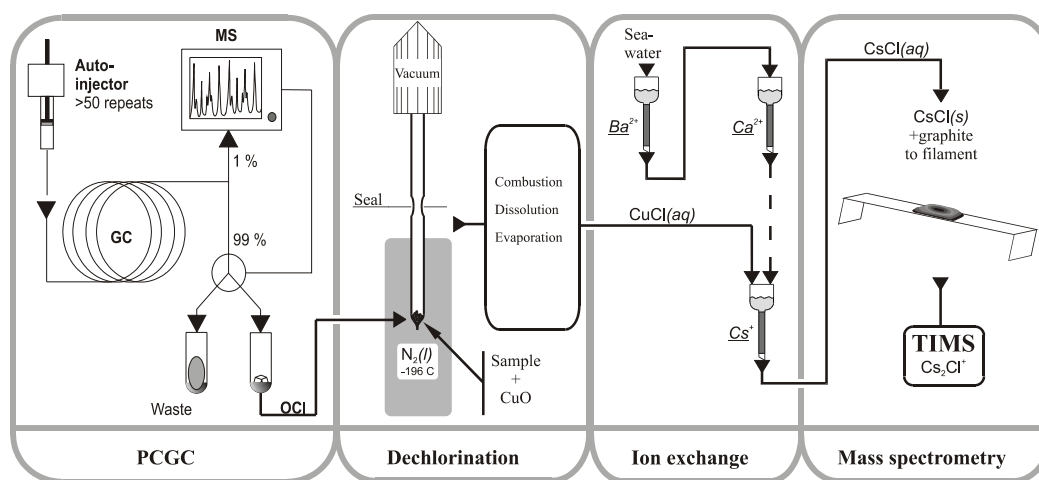

Figure 2. The novel analytical chain for preparation of compound-specific chlorine isotope analysis by thermal ionisation mass spectrometry (TIMS).

Preparative capillary gas chromatography (PCGC): Sovlent extracts are first extensively cleaned-up with e.g. preparative HPLC prior to being subjected to separation and harvesting of individual organochlorine compounds on a PCGC instrument[6,7]. Hundreds of large-volume autoinjections (5 ul) through the Gerstel Cold Injection System (CIS) is eluted through a megabore GC column and target compounds are cryogenically trapped in the Gerstel Preparative Fraction Collector. See also poster by Mandalakis and Gustafsson for specific PCGC details.

Dechlorination: Organochlorine samples yielding 0.7 µmol (25 µg) chlorine were dissolved in hexane and transferred to glass tubes. The solvent was evaporated by means of a nitrogen gas stream, followed by addition of 0.5 g CuO in wire form (ACS, Alfa Aesar). The tube was evacuated to a pressure of 1×10^{-5} mbar and sealed with a butane torch. Combustion was carried out in a programmed furnace at a temperature of 630 °C for the duration of 2 h[8,9].

Ion exchange chromatography: Extraction of the formed CuCl was performed by breaking the glass tube in 40 mL of H_2O, allowing 24 h for complete dissolution. The solution was evaporated to ~3 mL and loaded on a teflon column, holding 40 mg AG50W-X8 (Bio-Rad) in its Cs form. The CsCl solution was evaporated to dryness and redissolved to 1 µg/µL. Seawater was treated according to the same principles, involving Ba^{2+}, Ca^{2+} and Cs^+ resins[10].

Thermal ionisation mass spectrometry: Measurements were performed on a Finnigan MAT261, using degassed rhenium filaments. 50 µg of graphite from a slurry was added to the filament and mixed with an aliqout holding 6 µg Cl from the CsCl solution[11]. Measurements were performed on masses 301 and 303 of the Cs_2Cl^+ ions using electron multiplier and cyclic magnetic field. Data acquisition typically lasted for 3 h under which 275 ratios were collected. $Cs^+/Cs_2{}^{35}Cl^+$ was checked before and after each run.

Results and discussion

Blanks and yields for chloride were measured by ion chromatography. Dechlorination blanks while using 0.5 g CuO has been determined to ~0.8 µg Cl, mainly attributed to the CuO itself. Reducing the blanks may be achieved by optimising the amount and grade of CuO in the reaction. Yields for dechlorination of DDT ranged 50-100 %, implying complete combustion of sample material. Losses could arise from either incomplete dissolution or co-precipitation during evaporation.

Blanks for ion exchange chromatography were <10 ng Cl for dechlorinated samples and <30 ng Cl for seawater samples. Most of the blank material comes from the surrounding air and is incorporated into the sample during evaporation. Rinsing the AG50W-X8 in order to obtain low blanks also helps to remove degradation products in the chromatography process, the effect being improved ionisation during TIMS. Yields for seawater during ion exchange chromatography were determined to >95 %.

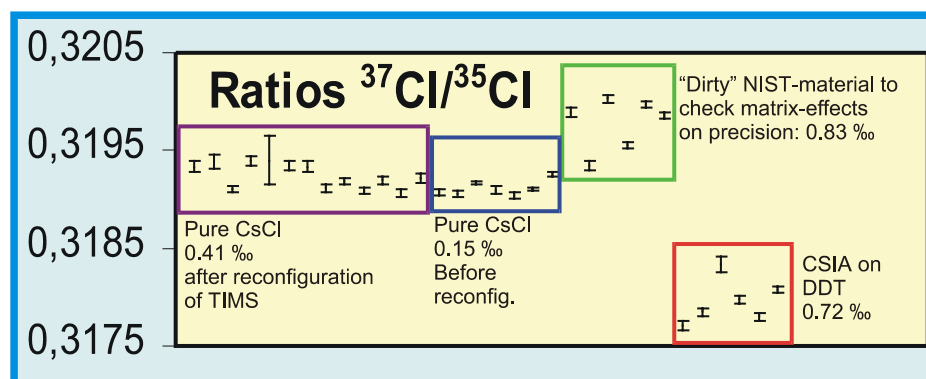Reproducibility in TIMS was <0.25 ‰ (1σ) with in-run precision of ~0.35 ‰ (2σ) (Figure 3).

Figure 3. External precision, using 4 µg Cl for each ratio, indicates the need for pure samples.

Fractionation was in the order of $1\text{-}4\times10^{-6}$ min^{-1} with a $Cs^+/Cs_2{}^{35}Cl^+<1.5$ (ref. 12). Upcoming work will focus on reproducibility, the effect of cation/anion balance on fractionation and $Cs^+/Cs_2{}^{35}Cl^+$, as well as a cross-calibration of TIMS vs. EIMS.

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