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New IRMS method of precise d^{37}Cl measurement

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Chlorine isotope ratios for stable isotope geochemistry have to be measured with the highest precision, preferably with 0.01 permil or better, due to very small range of natural variation, cf. Sharp 2006. The most precise method described by far employed an IRMS and chlorine quantitatively converted to chloromethane, CH_3Cl (Eggenkamp 2004). This gas can be easily produced from several chlorine compound and analyzed on IRMS. However the mass spectrum of this gas is complicated and the ratio of the most abundant peaks (mass-52/mass-50) differs from the $^{37}Cl/^{35}Cl$ isotope ratio. Moreover the measured ratio may be influenced by varying deuterium contents in the measured molecular species.

To overcome this difficulty, we have devised a negative ion mass spectrometer in which we retained all the facilities of IRMS (including dual inlet system with changeover valve, dual collector assembly and CH_3Cl gas as analyte) by modifying the ion source only. In the ion source we have replaced the ionization chamber with electron beam by a metal tube with a hot filament inside. In this tube $^{35}Cl^-$ and $^{37}Cl^-$ ions are produced with efficiency dependent on filament material and its temperature. No other ion species were found in the mass spectrum except of traces at masses 26 and 28 at ppm level, likely due to formation of $CN^-$and CO^-.

Ordinary electrometers with resistors 10 GΩ each produced analogue signals about 3 and 1 volts, respectively. These signals were converted to digital form and integrated over desired time (typically 20 seconds). The obtained precision of d^{37}Cl from 10 sample-to-standard alterations was typically 0.01 permil. Brakes after each alterations were set on 10-15 seconds in order to avoid any visible cross-contamination.

Details on our new approach will be presented.