



## Measuring Hg isotopes in bio- geo-environmental reference materials

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Hg is a highly toxic heavy metal, in higher abundance in metal ores and fossil fuel like coal. The use of these resources lead to Hg emissions in the environment, a lot of which is cycling through the atmosphere. Hg comprises 7 isotopes from mass 196 to 204. Its exact atomic weight, estimated from the relative abundance of its isotopes, was first evaluated by Alfred Nier in 1950. In the last 10 years, other analysts have reported the relative isotope abundance of "terrestrial mercury", using various samples, such as cinnabar from the Almaden mines or Hg from NIST Reference Materials (RM 1641d & RM 3133).

Although MC-ICP-MS measurements of Hg isotopic composition may be precise to fractions of permil, the determination of an absolute ratio is a difficult task. Indeed, whereas individual measurement of  $^{202}\text{Hg}/^{198}\text{Hg}$  have low reported uncertainties, variations of a few permil on that ratio may be calculated from one group to another for the same Hg samples. This highlight the fact that the best way to express the Hg isotopic composition is to use delta values relative to a common RM, the primary delta zero. The NIST 3133 was proposed. Secondary RM will be needed for checking on accuracy and comparisons between laboratories. These samples must be isotopically fractionated from the delta zero RM and should comprise both mono-elementary Hg solutions and more complex natural samples having various matrices. Using cold-vapour generation coupled to MC-ICP-MS (LMTG in Toulouse), we measured, relative to NIST 3133, the  $\delta^{202}\text{Hg}$  of two mercury samples from liquid Hg evaporation-condensation experiments. Although preliminary measurements are not highly precise ( $F65A = -3.8 \pm 0.6\text{permil}$ ;  $RL24H = 2.7 \pm 0.3\text{permil}$ ), the range in com-

position of these samples cover almost the whole range of reported values for terrestrial samples. Our measurement of the Almaden Hg ( $-0.58 \pm 0.05$ permil) is identical to the literature value. We also analysed various RM (soils, sediments, fly ash and lichens) presenting a large span of Hg contents and matrix compositions. To check on any matrix effect during analysis, a basalt (BE-N) and a fly ash (BCR 176) were first heated to  $900^{\circ}\text{C}$  to volatilise Hg. They were then doped with the NIST 3133 Hg and some other major and trace elements before acid digestion and analysis. All the samples yielded a  $\delta^{202}\text{Hg}$  of 0 within error, suggesting that the sample preparation and matrix did not alter the measured isotopic composition. The  $\delta^{202}\text{Hg}$  measured for all RM are mostly negative (0.25 to  $-1.9$ permil). Although delta values involving even isotopes follow a mass fractionation law, odd isotopes ( $^{199}\text{Hg}$  and  $^{201}\text{Hg}$ ) present anomalies relative to mass fractionation ( $\text{D}^{199}\text{Hg}$  and  $\text{D}^{201}\text{Hg}$ ). These capital delta values have a 1:1 relationship and strongly suggest a more or less important atmospheric cycle for Hg according to the nature of the studied sample.