Recent Developments on the Calibration of Raman Spectroscopic Systems for Quantitative Analyses of Geological Fluids

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For quantitative analyses of geological fluids, Raman spectroscopic system needs to be calibrated in terms of peak intensity (either height or area) or peak position. This is because (1) the quantification factor, which relates the intensity of Raman signal of the fluid species to its concentration based on the Placzek's ratio method, is system specific [1], and (2) Raman peak position is a very sensitive indicator for the density (or pressure) of some fluids, such as CH_4 [2] and CO_2 [3]. Three different types of standards in fused silica capillaries were prepared by Chou *et al* [4] for the calibration of Raman systems, and they were: (1) high-pressure optical cell [5], (2) cold-sealed fused silica capillary capsule (FSCC), and (3) flame-sealed FSCC. Even though the 1st type is bulky and not convenient for inter-laboratory calibration, it is the most reliable one in terms of composition and total pressure. In addition to the low-pressure limitation described previously for the 2nd type [4], the potential reaction between the sample fluid and epoxy tends to limit its shelf life. On the other hand, the application of the newly designed heating-cooling stage (either Linkam CAP500 or INSTEC) to the 3rd type greatly simplified the calibration procedures, because the well-controlled temperature of the fluid standard in the FSCC on the heating-cooling stage accurately defined the density of the fluid, either as a single phase or coexisting liquid and vapor phases, and provided excellent density standards [6]. The secondary standards, such as cyclohexane, can also be applied to calibrate Raman peak position after they are calibrated by the primary standards, such as Ne lines.

[1] Chou, Pasteris & Seitz (1990) *Geochim. Cosmochim. Acta*, **54**: 535-543, and references therein. [2] Lu, Chou, Burruss & Song (2007) *Geochim. Cosmochim. Acta*, **71**: 3969-3978 [3] Wang, Chou, Hu, Burruss, Sun & Song (2011) *Geochim. Cosmochim. Acta*, **75**, 4080-4093 [4] Chou, Lu, Chi & Burruss (2011) *Geol. Soc. of Amer. Abstr. with Progr.,* **43(5)**: 232 [5] Chou, Burruss & Lu (2005) in *Advances in High-Pressure Technology for Geophysical Applications*. Chapter 24: 475-485. Elsevier. [6] Chou, Wang & Burruss (2012) Abstract in *10th GeoRaman*, Nancy, France: 65-66