

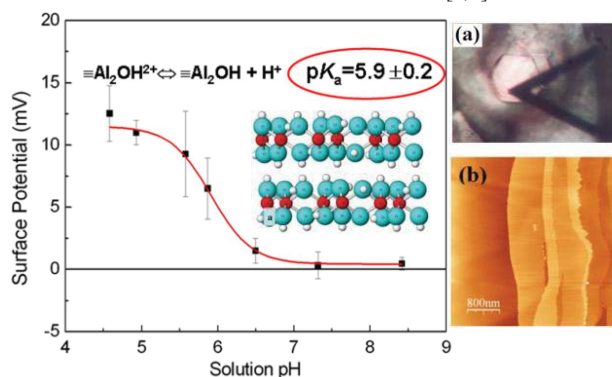
# Intrinsic Proton Activity of Surface Hydroxyl Groups of Single-crystal (Hydr)oxide Minerals: Insights from Recent AFM Studies

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Regardless of intensive interests in the surface chemistry of (hydr)oxide minerals, the surface charging behavior in aqueous solution is still not well understood. Using skillfully both AFM high-resolution imaging [1] and reliable colloidal probe technique [2, 3], we showed unambiguously that the basal plane of gibbsite developed significant net positive charge in the acidic pH range (Fig. 1) [4], and that the PZC of polished corundum single-crystals was sensitive to the change in off-cut angle of samples [5]. These results demonstrated that using samples with well-defined structures was essential towards a better understanding of the charging properties of gibbsite and corundum, particularly the intrinsic proton activity of surface hydroxyl groups like  $\text{Al}_2\text{OH}$  and  $\text{AlOH}$  [6].

Preparation contaminant-free surface of single-crystal corundum substrates, without resorting to vacuum annealing, is the prerequisite for studying the charging properties of corundum/water interface; however, after critical evaluation we found that existing wet/UV/plasma cleaning methods were not valid in terms of removing both organic and particulate contaminants. We proposed a modified RCA method which is reliable for producing contaminant-free surface with well-defined surface structures [7,8].



**Figure 1:** Diffuse layer potential of gibbsite (001) basal plane (the sample and an AFM image are shown on the right) in 1 mM NaCl at various pH obtained from fitting the AFM force curves. The red solid line is the fitting result based on a single-pKa protonation model shown in the inset ( $\text{pK}_a=5.9$ ). Also shown in the inset is the structural mode of gibbsite.

[1] Gan (2009), *Surf. Sci. Rep.*, **64**, 99. [2] Gan (2007), *Rev. Sci. Instrum.*, **78**, 081101. [3] Gan & Franks (2009), *Ultramicroscopy*, **109**, 1061. [4] Gan & Franks (2006), *Langmuir*, **22**, 6087. [5] Zhang, Wang & Gan (2012), to be submitted. [6] Franks & Gan (2007), *J. Am. Ceram. Soc.*, **90**, 3373. [7] Gan & Franks (2005), *J. Phys. Chem. B*, **109**, 12474. [8] Zhang & Gan (2012), to be submitted.

# Determination of trace mercury in geological samples by photo induced chemical vapour generation with isotope dilution inductively coupled plasma mass spectrometry

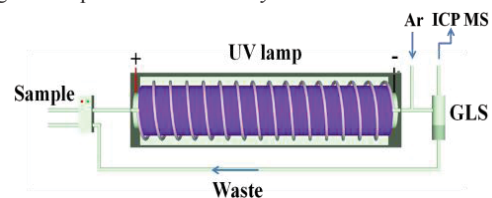
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## Abstract

Mercury is ubiquitous in the environment. Anthropogenic activities take the major responsibility for the significantly elevated mercury emission as a result of more and more human activities<sup>[1]</sup>. Much concern has been attracted to the determination of mercury due to their high toxicity and biomagnification<sup>[2]</sup>. The increasing mercury emission directly resulted in sediment and soil Hg contamination. To assess the toxicity and health risks of mercury, the accurate determination of Hg in sediment and soil is of great importance. However, the extremely low concentration of mercury and the complex sample matrix of soil and sediment samples make the accurate mercury determination troublesome. Furthermore, the severe memory effect of mercury determination by ICP MS is a rather difficult problem to overcome.

A simple, rapid and selective method was developed for the accurate determination of trace mercury in soil and sediment samples by photo induced chemical vapor generation (PVG) with isotope dilution inductively coupled plasma mass spectrometry determination (ID ICPMS). After microwave assisted acid digestion, sample solution was subjected to UV irradiation in the presence of formic acid. Mercury was thus efficiently converted into  $\text{Hg}^0$  without the addition of any other reductants. Subsequently, the generated mercury vapor was rapidly separated from the matrix by an argon flow and swept into ICPMS for quantification. Under the optimal experimental conditions, the limit of detection of  $0.6 \text{ ng L}^{-1}$  was obtained. Compared to traditional CVG, the PVG systems have superior detection sensitivity and tolerance ability to transition metal ions. Up to 5000 folds of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Zn}^{2+}$  have no significant interferences for mercury determination. The method was applied to the determination of mercury in geological samples with satisfactory results.



**Fig. 1** Schematic diagram of the experimental set-up, gas/liquid separator (GLS).

[1] Lin et al., (2010), *Applied Geochemistry*, **25**, 60-68. [2] Lubick et al., (2009), *Nature*, **459**, 620-621.