# An Electrochemical Approach to Improving the TIMS ion source

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## Overview:

Thermal ionization mass spectrometry (TIMS) is the method of choice for high precision isotope ratio measurements. However, demands for smaller sample sizes (subnanogram) in geochronology and isotope tracer studies are challenging the current capabilities of TIMS instrumentation. We have focused our efforts in attempting to improve the thermalized ion source in order to increase ionization efficiencies of typically analyzed elements, such as Pb. The current state of the thermalized ion emitter is a boro- or phosho- silica gel doped with the element of interest and loaded onto a resistively heated Re or Ta filament. The silica gel method is favorable because it is thought to suppress the volatility of the element to be analyzed. However, to date, little is known on the actual ion formation mechanism in the silica gel, and typical ionization efficiencies for elements such as Pb, Cr, Ru, and Ag are in the range of 0.05-2%. Kessinger et al. (1995) found that Ag-doped borosilicate glasses heated under high vacuum emitted monatomic metallic species, predominately $Ag^0$ with subordinate $Ag^+$. As suspected, under low $fO_2$ conditions, such as those in the sample chamber of the mass spectrometer, elements exist in their reduced state. We are attempting, therefore, to use modern electrochemical methods to increase the abundance of oxidized metal ions emitted from the molten borosilicate glass ion emitter. By treating the molten borosilicate glass as the electrolyte in the electrochemical cell, and varying the voltage to Pt reference and counter electrodes, we hope to find the potential range to oxidize the doped metal element from neutral to ionized species, and therefore increase the number of analyzable ions within the mass spectrometer, and thereby directly increase the ionization efficiencies and analytical precision of measured isotope ratios.

## Electrochemistry Background:

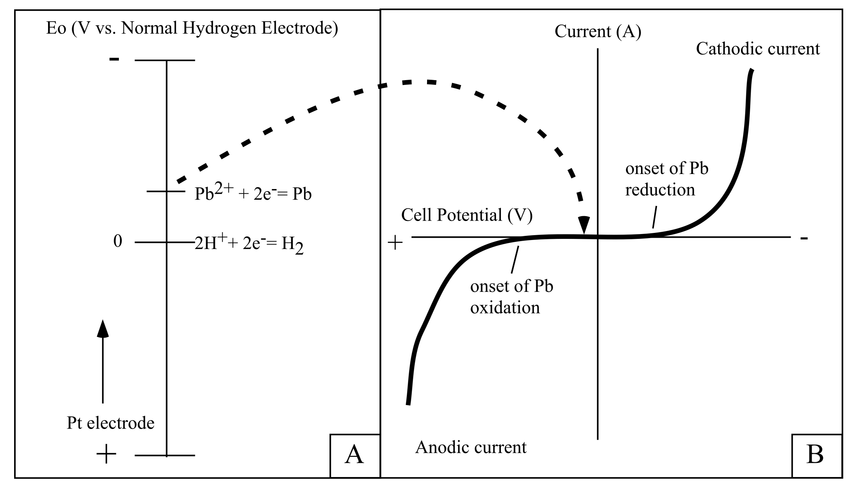


**Figure 1 a)** A conventional potential diagram for voltage of a Pt electrode relative to a normal hydrogen electrode, showing the hypothetical position of Ph reduction reaction.

**b)** A cell potential vs. current diagram showing the hypothetical variation in current associated with reduction and oxidation of Pb.

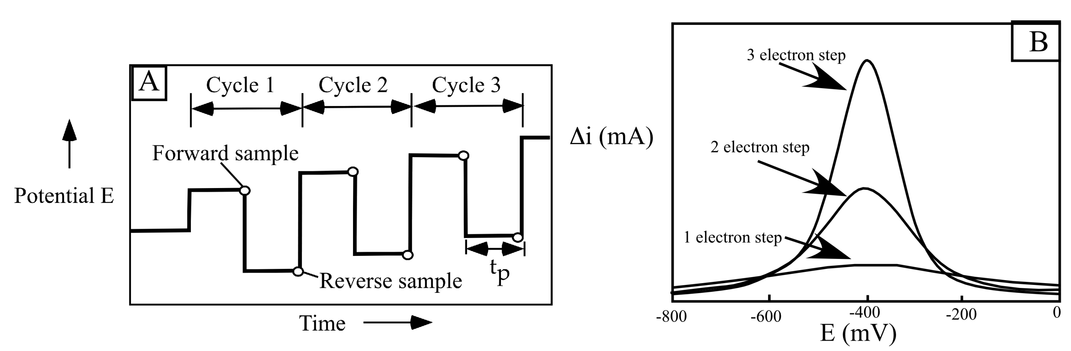


**Figure 2 a)** Typical pulsed potential ramp used in square wave voltammetry. $t_p$ is pulse time. Current is measured both at the top (forward) and bottom (reverse) of potential square wave, while average potential is ramped up between each "cycle".

**b)** On a di vs. E plot, the difference in current measured between forward and reverse position is related to the number of electrons transferred during a given oxidation-reduction reaction.

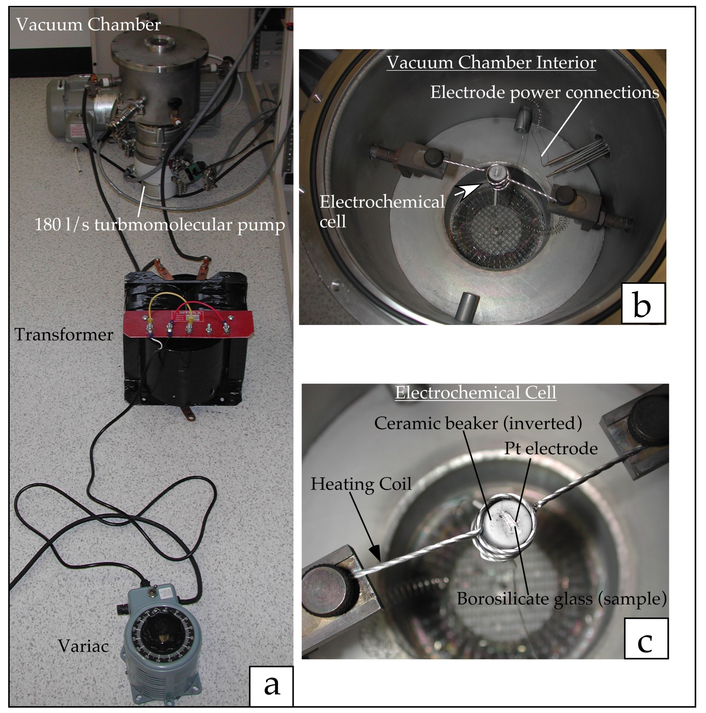


**Figure 3.** Test chamber used for electrochemical experiments and for testing miniature electrochemical cell for using in TIMS. Chamber is powered by a step-down transformer and vaciac and is pumped to vacuum using a turbomolecular pump (A). Electrodes are controlled with Ni wires connected to electrical feedthrough (B). Silica glass is heated on an inverted ceramic electrode wrapped with a resistively heated coil (C).

## Impact:

Following further work with the test chamber, including varying the current experimental set-up to produce a molten glass, we intend to perform electrochemical experiments, such as determining the potential in which to oxidize a doped metal element, such as Pb. Provided we achieve positive results with the test chamber, we will eventually miniaturize our electrochemical cell so that it may function as the ion source within the sample chamber of the mass spectrometer.

**Figure 4.** Preliminary design for the miniaturized electrochemical cell for use in the TIMS. Mounting posts are the filament posts currently used in the mass spectrometer.

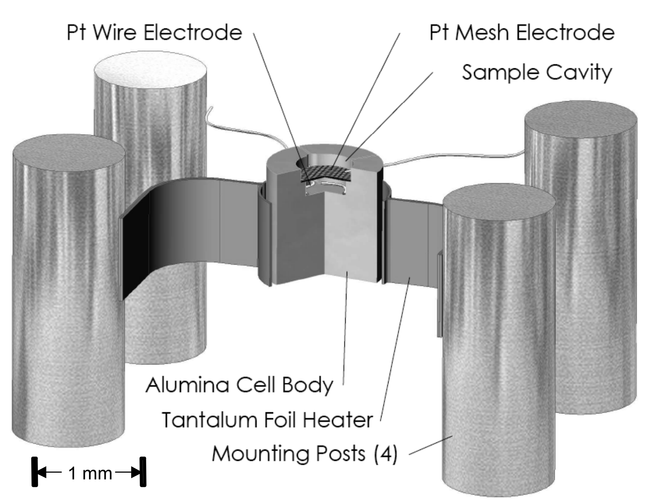


Figure courtesy of D. David (CIRES)