Section 1: Introduction

The Dickson Titrator is a high quality potentiometric titration system specifically designed to measure the Total Alkalinity of sea water. While it has been developed and tuned to give the best possible results for this media, it has also been successfully used on other types of water, including those from estuaries, lakes, rivers, and hot springs.

The system consists of a high quality dosing instrument (Metrohm Dosimat 876 Plus) to deliver acid, a pH electrode and accompanying amplifier, a multichannel digital volt meter (Agilent 34970A) to measure temperatures and emf, a stirrer, and a computer with software to run the system and calculate the results.

1.1 General Method Description

The Dickson Titrator utilizes the open cell method for the measurement of total alkalinity (TA). A known amount of seawater is acidified with dilute hydrochloric acid in a sodium chloride background to a pH of just over 3.5. The sample is stirred vigorously for five minutes with air bubbling through it to remove most dissolved CO2. Approximately 20 small increments of the same acid are then added with the emf and the temperature of the solution recorded at each step. These increments will take the pH to just below 3.0.

The TA of the sample is then computed from the sample's mass and salinity, the mass of the acid added at each point, the acid's concentration, and the temperature of the cell. All of these are fed into non-linear least squares fitting procedure that uses the methods described in detail in SOP 3b of The Guide to Best Practices for Ocean CO_2 Measurements (Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007) to calculate both TA and E^0.

1.2 Application of the Method

The methods described above are applied in a unique manner. Specifically, the Dickson software automatically determines the correct amount of acid to add for the initial dose. This is done in one of two ways, dependent on whether a Certified Reference Material (CRM) of known TA or a sample of unknown TA is being titrated.

For a CRM, the amount of acid necessary to bring the pH of the sample to 3.57 is added in a single aliquot. The amount is straightforwardly computed from the mass of the sample, the sample's certified TA and salinity, and the concentration of the titrant.

For a sample of unknown concentration, acid is added rapidly until an emf equivalent to a pH of approximate 4.0 (the pH is computed from the emf of the electrode and a knowledge of that electrode's E^0). The sample is allowed to stir for a short time, and more acid is added (in two increments) to bring the pH of the sample to 3.57.

In both cases, an initial pH of approximately 3.57 will yield a 0^{th} titration point (the point after the first fine addition) of a pH just outside the desired 3.5 to 3.0 range. The system will calculate how many fine additions will be needed to go just beyond that range and add them accordingly.

1.3 Method Refinements

The Dickson Titrator uses several refinements to achieve the high level of precision and accuracy it offers. These refinements include not only the use of high quality components, but also the calibration of these component's performance (where needed) to ensure they are indeed giving accurate results.

Most notable is the careful calibration of the volume delivered by the Dosimat. While Metrohm Dosimats are reliably very precise (usually around 0.01%), they're accuracy is much larger (around 0.3%). This is overcome by carefully weighing the amount of water delivered from the burette at a few nominal volumes, calculating the volumes of each delivery from its mass and density (computed from its temperature), and calculating a function that allows the actual volume to be computed from the nominal volume. This allows a usable accuracy of the acid delivery to be nearly at the same level of the Dosimat's precision.

The use of a unique high quality high impedance amplifier allows the titrator to use a 6.5 digit volt meter (readable to 0.000001 volts) to sense the emf of the pH electrode, minimizing the error contributed by the voltage sensing system.

The performance of the temperature sensors is also checked at the time of initial assembly to ensure they are within a suitable range. These are read to 0.01°C and are guaranteed to be accurate to better than 0.1°C, which corresponds to a maximum error in TA of around 0.01%.