Alkalinity titration system

The Scripps total alkalinity titration system has been designed and optimized for accurate measurement of the total alkalinity of discrete seawater samples. It is essentially identical to the system currently used in the Scripps CO_2 Reference Material Program to assign total alkalinity values to our CO_2 in seawater reference materials. The same design of system is also used for at-sea measurements of total alkalinity made during the US Repeat Hydrography Program.

Approach

This titration system implements a modified version of a published potentiometric titration method that has been detailed in SOP 3b of the *Guide to Best Practices for Ocean CO_2 Measurements*. A known amount of sample is acidified to a pH of ~3.6, the evolved CO_2 is removed, and the titration continued to a pH of ~3. The equivalence point corresponding to the total alkalinity is evaluated from titration points in the pH region 3.0 – 3.5 using a non-linear least-squares procedure that corrects for the reactions with sulfate and fluoride ions that are present in the seawater.

Specifications

The titration system is based around a Metrohm 876 Dosimat Plus (with a calibrated 5 mL exchange unit) and an Agilent 34970A Data Acquisition / Data Logger Switch Unit with a custom-made unity gain amplifier for the glass pH electrode cell.

The standard system includes a low profile desktop computer with a serial (RS-232) card adapter. The control software, written in LabVIEW 2013, is provided as an executable.

The recommended titration temperature is 20 °C, and requires a refrigerated temperature control bath that is capable of maintaining 20.00 ± 0.05 °C, and of pumping water externally through a closed loop (>10 L min^{-1}). ***The bath is not included in the system.***

The recommended pH electrode is the Metrohm Ecotrode Plus; the system is supplied with one such electrode that has been tested to ensure it is operating appropriately.

Sample volume	~125 mL
Repeatability (1 std. dev.)	~0.5 μmol kg^{-1}
Combined standard uncertainty*	~1.5 μmol kg^{-1}
Initial start-up (from cold)	< 1 hour
Measurement throughput:	4–6 per hour
Titration temperature probe	± 0.05 °C
Burette temperature probe	± 0.1 °C
Air temperature probe	± 0.1 °C
Power supply:	120 V
Power line frequency	60 Hz
Power cord/plugs	NEMA 5-15
Power outlets required	5
(Other power options are available)	

* Achieving this uncertainty (specified at a salinity of ~33) requires use of an acid titrant, whose density is known as a function of temperature, and that has been calibrated with a relative uncertainty of ~0.02%; as well as careful adherence to a suitable QA/QC program.

Optional Accessories/Services

- Metrohm Ecotrode Plus pH electrode, tested to demonstrate suitability for performing accurate total alkalinity titrations of seawater (with certificate).
- Second cell and stirrer; required to enable highest sample throughput.
- Extended support (provided by email and/or telephone).
- Alkalinity reference materials, and calibrated titration acid (available from co2crms@ucsd.edu).

Contact for further information

Professor Andrew G. Dickson
Scripps Institution of Oceanography
University of California, San Diego

Telephone: +1 (858) 822 2990
Fax: +1 (858) 822 2919

Email: adickson@ucsd.edu