SOP 14

Electronic calibration of the UIC Model 5011 coulometer

1. Scope and field of application

This procedure details how to determine the internal electronic calibration factor of the coulometer used in the determination of the total dissolved inorganic carbon in sea water (*i.e.* the UIC Model 5011—SOP 2). Doing this allows the performance of the current integrating circuitry of the coulometer to be assessed independently of any chemical procedures thus providing a valuable diagnostic check, particularly if there is a sudden unexplained change in calibration factor. Changes in the electronic calibration can indicate problems with the coulometer circuitry.

2. Principle

The internal circuitry of the coulometer uses a precision resistor in series with the external coulometer cell. The voltage across this resistor is input to a voltage to frequency converter module. This module then produces a stream of pulses whose frequency depends on the instantaneous voltage across the resistor, *i.e.* the current. The rate of pulse generation is adjusted at the factory to be 10 000 pulses s^{-1} when the current is 200 mA. The pulses are counted and the total number produced in a particular time interval is thus proportional to the total charge passed in that time interval.

To check the electronic calibration, the coulometer is adjusted to provide a constant current through an external precision resistor. This current is integrated by the coulometer for an accurately known time period. Simultaneously, the average voltage is measured across the external resistor.

The number of counts displayed is then compared with the number of counts that would correspond to the average current which is measured in the external circuit.

Measurements are carried out at at least two different current levels and the results obtained are used to assess the performance of the charge measuring circuitry in the coulometer. The simple calibration described here checks the current at two values: at ~50 mA and at ~2 mA. If desired, a more detailed calibration can be done using a variety of currents. The coulometer circuitry uses a different gain stage for measuring currents below and above 12 mA and thus a more detailed investigation may find that a slight change in the calibration occurs at that point.

3. Apparatus

3.1 Coulometer to be checked.

3.2 A high quality $5^{1}/_{2}$ digit voltmeter (± 0.01%) which can be read from a computer at a frequency of at least 2 Hz. The voltmeter calibration should have been adjusted against a suitable voltage standard.

3.3 A high quality four-lead standard resistor (nominally 10 Ω) whose resistance (R_S) is *certified* to better than ± 0.01%. The value should be stable with respect to the self-heating caused by the passage of current (*i.e.* have a low temperature coefficient of resistance).

3.4 Computer with suitable interface for reading the digital voltmeter at a frequency of at least 2 Hz.

4. Procedure

4.1 Initial setup

4.1.1 Allow the coulometer and the digital voltmeter to warm up for at least one hour prior to making measurements.

4.1.2 Connect the standard 10 Ω resistor as part of the external coulometer circuit in place of the coulometer cell and connect the voltmeter to measure the voltage across it.

4.2 Measurement procedure using Mode 0 of the coulometer

Mode 0 of the UIC coulometer is the normal counts mode. Use of the thumbwheel controlled timer is not recommended in this mode. The coulometer is thus read under computer control, with the time interval measured by the computer. As the resolution of the typical computer clock is ~0.01 s, a time period of 300 s is used to minimize timing uncertainties.

The following series of steps are repeated first for the “high” current (~50 mA—Note 1) and then for the “low” current (~2 mA —Note 2) settings of the coulometer. These currents can be obtained either by using the switch SW1 inside the coulometer or by adjusting the %T control on the coulometer front panel.

4.2.1 Set the coulometer in Mode 0.

4.2.2 Ensure that the TIME SET thumb-wheel is at 00.0.

4.2.3 Set the RUN/LATCH switch to the RUN position.

4.2.4 Set the desired current flowing (Note 3).

4.2.5 Reset the coulometer from the computer (ctrl-R).

4.2.6 Start the timer in the computer and read the coulometer immediately (ctrl-E).

4.2.7 Read the voltage across the standard resistor continuously during the period of measurement (~299 s).

4.2.8 Monitor the computer timer (Note 4). As soon as it reaches 300 s, read the coulometer again (ctrl-E).

4.2.9 The difference between the two coulometer readings is the number of pulses counted in the 300 s interval.

4.3 Alternate approach using Mode 15 of coulometer (Note 5)

Mode 15 of the UIC coulometer is optimized to provide an accurate timer function (1 in 100 000). The counter thus becomes an accurate frequency counter with the thumbwheel switch setting the gating period in seconds, and the pulses can be counted for a shorter time interval.

The following series of steps are repeated first for the “high” current (~50 mA—Note 1) and then for the “low” current (~2 mA —Note 2) settings of the coulometer. These can be obtained either

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1 The high current is adjusted to 50 mA (see coulometer instruction manual p. 22) to ensure optimal coulometer stability.

2 Caution, the voltage / frequency response of the coulometer circuitry becomes non-linear at currents below 2 mA.

3 Watch to make sure that the low current does not shut off during the measurement period.

4 To ensure an accurate time interval measurement, this should be done with a carefully optimized software.

5 The use of Mode 15 as described in the UIC coulometer manual cannot be used to verify the calibration as it employs no external standard.

by using the switch SW1 inside the coulometer or by adjusting the %T control on the coulometer front panel.

4.3.1 Set the coulometer to Mode 15.

4.3.2 Set the TIME SET thumb-wheels to 20.0 seconds.

4.3.3 Set the RUN/LATCH switch in the LATCH position.

4.3.4 Set the desired current flowing (Note 3).

4.3.5 Reset the coulometer using the front panel button (Note 6).

4.3.6 Read the voltage across the standard resistor continuously during the period of measurement (Note 7).

4.3.7 Write down the coulometer reading at the end of the time period (Note 8) for use in the subsequent calculations.

4.3.8 Ensure that the coulometer is returned to Mode 0, with the TIME/SET thumbwheels set to 00.0 and the RUN/LATCH switch to RUN before using the coulometer for normal measurements.

5. Calculation and expression of results

5.1 Average current measured across standard resistor

The average current measured passing through the standard resistor in the external circuit over the time interval:

$$\bar{I} = \frac{\bar{V}}{R_S} \, , \tag{1}$$

where

$\bar{V}$ = the average voltage across the standard resistor:

$$\bar{V} = \frac{1}{n} \sum_{i=1}^{n} V_i \, , \tag{2}$$

R_S = the certified value of the standard resistor.

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6 The coulometer will not respond to serial commands in Mode 15.

7 This period will necessarily only approximate the period counted by the coulometer as the computer is independent from the coulometer.

8 As the coulometer has been optimized for time measurement it does not update the count total in real time. Instead the count total is displayed and latched at the end of the time period. The counter immediately proceeds to accumulate the next count in a free running manner.

5.2 Expected number of counts

The expected number of counts corresponding to an average current $\bar{I}$ passing for a time interval of t seconds:

$$N' = t \times \bar{I} \times 10^4 / 0.2 \quad , \tag{3}$$

where $10^4/0.2$ is the nominal conversion factor for the voltage to frequency converter (10^4 counts at 0.2 A).

5.3 Calculation of voltage / frequency performance

Ideally, the number of counts displayed by the coulometer (N) is equal to (or at least proportional to) the number of counts calculated from the measured current (N'). The slope and intercept for a straight line are thus calculated from the data:

$$N = a\,N' + b \ . \tag{4}$$

Hence

$$a = \frac{N_{HI} - N_{LO}}{N'_{HI} - N'_{LO}} \tag{5}$$

$$b = N_{LO} - a\,N'_{LO} = N_{HI} - a\,N'_{HI} \ , \tag{6}$$

where the subscripts HI and LO refer to measurements at high and low current respectively. For the ideal case, $a = 1$ and $b = 0$ (Note 9). A value of the slope that is not exactly unity is not significant as the coulometer is calibrated for use with CO_2 directly. A value of the intercept that is far from zero is cause for concern (Note 10).

5.4 Example calculation

Time period, t = 300 s

Standard resistor, R_S = 10.00098 Ω

Number of counts on low current setting, N_{LO} = 44 167

Average voltage on low current setting, $\bar{V}_{LO}$ = 0.029408 V

Number of counts on high current setting, N_{HI} = 751 858

Average voltage on high current setting, $\bar{V}_{HI}$ = 0.500932 V

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9 The slope and intercept can be adjusted in the coulometer circuitry. The slope is the voltage to frequency response (RV5) and the intercept the offset (RV6)— see pp. 24–25 in the coulometer manual.

10 The magnitude of the problem for the calculation of C_T can be seen by converting the value of the intercept (b) into units of μmol·min^{-1}: $b/(4825.54 \times 5)$. Note that this correction only applies for the period during which the titration current is above 2 mA.

Hence:

$$N'_{LO} = 300 \times \frac{0.029408}{10.00098} \times \frac{10^4}{0.2} = 44108 \ \text{counts} \ , \tag{7}$$

$$N'_{HI} = 300 \times \frac{0.500932}{10.00098} \times \frac{10^4}{0.2} = 751325 \ \text{counts} \ , \tag{8}$$

(9)

and

$$a = \frac{751858 - 44167}{751325 - 44108} = 1.00067 \ ,$$

$$b = 751858 - 1.00067 \times 751325 = 29.6 \ ;$$

b is thus equivalent to a background of 0.0012 $\mu mol \cdot min^{-1}$.

6. Quality assurance

The digital voltmeter and the external standard resistor are independently calibrated and certified. They thus provide an external standard against which the coulometer can be judged. Control charts should be kept of the values obtained for the slope and the intercept. Out of control behavior may indicate a problem with the coulometer circuitry.

References

Johnson, K. M., K. D. Wills, D. B. Butler, W. K. Johnson & C. S. Wong (1993) Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated continuous gas extraction system and coulometric detector. *Marine Chemistry* **44**, 167–187.

UIC Inc. (1985) Instruction manual; model 5011 CO_2 coulometer.