



Instruments and methods

Simplified seawater alkalinity analysis: Use of linear array spectrometers

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Abstract

Modified spectrophotometric procedures are presented for the determination of seawater total alkalinity using rapid scan linear array spectrometers. Continuous monitoring of solution pH allows titrations to be terminated at relatively high pH, whereby excess acid terms are very small. Excess acid concentrations are quantified using the sulfonephthalein indicators, bromocresol green and bromocresol purple. The outlined spectrophotometric procedures require no thermal equilibration of samples. Using bromocresol green, solution pH_T ($[\text{H}^+]_T$ in moles per kg of solution) is given as:

$$\text{pH}_T = 4.2699 + 0.002578(35 - S) + \log((R(25) - 0.00131)/(2.3148 - 0.1299R(25))) \\ - \log(1 - 0.001005S)$$

and $R(25) = R(t)\{1 + 0.00909(25 - t)\}$, where $29 \leq S \leq 37$, $13^\circ\text{C} \leq t \leq 32^\circ\text{C}$, and $R(t)$ is the absorbance ratio (A_{616}/A_{444}) at temperature t and salinity S . Using bromocresol purple, the solution pH_T is given as $\text{pH}_T = 5.8182 + 0.00129(35 - S) + \log((R(25) - 0.00381)/(2.8729 - 0.05104R(25)))$ and $R(25) = R(t)\{1 + 0.01869(25 - t)\}$, where $29 \leq S \leq 37$, $13^\circ\text{C} \leq t \leq 32^\circ\text{C}$, and $R(t) = A_{589}/A_{432}$. Alkalinity measurements using bromocresol purple had a precision on the order of $0.3 \mu\text{mol kg}^{-1}$ and were within $0.3\text{--}0.9 \mu\text{mol kg}^{-1}$ of the alkalinities of certified seawater reference materials. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

Seawater alkalinity, defined (DOE 94) as a difference between the excess concentrations of proton acceptors over proton donors in 1 kg of seawater, is a cornerstone in

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analytical assessments of oceanic CO₂ cycling. Among the four fundamental CO₂ system measurements (alkalinity, total inorganic carbon, CO₂ fugacity and pH) alkalinity is unique in its invariance during CO₂ (gas) exchange with the atmosphere. Largely as a result of this property, the time scale for alkalinity variations in seawater is much larger than is the case for other CO₂ system variables. As a consequence of the comparatively low 'reactivity' of alkalinity in the oceans, it has been possible to describe (Millero *et al.*, 1998) the water mass characteristics of alkalinity as simple functions of temperature (*T*) and salinity (*S*) for much of the surface ocean. Although complete CO₂ system characterization requires at least two of the four fundamental CO₂ system measurements, *T*–*S* parameterizations of alkalinity allow full CO₂ system characterization via *T*–*S* and an additional measurement among the three remaining types. Ultimately, with sufficiently accurate *T*–*S* parameterizations of alkalinity, it should become possible to obtain full CO₂ system characterizations via a network of *in situ* pH or CO₂ fugacity sensors plus *in situ* measurements of temperature and salinity. The accuracy of such characterizations is directly linked to the quality of the many thousands of seawater alkalinity determinations that have been obtained through shipboard analyses. The accuracy and precision of shipboard alkalinity analysis, ± 4 and $\pm 2 \mu\text{mol kg}^{-1}$ (Millero *et al.*, 1993a), is substantially poorer than the corresponding uncertainties for total inorganic carbon measurements, which are not as amenable to *T*–*S* parameterization. However, through the use of shore-based facilities such as HOT (Hawaii Ocean Time-series) and BATS (Bermuda Atlantic Time-series Study), laboratory measurements of seawater alkalinity can be used to supplement shipboard measurements and significantly refine global *T*–*S* parameterizations of alkalinity based solely on shipboard analyses. Improvement in the quality of shore-based, gravimetric measurements of seawater alkalinity is the primary objective of the work described below.

Analytical methodologies for seawater alkalinity determinations have included (a) single-step acid addition with potentiometric determination of excess acid (Culberson *et al.*, 1970) and (b) stepwise addition of acid to a closed titration cell and use of chemical algorithms to determine the equivalence points on the titration curve (Dyrssen and Sillen, 1967; Edmond, 1970; Hansson and Jagner, 1973). The multi-step method has been widely used for shipboard measurement due to its high precision and autonomous operation (Bradshaw *et al.*, 1981; Bradshaw and Brewer, 1988; Millero *et al.*, 1993b). Breland and Byrne (1993) updated the single-step alkalinity procedure of Culberson *et al.* (1970) by combining the speed and conceptual simplicity of the single-step addition method with the precision of spectrophotometric pH determinations.

The procedures of Breland and Byrne (1993) involved the use of bromocresol green to measure the pH of acidified seawater samples. Their procedure involves three steps: (a) seawater and strong acid are combined in an approximately constant ratio, (b) the resulting homogenized solution is purged of CO₂ with a stream of N₂, and (c) the excess acid concentration is measured, allowing calculation of alkalinity from the difference between added acid and excess acid terms. The procedures that we describe in this work are straightforward, but important, extensions of those reported

previously by Breland and Byrne (1993). Use of rapid scan array spectrometers in this work, rather than classical spectrophotometers (which involve measurements via a photomultiplier tube and a movable grating or prism), allows the acid addition process to be continuously monitored. Consequently, the previous single-step procedures are improved by allowing titrations to be terminated when a seawater sample's hydrogen ion concentration exceeds the seawater's residual bicarbonate concentration. In this case, subsequent to purging, excess acid terms become very small. The work of Breland and Byrne (1993) demonstrated that analytical precision and accuracy are dependent on the accuracy of both spectrophotometric and gravimetric (or volumetric) measurements. Through the use of linear array spectrometers, as described below, analytical precision and accuracy are strongly dominated by only gravimetric (or volumetric) analytical accuracy. If, for example, a seawater sample is titrated to pH 4, the residual HCO_3^- concentration prior to N_2 purging will be approximately $30 \mu\text{mol kg}^{-1}$ or less. Subsequent to purging, the excess H^+ concentration will be on the order of $70 \mu\text{mol kg}^{-1}$. The precision of spectrophotometric pH analysis is ± 0.0004 pH units, whereupon H^+ concentrations are precise to 0.1%. As such, the imprecision in the excess acid term for a seawater sample titrated to pH 4.0 is smaller than $0.1 \mu\text{mol kg}^{-1}$. This imprecision is so small that it is unnecessary to conduct analyses at constant temperature. Since thermal equilibration of samples is generally the rate-determining step in spectrophotometric pH determinations, the procedures described below are both fast and precise. Through the use of gravimetric analysis, with carefully standardized acid, the procedures described below provide for analyses with conceptual simplicity and substantial accuracy.

2. Theory

The alkalinity (A_T) of a seawater sample that has been acidified and purged of CO_2 can be written as follows:

$$A_T M_{\text{SW}} = N_A M_A - [\text{H}^+]_{\text{ASW}} M_{\text{ASW}} - [\text{HI}]_{\text{total}} \Delta(\text{HI}) M_{\text{ASW}}, \quad (1)$$

where A_T is the alkalinity (mol kg^{-1} (seawater)) of a seawater sample, M_{SW} is the mass of the seawater sample (kg), N_A is the concentration of the added acid (mol kg^{-1} (solution)), M_A is the mass of the added acid, $[\text{H}^+]_{\text{ASW}}$ is the excess hydrogen ion concentration in the acidified seawater (mol kg^{-1} (seawater)), M_{ASW} is the mass of the acidified seawater calculated as $M_{\text{SW}} + M_A$, $[\text{HI}]_{\text{total}}$ is the total concentration of indicator in both protonated and unprotonated forms (mol kg^{-1} (acidified seawater)), and $\Delta(\text{HI})$ is a term that accounts for the moles of H^+ gained or lost by the indicator in the final acidified seawater relative to the stock solution from which it is added.

The term $\Delta(\text{HI})$ is derived as follows:

$$\Delta(\text{HI}) = \alpha_{\text{HI}}(2) - \alpha_{\text{HI}}(1), \quad (2)$$

where $\alpha_{\text{HI}}(2)$ refers to α_{HI} in the acidified seawater, $\alpha_{\text{HI}}(1)$ refers to α_{HI} in the stock indicator solution, and

$$\alpha_{\text{HI}} = \frac{[\text{HI}^-]}{[\text{HI}^-] + [\text{I}^{2-}]} = \frac{1}{1 + [\text{I}^{2-}]/[\text{HI}^-]} \quad (3)$$

For the protonation reaction



with a protonation constant given as

$$K_1 = [\text{HI}^-]/([\text{H}^+][\text{I}^{2-}]) \quad (5)$$

the solution pH can be described as follows (Clayton and Byrne, 1993):

$$\begin{aligned} \text{pH} = -\log[\text{H}^+] &= \log K_1 + \log[\text{I}^{2-}]/[\text{HI}^-] = \log K_1 \\ &+ \log((R - e_1)/(e_2 - Re_3)) \end{aligned} \quad (6)$$

where e_i are molar absorptivity ratios (Clayton and Byrne, 1993) and R is an indicator absorbance ratio. Eq. (6) shows that the indicator concentration ratio, $[\text{I}^{2-}]/[\text{HI}^-]$, can be written as

$$\frac{[\text{I}^{2-}]}{[\text{HI}^-]} = \frac{R - e_1}{e_2 - Re_3} \quad (7)$$

whereupon Eq. (3) can be written as

$$\alpha_{\text{HI}} = \frac{1}{1 + (R - e_1)/(e_2 - Re_3)} \quad (8)$$

Therefore

$$\Delta(\text{HI}) = \frac{1}{1 + (R_2 - e_1)/(e_2 - R_2e_3)} - \frac{1}{1 + (R_1 - e_1)/(e_2 - R_1e_3)} \quad (9)$$

where R_2 is the indicator absorbance ratio in the final acidified seawater solution and R_1 is the indicator absorbance ratio in the indicator stock solution.

Inspection of Eq. (9) shows that the sign of $\Delta(\text{HI})$ is positive if $R_2 < R_1$. This condition indicates that the indicator is more protonated in the acidified solution than in the indicator stock solution. Consequently, in this case, the indicator has acquired H^+ ions from the acid added to the solution. This acid, in the form of HI^- , does not appear in the term $[\text{H}^+]_{\text{ASW}} M_{\text{ASW}}$ in Eq. (1) and is instead accounted for as the final term in Eq. (1). Note that since $[\text{HI}^-]_{\text{total}} \approx 2.5 \mu\text{mol kg}^{-1}$ (acidified seawater) in typical titrations, the final term in Eq. (1) is no larger than $2.5 \mu\text{mol kg}^{-1}$. Furthermore, if R_1 in indicator stock solutions is adjusted near the values of R_2 in the final acidified seawater solutions (for example, $R_1 \approx 1.6$ and $\text{pH} \approx 4.0$ for BCG or $R_1 \approx 0.3$

and $\text{pH} \approx 4.8$ for BCP), the indicator term in Eq. (1) is very small ($< 0.2 \mu\text{mol kg}^{-1}$) and can be essentially ignored.

3. Method

Alkalinity calculations were performed using Eqs. (1) and (9). The $[\text{H}^+]_{\text{ASW}}$ and $\Delta(\text{HI})$ terms in Eqs. (1) and (9) were measured spectrophotometrically. Both $[\text{H}^+]_{\text{ASW}}$ measurements and $\Delta(\text{HI})$ measurements are determined through observations of sulfonephthalein absorbance ratios, R . With bromocresol green (BCG) R is given as $R = A_{\lambda_2}/A_{\lambda_1}$, where $\lambda_2 = 616 \text{ nm}$ and $\lambda_1 = 444 \text{ nm}$; with bromocresol purple (BCP) R is given as $R = A_{\lambda_2}/A_{\lambda_1}$, where $\lambda_2 = 589 \text{ nm}$ and $\lambda_1 = 432 \text{ nm}$.

Absorbance measurements were made with both an Ocean Optics S1000-TR spectrometer and an HP 8453 spectrophotometer. Raw absorbance data obtained using both spectrometers are shown in the appendix A. The A_{444} , A_{616} , A_{432} , and A_{589} data shown in Appendix A have not been corrected for baseline shifts monitored via absorbance measurements at 750 nm (A_{750} , columns 6 and 7). All titrations and absorbance measurements were performed in the same $6.5 \text{ cm} \times 6.5 \text{ cm} \times 6.0 \text{ cm}$ glass cell (Hellma Cells, Inc.). In measurements involving the HP 8453 spectrophotometer, the titration cell was placed in the spectrometer cell compartment. In measurements involving the Ocean Optic S1000-TR spectrometer, light was passed through the titration cell via collimating lenses (OO # 74-VIS) connected to the spectrometer with optic fibers. The amount of seawater and HCl used for titrations was measured gravimetrically with an accuracy of 0.01 and 0.0001 g, respectively.

Subsequent to a baseline determination with a known amount of seawater ($\sim 130 \text{ g}$) in the cell, BCG stock solution ($\sim 3 \times 10^{-3} \text{ M}$) or BCP stock solution ($\sim 4 \times 10^{-3} \text{ M}$) was added, making final solutions approximately $2\text{--}3 \mu\text{M}$ in BCG or BCP. The solution was stirred and titrated with HCl, while the pH of the solution was continuously monitored. An Ocean Optics S1000-TR spectrometer and an HP 8453 spectrophotometer were programmed such that they continuously measured and displayed the pH of the solution during acid titration. Additions of 0.100 M HCl were made with a plastic syringe filled with a flexible Teflon syringe needle. Acid additions were determined gravimetrically as the difference between the mass of the syringe and its contents before and after the acid addition. The titration was terminated at a solution $\text{pH} \sim 4.2\text{--}3.9$ for runs with BCG and at solution $\text{pH} \sim 4.3\text{--}4.2$ for runs using BCP. After the solution was vigorously purged with N_2 for at least 5 min , absorbance measurements were made, and then the temperature of the solutions was measured with a Testo Term 7000 digital thermometer. For longer bubbling times, presaturation of the N_2 stream with H_2O is recommended in order to prevent solution dehydration with concomitant overestimation of $[\text{H}^+]_{\text{ASW}}$. This effect was negligible for our analytical conditions (mass loss $< 0.2\%$).

The HCl solutions were from J.T. Baker standards ($0.100 \pm 0.001 \text{ M}$). The concentration of this acid was determined coulometrically ($0.10036 \pm 0.00001 \text{ mol/kg}$ solution) in the laboratory of Dr. Andrew Dickson (Scripps Institution of Oceanography).

4. Temperature and salinity dependence of pH measurements

4.1. Bromocresol green

Using bromocresol green, solution pH_T is given as (Breland and Byrne, 1993)

$$\text{pH}_T = 4.2699 + 0.002578(35 - S) + \log((R(25) - 0.00131)/(2.3148 - 0.1299R(25))) - \log(1 - 0.001005S) \quad (10)$$

and

$$R(25) = R(t)\{1 + 0.00909(25 - t)\} \quad (11)$$

where $29 \leq S \leq 37$ and $13^\circ\text{C} \leq t \leq 32^\circ\text{C}$. The bromocresol green dissociation constant $K(\text{BCG})$ in Eq. (10) ($-\log K(\text{BCG}) = 4.2699$ at $S = 35$ and $t = 25^\circ\text{C}$) was originally measured on the molal concentration scale. The final term in Eq. (10) is added to provide total excess acid concentration ($[\text{H}^+]_{\text{ASW}}$) in moles per kg of solution ($\text{pH}_T = -\log[\text{H}^+]_{\text{ASW}}$).

The salinity dependence of the bromocresol green dissociation constant in seawater is given as the second term in Eq. (10) ($0.002578(35 - S)$). The absorbance ratio at 25°C in Eq. (10) is calculated from BCG absorbance at temperature t using Eq. (11) with $R(t) = A_{616}/A_{444}$. Eq. (11) represents a redetermination of the Equation developed by Breland and Byrne (1993) and extends their determination to lower temperatures.

4.2. Bromocresol purple

Using bromocresol purple, solution pH_T is given as (Breland and Byrne, 1992)

$$\text{pH}_T = 5.8182 + 0.00129(35 - S) + \log((R(25) - 0.00381)/(2.8729 - 0.05104R(25))) \quad (12)$$

and

$$R(25) = R(t)\{1 + 0.01869(25 - t)\}. \quad (13)$$

where $29 \leq S \leq 37$ and $13^\circ\text{C} \leq t \leq 32^\circ\text{C}$. Eq. (12) provides acid concentrations directly in terms of moles per kg of seawater ($\text{pH}_T = -\log [\text{H}^+]_{\text{ASW}}$). Eq. (13) was experimentally derived from CO_2 -free seawater in the present work using the procedures of Breland and Byrne (1993). $R(t)$ in Eq. (13) is the absorbance ratio $R(t) = A_{589}/A_{432}$.

5. Results and discussion

5.1. Measurement precision

Table 1A and B provide the results of replicate analysis on an unthermostated seawater sample using bromocresol green (Table 1A) and bromocresol purple

Table 1
Replicate alkalinity measurements on seawater^a

Replicate	Temp (°C)	Final pH _T		A _T	
		(HP)	(OO)	(HP)	(OO)
A. Analysis using BCG					
1	23.9	4.415	4.369	2461.9	2457.5
2	24.3	4.192	4.177	2461.0	2458.6
3	24.9	4.370	4.342	2460.5	2457.6
4	21.4	4.229	4.199	2462.3	2457.9
5	22.3	4.223	4.195	2462.3	2458.2
6	22.5	4.209	4.186	2462.7	2459.2
7	22.5	4.165	4.154	2460.6	2458.8
			Average:	2461.6	2458.2
			S.D:	0.9	0.6
B. Analysis using BCP					
1	24.9	4.572	4.545	2460.3	2458.6
2	22.4	4.776	4.748	2459.5	2458.4
3	23.7	4.652	4.631	2459.8	2458.6
4	24.6	4.856	4.831	2459.5	2458.6
5	23.0	4.594	4.571	2460.1	2458.7
6	22.7	4.991	4.971	2459.8	2459.2
7	23.0	4.689	4.666	2459.6	2458.5
8	22.7	4.713	4.686	2459.4	2458.2
			average:	2459.8	2458.6
			S.D.	0.3	0.3

^a Final pH_T was calculated at 25°C in mol kg⁻¹ SW scale; pH_T(HP) and A_T(HP) were measured using the Hewlett Packard spectrophotometer; pH_T(OO) and A_T(OO) were measured using the Ocean Optics spectrometer. A_T is in μmol kg⁻¹ seawater.

(Table 1B). The tests shown in these tables were designed to test the reproducibility of our procedures. Taken together, the results in Table 1 show that our outlined procedures for seawater alkalinity determinations are capable of precisions better than 1 μmol kg⁻¹. Furthermore, using bromocresol purple our procedures provide precisions better than 0.5 μmol kg⁻¹. The improved precision in Table 1B compared to Table 1A results from the reduced importance of the excess acid term in Eq. (1) in analyses using bromocresol purple. This indicator has a higher pH indicating range than bromocresol green, allowing analysis to be conducted at relatively high pH. Using bromocresol purple the agreement between A_T results obtained using the two spectrometers is substantially improved. In Table 1B the difference in the average A_T results (A_T(HP) – A_T(OO)) is 1.2 μmol kg⁻¹.

The observed systematic difference between A_T(HP) and A_T(OO) is attributable to differences in spectrophotometer performance. In view of observed excellent absorbance agreement among our laboratory's four spectrophotometers that do not involve the use of fiber optics (two HP 8453 instruments and two Varian, Cary 1 and Cary 3, spectrophotometers) it is probable that our observed small A_T(HP) – A_T(OO) differences are caused by errors in pH_T(OO). Resolution of such problems (i.e. measurement

discrepancies on the order of $1\text{ }\mu\text{mol kg}^{-1}$) may best be pursued by directly monitoring the linearity of spectrometer absorbance response. Absorbance standard reference materials for this purpose are available from NIST (e.g. SRM 930D). The performance of our HP8453 spectrophotometers indicates that $[\text{H}^+]_{\text{ASW}}$ measurements obtained with these instruments can be used directly in Eq. (1) with the expectation of obtaining excellent agreement with certified standards. In the context of the excellent precision obtained using the Ocean Optics instrument and the small magnitude of the $A_{\text{T}}(\text{HP})$ and $A_{\text{T}}(\text{OO})$ difference obtained using bromocresol purple, we suspect that with regular use of certified A_{T} standards, as well as absorbance reference materials, the small A_{T} measurement problems encountered with the Ocean Optics spectrometer can be characterized and eliminated.

5.2. Measurement accuracy

The accuracy of our alkalinity procedures was assessed using certified alkalinity standards prepared at SIO’s Marine Physical Laboratory under the direction of Dr Andrew Dickson. Table 2 shows the results of determinations using bromocresol green and bromocresol purple with the HP 8453 spectrometer. No measurements were made with the Ocean Optics spectrometer because of the limited volumes of seawater in the certified standard. Alkalinity measurements with both indicators are in good agreement. The difference between the A_{T} averages using the two indicators is $1.1\text{ }\mu\text{mol kg}^{-1}$. This difference may, in part, reflect differences in the accuracies of bromocresol green and bromocresol purple pK_2 determinations. More importantly, the alkalinity of the certified reference material is given as

$$A_{\text{T}} = 2234.92 \pm 0.44\text{ }\mu\text{mol kg}^{-1} (S = 33.78).$$

Our measured alkalinity using BCG is $0.5\text{ }\mu\text{mol kg}^{-1}$ higher than the certified value, and using BCP our measured alkalinity is $0.6\text{ }\mu\text{mol kg}^{-1}$ lower than the certified value.

Table 2
Measurements (using HP8453) on certified reference material (proposed value of $A_{\text{T}} = 2234.92 \pm 0.44\text{ }\mu\text{mol kg}^{-1}$)

Run No.	Temp (°C)	Final pH _T	A_{T} ($\mu\text{mol kg}^{-1}$)
A. Analysis using BCG			
1	21.7	4.170	2235.5
2	22.0	4.067	2235.8
3	22.8	4.194	2234.9
		Average:	2235.4
		Range:	0.9
B. Analysis using BCP			
1	22.1	4.718	2234.6
2	22.2	4.777	2234.4
3	22.6	4.745	2234.0
		Average:	2234.3
		Range:	0.6

6. Conclusions

The alkalinity measurement technique that we have proposed emphasizes the most fundamental aspect of alkalinity analysis (gravimetric measurement) and greatly diminishes the excess acid term, whose precise and accurate quantification requires more analytical skill and sophistication. The procedures that we have outlined are fast, precise and accurate. Improvements in rate of sample throughput are gained largely because no thermal equilibration is required in these analysis. Our sample processing times are on the order of 12 min. The processing time using previous techniques, which require thermostated solutions, is approximately 20 min or more per sample. The precision of our analyses using bromocresol purple is approximately $\pm 0.5 \mu\text{mol kg}^{-1}$. This represents a factor of three improvement over the spectrophotometric A_T precision ($\pm 1.5 \mu\text{mol kg}^{-1}$) of Breland and Byrne (1993), which was also obtained through gravimetric analysis. Use of the Breland and Byrne (1993) procedures at sea, with volumetric analysis of large samples, produced A_T precision equal to $\pm 1.8 \mu\text{mol kg}^{-1}$ (Clayton *et al.*, 1995). The precision of potentiometric A_T measurements obtained by titration of weighed samples is on the order of $\pm 2.5 \mu\text{mol kg}^{-1}$ (Millero *et al.*, 1993). The excellent accuracy of our outlined procedures is highlighted by the observation that none of the A_T measurements shown in Table 2 deviate from the certified reference material by more than $\pm 0.9 \mu\text{mol kg}^{-1}$. In addition to noting the speed, precision and accuracy of our outlined A_T measurements, it should be emphasized that our procedures simplify the analytical requirements for A_T measurements by eliminating the use of thermocirculators.

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Appendix

Raw absorbance data obtained on HP8435 and Ocean Optics spectrometers
(a) BCG

Replicate	<i>A</i> ₄₄₄		<i>A</i> ₆₁₆		<i>A</i> ₇₅₀	
	(HP)	(OO)	(HP)	(OO)	(HP)	(OO)
1	0.0414	0.0519	0.1096	0.1140	– 0.0005	0.0075
2	0.0548	0.0575	0.0911	0.0906	0.0013	0.0048
3	0.0449	0.0531	0.1084	0.1113	0.0003	0.0082
4	0.0587	0.0720	0.1044	0.1126	– 0.0009	0.0106
5	0.0577	0.0598	0.1017	0.0988	– 0.0002	0.0007
6	0.0574	0.0594	0.0975	0.0959	0.0010	0.0015
7	0.0565	0.0611	0.0882	0.0905	– 0.0002	0.0052

BCP

Replicate	<i>A</i> ₄₃₂		<i>A</i> ₅₈₉		<i>A</i> ₇₅₀	
	(HP)	(OO)	(HP)	(OO)	(HP)	(OO)
1	0.4364	0.4318	0.0723	0.0698	– 0.0001	0.0028
2	0.3900	0.3826	0.0982	0.0946	0.0003	0.0058
3	0.4353	0.4486	0.0846	0.0931	– 0.0001	0.0122
4	0.3868	0.3877	0.1212	0.1211	0.0003	0.0090
5	0.4502	0.4469	0.0761	0.0754	0.0003	0.0047
6	0.3820	0.3847	0.1572	0.1560	0.0005	0.0085
7	0.4400	0.4420	0.0909	0.0930	– 0.0012	0.0068
8	0.4189	0.4203	0.0919	0.0939	0.0004	0.0092