
RESEARCH METHODS AND FACILITIES

Intercalibration of Bruevich's Method to Determine the Total Alkalinity in Seawater

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Abstract—In 2000, the Carbon Dioxide in the Ocean working group of the North Pacific Marine Science Organization (PICES) performed an international experiment on the intercalibration of the measurements of the total alkalinity in seawater using certified reference materials (CRM). Taking part in this experiment, Russian specialists presented the method by Bruevich. The results of the intercalibration showed that the alkalinity values obtained by Bruevich's method using modern burettes, an Na₂CO₃ reactant of high purity as a standard to ascertain the acid titre, and corrections for the acid density and for the weights of the acid and seawater samples in vacuum are in agreement with the standard within $\pm 1 \mu\text{M}/\text{kg}$.

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The total alkalinity (TA) of seawater is considered to mean the sum of the concentrations of weak acid anions contained in the water that are neutralized by titration with a strong acid [2, 4]. The TA value is measured by the amount of hydrochloric acid equivalents required to neutralize 1 l (or 1 kg) of seawater to the final point conforming to the transformation of hydrocarbonate ions into carbonic acid. The alkalinity is considered not only as a hydrochemical characteristic of the environment but also as a parameter of the carbonate system. Jointly with one of the three other carbonate parameters now measurable experimentally (the pH value, total inorganic carbon, and partial pressure of carbon dioxide), the total alkalinity is used to calculate the concentrations of its principal components: the carbonic acid ions (HCO₃⁻ and CO₃²⁻), the free CO₂ concentration, and the carbonate parameters that were not measured experimentally [1, 5].

The variability of the alkalinity and other carbonate system parameters in the surface layer of the World Ocean is not strong. Thus, for example, the increase in the concentration of inorganic carbon caused by the growth of the CO₂ content in the atmosphere is as low as 0.05% per year [8], and the standard deviation of the alkalinity linear dependence on the salinity for the surface waters of the World Ocean is 10 $\mu\text{M}/\text{kg}$ or lower [17]. This gives an estimate of the requirements imposed on the accuracy of measurements and calculations of the carbonate system parameters. The key problems such as the ocean climate changes, the biogeochemical cycle of carbon, and the variations of the primary salinity composition of the ocean may not be studied until the systematic errors of the experimental

procedures are reduced to the level of random errors. That is why the problem of the development of high-precision methods for the measurement of the carbonate system parameters now receives much attention within a series of important international programs: the LOICZ (Land–Ocean Interaction in the Coastal Zone), GEMS (Geochemistry of Marine Sediments), JGOFS (Joint Global Ocean Flux Studies), and WOCE (World Ocean Circulation Experiment). Within the frameworks of these programs, the works on the intercalibration of the measurements of the carbonate system parameters are performed for years, which allows one to evaluate the quality of the data obtained using different methods at different laboratories. The matching of the alkalinity data obtained by different specialists during different marine expeditions has its long-term history [15, 20], which showed that the interlaboratory discrepancy between different methods for the alkalinity determinations in seawater, as a rule, considerably exceeds the reproducibility of these methods. Thus, for example, the intercalibration of alkalinity measurements in a closed cell using the procedure by Edmond [12] performed at several laboratories in 1987 [20] gave disappointing results. The scattering of the data obtained at different laboratories amounted to about 200 $\mu\text{M}/\text{kg}$ (with the declared accuracy of the method of $\pm 2 \mu\text{M}/\text{kg}$); i.e., it was quite equal to the variability range of the alkalinity in the ocean.

A notable advance was made in this field owing to the Carbon Dioxide in the Ocean working group (WG13) founded in 1998 under the PICES North Pacific Marine Science Organization. This group headed by Prof. A. Dickson (Scripps Institution of

Table 1. Participants in the international experiment on the intercalibration of the methods for the total alkalinity determination in seawater performed by the WG13 working group of the PICES International Committee in 2000

Country	Institution	Participant name
Canada	Institute of Ocean Sciences, Sidney, B.C.	W.K. Johnson
Korea	Seoul National University, Seoul	D.-J. Kang
Russia	Il'ichev Pacific Oceanological Institute, Far East Division, Russian Academy of Sciences, Vladivostok	G.Yu. Pavlova
USA	NOAA Pacific Marine Environmental Laboratory, Seattle	R.A. Feely
	Scripps Institution of Oceanography, San Diego	A.G. Dickson
	University of Hawaii, Honolulu	Dore, John
Japan	Central Research Institute of Electric Power Industry, Abiko	K. Shitashima
	Hokkaido University, Sapporo	S. Watanabe
	Japan Marine Science and Technology Center, Yokosuka	A. Murata
	CREST: Japan Science and Technology Corporation & Hokkaido University, Sapporo	N. Tsurushima, S. Watanabe, Y. Nojiri
	& National Institute for Environmental Studies, Tsukuba	
	Kansai Environment Engineering Center Ltd., Osaka	K. Goto, K. Harada
	& National Institute for Resources and Environment, Tsukuba	
	University of the Ryukyus	H. Fujimura

Oceanography, USA) performed an international experiment on the intercalibration of the methods for measurements of carbonate system parameters using certified reference materials (CRM). The CRM are stable seawater samples in which the salinity, total inorganic carbon, and alkalinity were determined by means of high precision procedures.

In 2000, the WG13 carried out an experiment on the intercalibration of the total alkalinity measurements in seawater with the first participation of Russian specialists, who presented the procedure by Bruevich [2, 4]. Within the experiment, twelve laboratories were involved: six from Japan, three from the USA, and one from Canada, South Korea, and Russia each (the participants are listed in Table 1). For the intercalibration, the following methods were presented: potentiometric titration in a closed [12] and open [10] cell, the single addition procedure by Culberson [9], and the method by Bruevich [2]. Each of the participants received four series of various seawater samples (each series of four samples) from Prof. A. Dickson, who headed the experiment. Two series (CRM 50 with $S = 33.411\text{‰}$ and CRM 51 with $S = 34.22\text{‰}$) were certified standards prepared at the laboratory of Prof. Dickson. The other two series were prepared by Japanese specialists (00–A1 with $S = 35.38\text{‰}$ and the Deep Water with $S = 34.59\text{‰}$). The samples of all four series consisted of filtered seawater sterilized by means of UV irradiation. The alkalinity in the samples examined was determined to $\pm 1 \mu\text{M/kg}$ at the laboratory of Prof. Dickson [10]. The alkalinity test in the CRM is based on the coulometric procedure (by which an acid titre was determined at the

National Institution for Standards of the USA) and on the potentiometric titration in an open cell [10]. By now, the procedure of potentiometric titration in an open cell is thought to be the most precise and reliable tool to determine the total alkalinity in seawater [14]. The participants in the experiment knew the alkalinity value in the CRM 50 equal to $2211.11 \pm 0.95 \mu\text{M/kg}$. Later, when processing the results obtained, the CRM 50 alkalinity values measured by each of the participants were used to adjust the data of the other series to a unified calibration scale. The true alkalinity values in the samples of the other series were unknown. Each of the participants determined the TA values in the samples received by his or her laboratory and sent the results to the chief of the experiment.

The experiment performed appeared to be successful: after the conversion of all the data obtained to the unified calibration scale, most of the results of the alkalinity determination (ten of the twelve laboratories involved) fell into the range of $5 \mu\text{M/kg}$ (Fig. 1) [14]. However, the information published doesn't allow one to identify the technique used for intercalibration and the name of the experiment maker because the participation in the intercalibration was anonymous. Each of the participants was assigned an individual label (the letters from A to L in alphabetical order, Fig. 1). Because of this, here, we present all the data obtained by us using the method by Bruevich (Table 2). As seen from the table, for the certified standards (CRM 50 and CRM 51), the TA values obtained with the Bruevich method agreed very well (within $\pm 1 \mu\text{M/kg}$) with those obtained using the method by Dickson [10]. For the

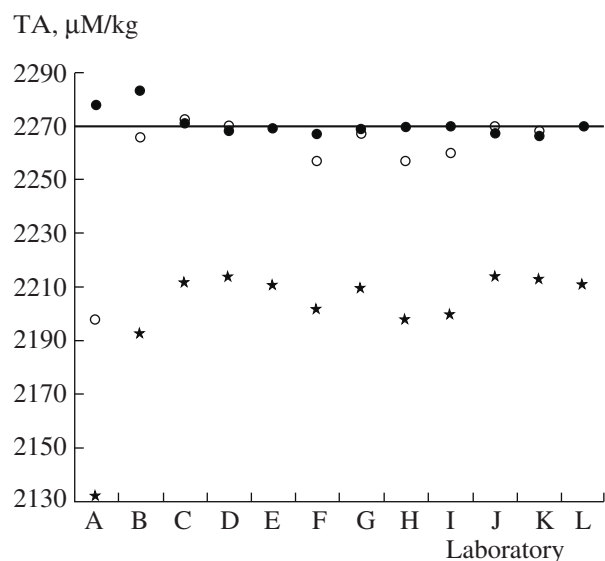


Fig. 1. Results of the alkalinity intercalibration (2000). The asterisks mark the values measured for CRM 50; the white circles mark the values measured for CRM 51; the black circles mark the values measured for CRM 51 and corrected to fit the common calibration scale. The horizontal line is the "true" alkalinity value in CRM 51. The figure is taken from [14].

samples prepared by the Japanese specialists, the discordance was greater and amounted to ± 3 $\mu\text{M}/\text{kg}$. As we suggest, this may be caused by the insufficient preparation accuracy of the Japanese samples. In some of the bottles, a sediment was observed; in others, microorganisms were found that were probably incompletely eliminated under the sterilization. The same causes, evidently, may explain the high value of the standard deviation (± 2.91 $\mu\text{M}/\text{kg}$) for the Deep Water sample (bottle 88). Unfortunately, the report on the intercalibration [14] did not consider the results obtained for the Japanese samples.

Thus, the intercalibration results showed that the Bruevich method agrees well with the commonly used procedures of potentiometric titration in a closed or open cell as well as with the single addition method.

Unlike the procedures of potentiometric titration, the Bruevich method is very easy and needs no complicated implementation (thermostating, expensive electrodes, computers). The method consists of the direct titration of 25 ml of seawater with 0.02N hydrochloric acid in an open cell [2]. To remove carbon dioxide, the titration was carried out under continuous blowing of the seawater samples with an inert gas or with air purified from carbon dioxide and ammonia. The end of the titration was determined visually from the solution color changing from greenish to light pink (pH 5.4–5.5 at the equivalence point). As an indicator, a mixture of methyl red and methylene blue alcoholic solutions was used. Because in the Bruevich method the equivalence point was determined visually by the changes in the

indicator color, the solutions of the acid and the standard were prepared with distilled water with low ionic forces. Hence, the error caused by the background alkalinity, which ranged from 10 to 30 $\mu\text{M}/\text{kg}$ [10] and appeared due to the commercial NaCl chemical used to prepare the acid solutions of high ionic force (0.7 M/kg), is absent within the Bruevich method. This strongly simplifies the procedure because the decrease in the background alkalinity requires a thorough purification of sodium chloride, including the recrystallization from the NaCl saturated solution in a chlorine atmosphere and drying at 550°C [10]. Unlike the methods of potentiometric titration, the alkalinity measurements using the Bruevich method contain no errors caused by the imperfect behavior of the measuring electrodes. It is known that the quality requirements for the measuring electrodes at potentiometric titration of alkalinity are high. Thus, for example, when using the procedure by Dickson, the pH measuring electrode is rejected if the value averaged over four or more alkalinity measurements in the CRM made during a day differs by more than 2 $\mu\text{M}/\text{kg}$ from the certified value or if the standard deviation of these measurements is over 1 $\mu\text{M}/\text{kg}$ [10]. The Bruevich method also provides a pronounced gain in the analysis quickness because the time required for the titration is about 10 min as compared to 20 min or more in the procedures of potentiometric titration.

Among the disadvantages of the Bruevich method, one must first note the visual fixation of the equivalence point, although the indicator color changes (i.e., the end of the titration occurs) under CO_2 blowing (pH ~ 5.4 , the condition for titration by the Bruevich method) at the sample overtitration by 0.0001 ml or below. According to our estimations, in this case, the variation in the pH value amounts to 0.040 units, which may be correctly determined even visually. As to the pH value change when 0.001 ml of HCl was added in excess of the equivalence point under titration in a closed cell (pH ~ 4.5), it amounts to about 0.004 pH units, which is quite difficult to register experimentally. The automation of the direct titration, i.e., either potentiometric or spectrophotometric detection of the equivalence point, is hindered due to the flow of air bubbles used during the titration. Moreover, we think that the automation of the direct titration of the alkalinity would simplify the measurement procedure for the analyst but not improve the quality of the measurements as such. Thus, at the potentiometric registration of the equivalence point, the experimenter should face the above-listed problems, and the spectrophotometric termination of the alkalinity titration would restrict the potentialities of the Bruevich method and make it unsuitable for turbid waters of rivers and estuaries.

The Bruevich method has been successfully used in Russian practice to determine the alkalinity in seawater for more than seven decades. When operating aboard a vessel, seawater samples are collected with an automatic pipette calibrated to ± 0.001 ml by weighing. To

convert the volumetric units into gravimetric units, the values of the seawater density at the temperature of the alkalinity determination are calculated. The titre of the hydrochloric acid is ascertained, as a rule, using a standard soda solution prepared by weighing, including the vacuum correction. For this purpose, the authors used Na_2CO_3 of 99.995% purity. The use of an automatic high-precision burette with a 0.001ml scale factor (BRINKMAN/Dosimat 665) allows one to determine the alkalinity in seawater by the Bruevich method with an accuracy up to ± 2.3 – $2.6 \mu\text{M/kg}$ under onboard conditions.

The CRM 50 and CRM 51 certified standards were titrated at a coastal laboratory with a lower error (± 0.54 – $1.68 \mu\text{M/kg}$, Table 2). When treating these samples, we made some modifications to the standard procedure of the alkalinity determination by the Bruevich method, which provided no worse measurement accuracy than the techniques used abroad:

(1) Weighed (accuracy to 0.0001 g) samples of seawater rather than aliquots were taken for the titration.

(2) The volumes of hydrochloric acid utilized for the titration were converted into weight units. To do this, the titrant temperature was registered throughout the titration process. The density of the 0.02N hydrochloric acid was determined by pycnometry. To calculate the acid density as a function of temperature, the temperature dependence for air-saturated water was used [11].

(3) All the weighed values (the seawater samples and the portions of hydrochloric acid and Na_2CO_3 used to determine the titre of the HCl) were used with the vacuum corrections.

(4) The burette used for the titrant supply was calibrated to ± 0.0007 ml.

(5) The titre of the hydrochloric acid was determined using three standard soda solutions of different concentrations and by four CRM samples (series 50, sample nos. 335, 358, 81, and 129). A comparison of the certified alkalinity value in the CRM 51 (sample 45) to that obtained by the Bruevich procedure and calculated using each of the seven titres obtained is shown in Fig. 2. As seen from the figure, the alkalinity values calculated in this way are in agreement with the standard within $\pm 1 \mu\text{M/kg}$, excluding the single value calculated using the titre found from CRM 129.

Thus, the validity of the usage of the express and simple Bruevich method to determine the alkalinity in seawater was first confirmed by an international experiment on intercalibration. The importance of this conclusion is mainly determined by the fact that foreign specialists are poorly informed about the Bruevich method, which often posed problems in the course of joint treatment of contemporary and historical data obtained by different procedures.

At present, the Bruevich method is the only tool to examine the alkalinity in interstitial solutions of marine sediments, because this method is suitable for analyzing small sample volumes and allows one to avoid the

Table 2. Results of the intercalibration experiment. The data are given in $\mu\text{M/kg}$ as the average value \pm standard deviation (number of analyses)

Sample	Certified alkalinity value	Alkalinity value obtained by the Bruevich method
CRM 50 (# 335)	2211.11 \pm 0.95	2211.03 \pm 1.36 ($n = 10$)
CRM 50 (# 358)		2209.78 \pm 0.67 ($n = 4$)
CRM50 (#81)		2211.95 \pm 1.68 ($n = 4$)
CRM 50 (# 129)		2210.41 \pm 1.08 ($n = 5$) average 2210.8
CRM 51 (#48)	2269.9	2268.48 \pm 1.37 ($n = 5$)
CRM 51 (#42)		2268.53 \pm 0.94 ($n = 5$)
CRM 51 (#45)		2269.95 \pm 0.56 ($n = 4$)
CRM 51 (#54)		2271.50 \pm 0.54 ($n = 3$) average 2268.5
Series 00-A1(#185)	2238.8	2233.91 \pm 0.61 ($n = 3$)
Series 00-A1 (# 045)		2230.23 \pm 0.16 ($n = 3$)
Series 00-A1 (# 086)		2232.26 \pm 1.24 ($n = 4$)
Series 00-A1(# 109)		2233.97 \pm 1.12 ($n = 3$) average 2232.6
Deep water series (no. 55)	2405.5	2410.89 \pm 1.30 ($n = 5$)
Deep water series (no. 30)		2409.67 \pm 0.98 ($n = 3$)
Deep water series (no. 88)		2399.7 \pm 2407.63 ($n = 6$)
Deep water series (no. 69)		2408.12 \pm 0.21 ($n = 3$) average 2410.3

errors caused by the oxidation of hydrogen sulfide during the titration.

The first determination of the alkaline reserve of interstitial solutions in marine sediments was probably made by Murray and Irvine [19]. However, systematic measurements of the alkalinity in interstitial water came to be carried out only by Soviet specialists. This became possible once S.V. Bruevich developed a procedure to determine the alkaline reserve in interstitial solutions based on the direct titration of small sample volumes (about 1 ml) in an open cell [3]. By means of this method, at the Institute of Oceanology of the Russian Academy of Sciences (Bruevich, Zaitseva, and Shishkina) and the All-Russia Scientific–Research Institute for Marine Fisheries and Oceanography (Gorshkova), a large data set was obtained on the alkaline reserve of interstitial solutions in the World Ocean. Foreign specialists, until the 1970s, paid no attention to the studies on the alkaline reserve in interstitial solutions. For example, reviews [13, 21] contain no data on the alkalinity determination. The studies on the alkaline reserve in interstitial waters were started abroad after

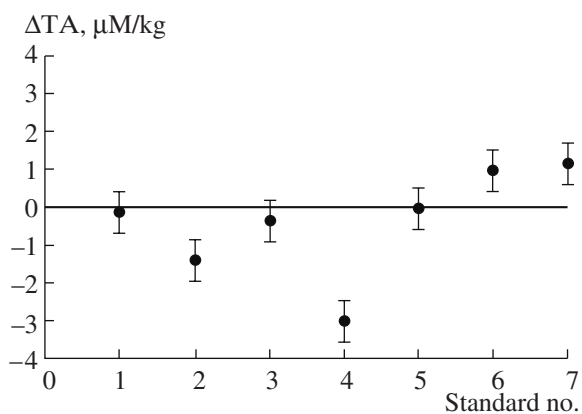


Fig. 2. Comparison of the certified alkalinity value in CRM 51 (sample 45) to the average TA values measured with the Bruevich method and calculated using the acid titres established with CRM 50 standards and soda solutions of different concentrations. The numbers comply with the following standards: 1—CRM 50 (no. 335); 2—CRM 50 (no. 358); 3—CRM 50 (no. 81); 4—CRM 50 (no. 129); 5—Na₂CO₃ no. 1; 6—Na₂CO₃ no. 2; 7—Na₂CO₃ no. 3.

Stumm and Morgan [23] proposed the method of potentiometric titration of the interstitial water alkalinity in a closed cell from small sample volumes (about 1 ml). As we think, the most interesting studies that used the method by Stumm to determine the alkalinity reserve of interstitial waters were performed by researchers from the USA [7, 18, 22] and Japan [16]. The fact that the oceanographic practice of the last decade includes almost no studies by foreign authors on the determination of the alkaline reserve in interstitial waters is probably related to the fact that the method by Stumm does not allow one to obtain any reproducible and reliable data, despite the declared accuracy of $\pm 0.5\%$.

We used the Bruevich procedure to determine the alkalinity in interstitial waters of the sediments from the Sea of Okhotsk in 1998–2004 [24–27]. The results obtained provided the basis for a series of modeling calculations and allowed us to better understand the processes of early diagenesis in reduced sediments [6, 28]. The experimental accuracy of the alkalinity determination in interstitial water using this procedure obtained by the authors from the analysis of parallel samples collected from the same layer was higher than that in seawater and amounted to $\pm 10 \mu\text{M/kg}$ (1σ) [25]. In the reduced sediments from the Sea of Okhotsk, for the first time, extremely high values of alkalinity and hydrogen sulfide were found (up to 120 and 15 $\mu\text{M/kg}$, respectively). The subject of our special study was the problem of the features of the alkalinity reserve determination in an environment with high H₂S contents [25]. Parallel tests of the samples using the Bruevich method showed that the alkalinity value of the interstitial water from reduced sediments decreased with the sample storage time. We think that the decrease in the alkaline reserve may be caused by two processes: carbonate pre-

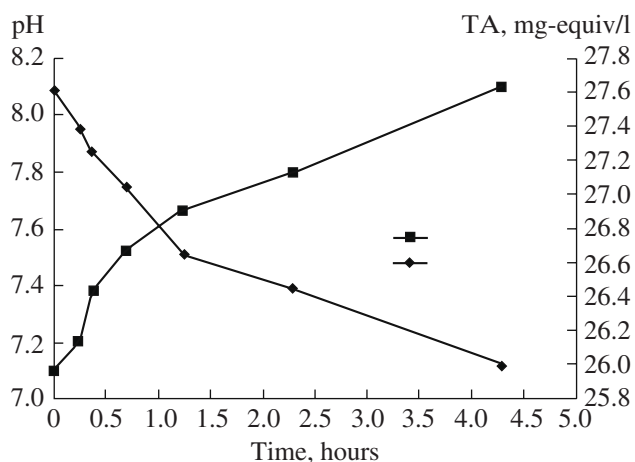
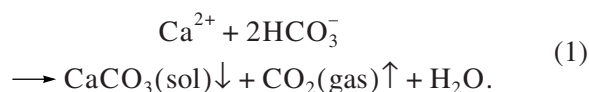
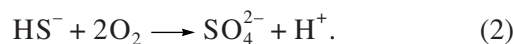


Fig. 3. Oxidation of a sulfide solution ($\sim 30 \mu\text{M}$ of H₂S in 0.5 M NaCl) under contact with the air at room temperature.

cipitation and sulfide oxidation. The precipitation of carbonates results from the removal of CO₂ and H₂S from the interstitial water to the atmosphere:



Sulfide is oxidized by molecular oxygen under contact with air:



The rate of sulfide oxidation and the effect of this process upon the total alkalinity value were studied by the authors under onboard conditions [25]. To do this, a 30-mM solution of Na₂S prepared in the background of 0.5 M NaCl was acidified to pH = 7.1 with a concentrated hydrochloric acid; then, aliquots of this solution were titrated with hydrochloric acid during several hours at a room temperature (24–25°C). The data presented in Fig. 3 show that the alkalinity value considerably decreases during several hours. The simultaneous increase in the pH value of the solution observed by us points to the fact that the release of CO₂ to the atmosphere (reaction 1) proceeds faster than the H₂S oxidation (reaction 2). As a rule, during a cruise, the alkalinity of reduced samples was determined two hours after the interstitial water squeeze. The data presented in Fig. 3 show that up to 10% of the total alkalinity may be lost in this short time. The actual alkalinity losses would be lower than the values obtained at room temperature because, after squeezing, the samples of interstitial water are kept in a refrigerator at a temperature of about 4°C. Nevertheless, it is desirable that the time from the squeezing of the interstitial water to the alkalinity determination in it should be minimal.

Thus, the results of the intercalibration showed that the alkalinity values obtained by the Bruevich method using modern burettes, Na₂CO₃ of high purification

degree as a standard to establish the acid titre, and applying correction for the acid density and for the weight of the acid and seawater samples in vacuum are in agreement with the standard within $\pm 1 \mu\text{M}/\text{kg}$. Under field conditions, the usual accuracy of the method for seawater analyses is equal to $\pm 2.5 \mu\text{M}/\text{kg}$. The method presented is easy and well applicable to the microanalysis of interstitial waters of marine sediments.

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