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# Validation of method for determination of total carbon, inorganic carbon and total organic carbon in marine waters

## Walidacja metody oznaczania węgla całkowitego, nieorganicznego i organicznego w wodach morskich

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**Abstract:** Validation is a process of setting parameters characterizing the proficiency of actions and limitations of a method and an assessment of its usefulness for particular purposes. As a result, it ensures that the analysis process is carried out in a reliable and precise way and gives reliable results. Marine water , as well as the addition of standard solutions were used for the validation process. Uncertainty in the results, limit of quantification, precision, repeatability and reproducibility, recovery and accuracy of the method were obtained. This paper discusses the results of the validation of the method for determination of total inorganic and organic carbon in marine waters. For this purpose, a Shimadzu analyser TOC-L was used. The discussed method is based on infrared detection NDIR. A halogen scrubber type B was used to determine the compounds. This allowed to shorten the analysis time at the stage of sample preparation. It increased the absorption of salt contained in a sample, as a result of which the dilution stage could be omitted, and the final result is affected by a smaller error. The method of validation of determination of total inorganic and organic carbon received accreditation of the Polish Centre for Accreditation and joined a wide range of the analyses carried out in the Laboratory of the Department of Environment Protection of the Marine Institute in Gdańsk.

**Keywords:** total organic carbon, seawaters, marine waters, total carbon, inorganic carbon, validation

**Streszczenie:** Walidacja jest procesem ustalania parametrów charakteryzujących sprawność działania i ograniczeń metody oraz sprawdzeniem jej przydatności do określonych celów. W efekcie można uzyskać pewność, że proces analizy przebiega w sposób rzetelny i precyzyjny oraz daje wiarygodne wyniki. Do procesu walidacji wykorzystano wodę morską, a także tą samą wodę z dodatkami wzorców. Walidacja metody pozwoliła na określenie takich parametrów, jak: niepewność wyników, granica oznaczalności, precyzja, powtarzalność i odtwarzalność, a także odzysk i dokładność metody. W niniejszej pracy omówione zostały wyniki walidacji metod oznaczania węgla całkowitego, nieorganicznego i organicznego w próbkach wody morskiej. W tym celu wykorzystano analizator TOC-L firmy Shimadzu. Omawiana metoda polega na detekcji w podczerwieni NDIR. Do przeprowadzenia badań zastosowano skruber halogenów typu B. Pozwolił on na skrócenie czasu analizy na etapie przygotowania próbki. Zwiększył on pochłanianie soli zawartej w próbce, w wyniku czego można było pominąć etap rozcieńczania, a wynik końcowy obarczony jest mniejszym błędem. Metoda oznaczania węgla całkowitego, nieorganicznego i organicznego uzyskała akredytację Polskiego Centrum Akredytacji i dołączyła do szerokiego grona analiz wykonywanych w Laboratorium Zakładu Ochrony Środowiska Instytutu Morskiego w Gdańsku.

**Słowa kluczowe:** ogólny węgiel organiczny, wody morskie, węgiel całkowity, węgiel nieorganiczny, walidacja



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## INTRODUCTION

Environmental pollution is one of the biggest problems resulting from the development of civilization. In order to determine the level of pollution, summary indicators of the pollution level are used; they include total, inorganic, and organic carbon [9].

The Baltic Sea is one of the shelf seas which play a significant role in organic matter exchange between the land, the ocean, and the atmosphere [3]. Inorganic matter in water has two sources: natural and anthropogenic. Natural sources may include humic compounds, matter exchange products, as well as river estuaries [3,4]. Anthropogenic compounds include: phenols, surfactants, polycyclic aromatic hydrocarbons, pesticides, oil-deriving compounds [4]. The analysis of total organic carbon (TOC) allows all organic compounds to be estimated in an analyzed sample [7]. This indicator is normalized by the Polish legislation [8]. The determination of total organic carbon (TOC) can take place with the use of various methods, e.g., infrared spectrophotometry, titration, conductometry [5].

Total organic carbon (TOC) is a physicochemical indicator which allows the condition of water to be assessed. The value of this indicator in transitional and coastal waters should be: ≤5 mg/dm$^3$ for class I waters, and ≤10 mg/dm$^3$ for class II waters. These parameters were defined in the Polish legislation as part of the implementation of the Marine Strategy Framework Directive. The purpose of achieving these values is to ensure the good condition of the marine water environment before 2020 [8]. The purpose of this article is to present the validation of a method for determination of total, inorganic and organic carbon in marine waters with the use of infrared spectrometry, based on Standard PN-EN 1484:1999 [5].

## MATERIAL AND METHODS

### Samples

Samples of seawater were collected in a cruise at the Baltic Sea. The sampling procedure followed the Standard PN-ISO 5667-3:2005, the samples were stored in glass bottles filled up to the cork. To avoid potential biological activity after sampling, the samples were acidified to pH=2, and then kept in a temperature of 2-5 oC [5]. For assessment of repeatability and reproducibility the following solutions were added to the seawater samples with salinity 7.5 PSU [11]: potassium hydrogen phthalate of Merck company, 122400X lot, sodium carbonate of POCH CAS: 497-19-8, and sodium bicarbonate of SIGMA-ALDRICH, lot SZBE2410V were used. The basic concentration of the standards was 1000 mg/dm$^3$, before the addition to the samples, the standards were diluted and the results are presented in the tables I-IV.

To determine correctness and accuracy, certified reference material QCI-040 lot 017494 from RTC, SIGMA-ALDRICH was used. The limit of quantification (LOQ) is the lowest possible concentration of an analyte that can be determined on an acceptable level of repeatability, precision, and correctness. The working range is a span between the minimum and maximum level of concentration obtained via a given research method keeping and acceptable level of repeatability, precision, and correctness [12].

The accuracy of measurement is the degree to which its result complies with a certain accepted true value of the quantity subjected to measurement [12].

Repeatability is the precision of determinations carried out by the same analyst, in the same laboratory, with usage of the same method and the same equipment within a short period of time [12].

### Research method

The content of organic carbon was determined after the combustion of organic compounds into carbon dioxide [2].

Total carbon, inorganic and organic, was determined with the catalytic oxidation method through combustion at a temperature of 6800C, with a TOC-L analyser of the Shimadzu corporation [1].

Determination of total carbon (TC)

The water sample entered into a combustion pipe, filled up with a platinum catalyst, where it was subjected to combustion into carbon dioxide at a temperature of 6800C. This gas was cooled down and drained, then it went to a halogen scrubber, where chlorine, among others, was removed. Infrared detection (NDIR) is the last stage of determination.

Determination of inorganic carbon (IC)

The sample is moistened with a reactive solution (25% orthophosphate acid). The sample acidified in such a way is blown with carrier gas to the IC reactor, where carbon dioxide is determined with an NDIR detector.

Determination of organic carbon (TOC)

Organic carbon is determined on the basis of calculations. It constitutes the difference between total and inorganic carbon.

$$TOC = TC - IC$$

### Results and Discussion

The limit of quantification LOQ is the smallest quantity of substance that can be determined quantitatively with the use of a certain analytical method with assumed accuracy and precision. The lower limits for total carbon, inorganic and organic were estimated on the basis of a series of analyses; the results are presented in Tables I.

A draft range for total inorganic and organic carbon is 0.5-500 mg/dm$^3$. Due to such a wide range of determination, calibration curves were divided into two parts (Fig. 1-4).

**Tab. I.** Summary of scores of the lower limit of quantification.

| FORM OF DETERMINED CARBON | STANDARD CONCENTRATION [mg/dm³] | PRECISION [%] | RECOVERY [%] | ABSOLUTE ERROR | MATRIX |
|---|---|---|---|---|---|
| TC | 0.50 | 2.72 | 104 | 0.038 | Deionized water with the standard addition |
| | 0.50 | 3.59 | 101 | 0.027 | Marine water with the standard addition |
| IC | 0.50 | 10.9 | 128 | 0.14 | Deionized water with the standard addition |
| | 0.50 | 8.87 | 97.8 | 0.04 | Marine water with the standard addition |
| TOC | 0.50 | 2.28 | 102 | 0.014 | Deionized water with the standard addition |
| | 0.50 | 3.53 | 106 | 0.03 | Marine water with the standard addition |

**Tab. II.** Summary of the validation scores for total carbon.

| DETERMINED VALUE [mg/dm³] | PRECISION [%] | RECOVERY [%] | ABSOLUTE ERROR | MATRIX |
|---|---|---|---|---|
| 1 | 2.72 | 104 | 0.038 | Deionized water with the standard addition |
| 1 | 3.59 | 101 | 0.027 | Marine water with the standard addition |
| 5 | 0.38 | 110 | 0.509 | Deionized water with the standard addition |
| 5 | 0.91 | 102 | 0.09 | Marine water with the standard addition |
| 10 | 0.94 | 112 | 1.23 | Deionized water with the standard addition |
| 10 | 1.41 | 97.2 | 0.28 | Marine water with the standard addition |
| 100 | 1.85 | 95.9 | 4.11 | Deionized water with the standard addition |
| 100 | 4.36 | 104 | 3.99 | Marine water with the standard addition |
| 500 | 1.18 | 107 | 37.3 | Deionized water with the standard addition |
| 500 | 6.34 | 103 | 25.77 | Marine water with the standard addition |

**Tab. III.** Summary of the validation scores for inorganic carbon.

| RECOVERY CONCENTRATION [mg/dm³] | PRECISION [%] | RECOVERY [%] | ABSOLUTE ERROR | MATRIX |
|---|---|---|---|---|
| 0.5 | 10.9 | 128 | 0.14 | Deionized water with the standard addition |
| 0.5 | 8.87 | 97.8 | 0.04 | Marine water with the standard addition |
| 2.5 | 2.24 | 106 | 0.15 | Deionized water with the standard addition |
| 2.5 | 2.69 | 99.4 | 0.05 | Marine water with the standard addition |
| 5 | 1.67 | 100 | 0.07 | Deionized water with the standard addition |
| 5 | 3.90 | 97.0 | 0.22 | Marine water with the standard addition |
| 50 | 0.36 | 99.0 | 0.52 | Deionized water with the standard addition |
| 50 | 3.07 | 106 | 3.08 | Marine water with the standard addition |
| 100 | 0.57 | 105 | 4.76 | Deionized water with the standard addition |
| 100 | 2.10 | 105 | 4.92 | Marine water with the standard addition |

## Precision, repeatability, accuracy

Accuracy is the degree of closeness of the score to the agreed true measured value [6].

Repeatability is the precision of determination analyses carried out by the same analyst, in the same laboratory, with the use of the same method and the same equipment, within a short period of time [6].

Validation values for total carbon in marine waters are presented in Table II. Obtained repeatability of the method within the range of 0-10 mg/dm³ was 9.5 %, and within the range of 10- 500 mg/dm³ - 3.0 %.

The validation scores for inorganic carbon in marine waters are presented in Table III. The obtained repetitiveness of the method within the range of 0-10 mg/dm³ was 23.4%, and within the range of 10-500 mg/dm³ - 8.1%.

The validation scores for organic carbon in marine waters are presented in Table IV. Repeatability of the method obtained within the range of 0-10 mg/dm³ was 14.2 %, and within the range of 10-500 mg/dm³ -26.2%. Organic carbon was calculated from the difference of total carbon and inorganic carbon.

Correctness was estimated through the comparison of obtained scores with the known value of the certified reference material and presented in Table V.



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**Tab. IV.** Summary of the validation scores for organic carbon.

| DETERMINED VALUE [mg/dm³] | PRECISION [%] | RECOVERY [%] | ABSOLUTE ERROR | MATRIX |
|---|---|---|---|---|
| 0.5 | 2.28 | 102 | 0.01 | Deionized water with the standard addition |
| 0.5 | 3.53 | 106 | 0.03 | Marine water with the standard addition |
| 2.5 | 1.46 | 114 | 0.35 | Deionized water with the standard addition |
| 2.5 | 5.38 | 102 | 0.11 | Marine water with the standard addition |
| 5 | 3.45 | 121 | 1.0 | Deionized water with the standard addition |
| 5 | 2.38 | 95.1 | 0.24 | Marine water with the standard addition |
| 50 | 3.34 | 93.0 | 3.5 | Deionized water with the standard addition |
| 50 | 8.00 | 100 | 3.3 | Marine water with the standard addition |
| 200 | 2.50 | 105 | 10.4 | Deionized water with the standard addition |
| 200 | 9.92 | 104 | 19.4 | Marine water with the standard addition |

**Tab. V.** Comparison of the results of the certified reference material analysis QCI-040 lot. 017494. Permissible range for total carbon: 93.1±1.57 mg/dm³.

| REFERENCE VALUE [mg/dm³] | DETERMINED VALUE [MG/DM³] | RECOVERY [%] | ABSOLUTE ERROR |
|---|---|---|---|
| 93.1 | 93.3 | 100 | 0.2 |
| 93.1 | 94.8 | 102 | 1.7 |
| 93.1 | 95.2 | 102 | 2.1 |
| 93.1 | 93.4 | 100 | 0.3 |
| 93.1 | 95.0 | 102 | 1.9 |
| 93.1 | 95.4 | 102 | 2.3 |
| 93.1 | 92.2 | 99.0 | 0.9 |
| Mean | 94.2 | 101 | 1.3 |
| SD | 1.21 | | |
| RSD | 1.29 | | |

**Tab. VI.** Results of proficiency research.

| NO. | ASSIGNED VALUE [mg/dm³] | STANDARD DEVIATION OF THE SURVEYS | DETERMINED VALUE [MG/DM³] | RELATIVE ERROR [%] | REPRODUCIBILITY [%] |
|---|---|---|---|---|---|
| 1 | 1065 | 273.7 | 1134 | 6.48 | 23.25 |
| 2 | 1065 | 273.7 | 1258 | 18.1 | |
| 3 | 1065 | 273.7 | 1188 | 11.6 | |
| 4 | 1065 | 273.7 | 1128 | 5.92 | |
| Mean | 1065 | 273.7 | 1177 | 10.5 | |

**Tab. VII.** Summary of the validation scores for marine waters.

| NO. | ASSIGNED VALUE [mg/dm³] | STANDARD DEVIATION OF THE SURVEYS | DETERMINED VALUE [mg/dm³] |
|---|---|---|---|
| TC | 0.5-10 mg/dm³ – 3.59 %<br>10-500 mg/dm³ – 6.34 % | 5 % | 0.5-10 mg/dm³ – 10 %<br>10-500 mg/dm³ – 20 % |
| IC | 0.5-10 mg/dm³ – 8.87 %<br>10-500 mg/dm³ – 3.07 % | 5 % | 0.5-10 mg/dm³ – 24 %<br>10-500 mg/dm³ – 20 % |
| TOC | 0.5-10 mg/dm³ – 5.39 %<br>10-500 mg/dm³ – 9.92 % | 5 % | 0.5-10 mg/dm³ – 17 %<br>10-500 mg/dm³ – 30 % |

## Comparative research results

The Laboratory of the Department of Environment Protection took part in an inter-laboratory comparative research organized by CLP-B LABTEST as part of validation of the method for organic carbon determination. The results of this research are presented in Table VI.

## Discussion and conclusion

The validation of the method allowed us to determine parameters such as: uncertainty in the results, limit of quantification, precision, repeatability and reproducibility, as well as recovery and accuracy of the method. The summary of the obtained values is presented in Table VII.

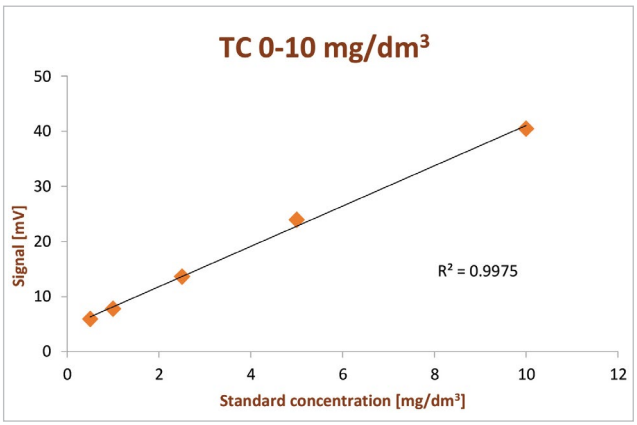


**Fig. 1.** Calibration curve of total carbon within concentration range of 0-10 mg/dm³.

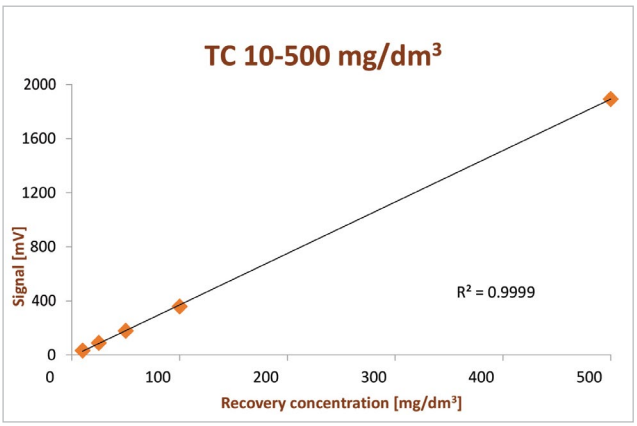


**Fig. 3.** Calibration curve of total carbon within concentration range of 10-500 mg/dm³.

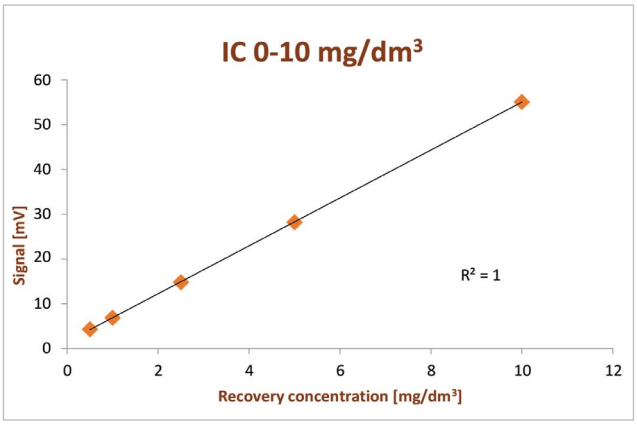


**Fig. 2.** Calibration curve of total inorganic carbon within concentrations range of 0-10 mg/dm³.

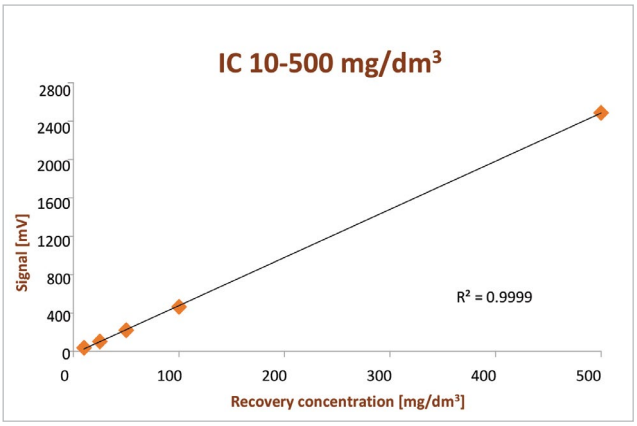


**Fig. 4.** Calibration curve of total inorganic carbon within concentration range of 10-500 mg/dm³.

Measurement uncertainty is characterizing the dispersion of the values attributed to a measured quantity [10]. Expanded uncertainty constitutes the product of a complex uncertainty which is calculated for many components, such as uncertainty of the standard, flask, certified material, precision [10].

Credibility and reliability of the developed testing procedures were confirmed by the positive results of the QCI-040 lot. 017494 certified reference material's analysis, and of comparative (interlaboratory) research. Table V and VI contains a summary of the results.

The studies carried out allowed the following conclusions to be drawn:

- in order to obtain better repeatability and precision of results, the analysis should be carried out as soon as possible (ideally within 24 hours), particularly if we expect low concentrations and the presence of volatile substances. If there is no other option, the sample should be frozen or acidified with concentrated sulfuric acid (VI) to pH = 2, and the determination should be carried out within 7 days,
- this method enables high recovery values to be achieved,
- in the case of samples with high salinity, e.g., marine waters, the use of type B halogen scrubber is a perfect solution. It stops higher concentrations of salt than a standard absorber, due to which it is possible to analyze samples with concentration of salt even up to 3%. This means that there is no need to dilute the sample earlier, and the final result itself is vitiated with a smaller error,
- the determination method of total inorganic and organic carbon joined the wide range of analyses carried out in the Laboratory of the Department of Environment Protection, and it received accreditation of the Polish Centre for Accreditation in 2016.

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