

TECHNIQUES FOR MEASURING THE CONTENT OF DISSOLVED ORGANIC CARBON IN NATURAL WATERS

S.V. Lyutsarev and V.V. Chubarov

*P.P. Shirshov Institute of Oceanology,
the Russian Academy of Sciences, Moscow*

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Variations of the dissolved organic carbon (DOC) in natural waters is important not only for studies of the Global Carbon Cycle but also in the optics of hydrosphere (color, turbidity, and fluorescence properties) and atmosphere (greenhouse effect). In this paper we present a short overview of basic techniques for the determination of the DOC and pay special attention to the lively discussion that takes place in the literature about the choice of an optimal measurement technique. Finally, we propose an original technique of measuring DOC and a facility to perform it, namely, the Lyutsarev carbon analyzer (LCA). Some results obtained with LCA during the expedition onboard "Il'ya Repin" ship on Volga river in summer of 1993 are discussed.

The task of assessing the store and concentration of organic matter in the hydrosphere in general and in terrain and ocean waters in particular is essential in tackling such problems of the atmospheric and ocean optics as the greenhouse effect of the atmosphere, the color of ocean water, water transparency in various spectral regions, underwater illumination, etc. The greenhouse effect, to which carbon dioxide makes the most significant contribution, is of particular importance. Accumulation of the CO₂ in the atmosphere, as a result of anthropogenic pollution, is partially eliminated by solution in natural surface waters, followed by transformations into the suspended and dissolved organic matter, as a result of photosynthesis by phytoplankton and higher plants. Besides, a significant portion of humic matter from land also comes to rivers and seas. An increasing inflow of organic matter to ocean waters affects the carbon cycle in the ocean—atmosphere system, which in the nearest decades is likely to cause a significant increase in the dissolved organic matter content of surface ocean waters.¹ Therefore, correct assessment of dissolved organic matter content of natural waters is of primary importance for understanding of the geochemical and physical processes occurring in the ocean and the atmosphere.

For nearly three decades the world scientific community have had discussions about the correctness of various chemical methods used for determination of total organic matter in natural waters, especially in sea waters. Since carbon is the main element of all organic compounds, the data on organic carbon content can serve as the most representative indicator of the organic matter content. The calculated ratio between organic matter and organic carbon weights for natural waters is approximately equal to two.

In recent years, however, the problem on unification of methods for determining the dissolved organic carbon (DOC) concentration in ocean waters has become a subject of discussions again. This problem has arisen because the instrumental express methods of wet persulfate or dry high-temperature oxidation (using fast probe injection), widely practised in other countries, turned out to be incorrect, although a great bulk of data has been compiled using these methods. On July 15–19, 1991 an international conference "Measurement of Dissolved Organic Carbon and Nitrogen" on this problem was held in Seattle (USA).²

Early in the 20th century, attempts to develop chemical methods for determination of organic carbon content were undertaken. However, neither P^UHttner nor the Raben method yielded satisfactory results. The major disadvantage to these methods is that the oxidation of sea water samples with a chromic mixture yields a large amount of pure chlorine along with the carbon dioxide what essentially distorts the results on measuring the carbon dioxide content.

The first technique provided the reliable results was the Krogh—Keys one.³ Specific feature of this technique is in separation out of the main portion of chlorides from a sea water sample as poorly soluble in water thallium chloride, prior to further chemical analysis. The sequence of the procedure steps described in Ref. 3 is as follows. First, a sea water sample analyzed is acidified with a strong mineral acid to eliminate carbon dioxide formed from carbonates. Then thallium sulfate solution is added to the reaction mixture to form thallium chloride and make it to precipitate that helps one to eliminate virtually all chloride ions. Following centrifugation, the precipitate formed is separated out and the mother solution is carefully evaporated till dry. In order to avoid penetration of extraneous impurities into the sample and to prevent any sputtering of the solution, the evaporation is accomplished by radiant heating. The resulting dry rest is transferred into a special flask and is subjected to "wet" combustion in the presence of cerium chromate mixture.

The oxidation of the organic matter in a sample results in a release of carbon dioxide, and thus formed in the combustion flask, CO₂ is swept off by the carrier gas and transported into Reberg absorption vessels to be absorbed by titrated BA(OH)₂ solution. The amount of BaCO₃ formed is determined by back titration of the excess of Ba(OH)₂.

Among the method's attractive features is the use of a catalyst-containing tube for gas—phase combustion of volatile carboniferous substances, mainly the carbon monoxide. Successive layers of platinum foil, copper oxide, and chromous lead heated to 400 ... 500°C serve as a catalyst.

Measurement error of the Krogh—Keys method is ±0.1 mg C/l. The method's instrumentation is relatively

simple. However, in order to provide a required precision, adequate skill of the analyst is needed in order to minimize the chance for sample loss and contamination. The procedure is not free of drawbacks. The use of a rare and highly toxic thallium salts, loss of organic substances as a result of occlusion by the thallium chloride precipitate, loss of volatile organics during evaporation of a sample to dryness; subjectiveness of visual titration are to be mentioned among such drawbacks.

Despite the said shortcomings, the Krogh–Keys method long remained the only available technique useful for analysis of saline and sea waters. Datsko^{4,5} and Skopintsev⁶ were the first who used this method in the USSR. They have also proposed a modified procedure.

In 1950 a combustion technique was proposed that was radically different than a conventional used, i.e., combustion in saltpeter melt.⁷ The method is based on the decomposition of saltpeter upon melting ($T_{\text{melt}} = 334^{\circ}\text{C}$) followed by a release of oxygen $2\text{KNO}_3 = 2\text{KNO}_2 + \text{O}_2$.

Analysis is performed by mixing the dry rest left after evaporation of the acidified sea water sample with saltpeter followed by heating the mixture in a special combustion flask till it melts down. As this takes place, oxidation of the organic carbon occurs to give carbon oxide and carbon monoxide and a small amount of nitrogen oxides, with only an insignificant amount of chlorides (if any) being subjected to decomposition under the reaction conditions. The evolving gases are swept off by the carrier gas (purified air) to be transported to the tube containing platinum and copper oxide catalyst heated to $400 \dots 450^{\circ}\text{C}$. The volatile products of incomplete combustion contact the catalyst are fully oxidized. The nitrogen and sulfur oxides are absorbed by sulfuric bichromate solution and concentrated sulfuric acid, while the chlorine is absorbed by the potassium iodine solution containing starch.

The gas free from impurities passes through the Reberg absorption vessels filled with titrated $\text{Ba}(\text{OH})_2$ solution. Then back titration of this solution is carried out using hydrochloric acid to determine the amount of CO_2 that released from a sample burnt and consequently the organic carbon content. The final step of the procedure is visual titration with $\text{Ba}(\text{OH})_2$ solution. Chief advantage of this method is the absence of silver and thallium chlorides precipitate. Among its drawbacks the loss of volatile compounds, visual titration, the necessity of introducing a correction for a blank test should be mentioned. Further development of this method in application to highly mineralized waters has been done by other research groups.

In 1957 Krylova proposed a technique for analysis of the organic carbon in natural waters based on burning dry residue that is left after sample evaporation to dryness.⁸ Later on the technique was elaborated especially for sea water analysis.⁹ The main feature of the technique essence is that after the evaporation to dryness of a sea water sample, acidified with a precise amount of mineral acid, carried out in a weighting bottle at temperature below 60°C , the resulting dry residue is kept till final analysis could be made at a coastal laboratory.

The dry residue is transferred into a special quartz beaker, great care being taken to avoid any loss of the material. The quartz beaker is placed into a widening section of a quartz tube of a combustion unit which is then blown through with air or oxygen free from carbon dioxide. Then the Reberg vessels containing $\text{Ba}(\text{OH})_2$ solution are connected to the unit and fast pyrolysis of the quartz beaker content is carried out, corresponding section of the quartz tube being heated with gas burner flame. The pyrolysis and

combustion are to be completed within 10 to 15 min. The combustion products flowing through the narrow section of the quartz tube pass over platinum foil which acts as a catalyst of full oxidation. This section of the quartz tube is heated by an electric furnace to 900°C .

Inside the tube before and after the platinum foil, metallic silver is placed for pre-trapping of chlorides and sulphur oxides. The carrier gas leaving the quartz tube sweeps off the carbon dioxide to get into a series of wash bottles where the remaining chlorine and sulfur and nitrogen oxides are trapped. The carbon dioxide is absorbed by $\text{Ba}(\text{OH})_2$ solution in the Reberg vessels. Upon completion of the combustion and blowing through of the unit with a fresh portion of the carrier gas, titration of $\text{Ba}(\text{OH})_2$ solution is carried out with 0.02 N hydrochloric acid. Thus, use of the back titration allows one to determine first the amount of the barium carbonate formed and then the organic carbon content in the sample analyzed.

The method's advantages are the absence of loss of organics as a result of occlusion by sparingly soluble chlorides precipitate, insignificant chlorine evolution, no correction for a blank trial required. The method's shortcomings are the loss of volatile organics at sample evaporation to dryness, prolonged evaporation of sea and ocean water samples in weighting flasks, necessity of taking special care to avoid extraneous organics getting into the sample during its prolonged evaporation, laborious operation of transferring the dry residue into a quartz beaker prior to combustion, and subjectivity of the visual titration. In a number of cases, these drawbacks are of secondary importance, therefore, new modifications of the "dry" combustion method still appear. Specifically, it has found a use in analysis of highly mineralized and underground waters.

In 1955 Forsblad described a version of "wet" combustion of the dry residue that is left after a sample evaporation.¹⁰ According to his method, evaporation of a 200 ml sample is carried out in a special flask into which a relevant quantity of phosphoric acid is added which is equivalent to the content of Cl^- , CO_3^{--} , and HCO_3^- . All of the aforementioned ions volatilize under evaporation conditions at a reduced pressure. Then the flask containing the dry residue is connected to an apparatus of simple design and 10 ml of an oxidizing mixture (1.5 g of KJO_3 , 15 g of CrO_3 , 30g of P_2O_5 , 130 ml of H_2SO_4 , and 25ml of H_3PO_4) is added into it. Oxidizing mixtures of this type have been proposed and improved by Van Slyke.¹¹ After the sample—oxidizer mixture is heated up to the boiling point for 10 min, the carbon dioxide evolved is absorbed by 20 ml of $\text{Ba}(\text{OH})_2$ solution which is then titrated by hydrochloric acid first to pH equal to 10 and then to 3.5. During the second titration barium carbonate decomposition occurs being unimpeded by the chlorides and sulfates present. The accuracy of measurement for a sample containing 2 mg of organic carbon is 1%, full time of analysis being 75 min (see Ref. 11).

Kay¹² used a "wet" combustion method to analyze natural samples. The method consists in the addition of an oxidizing mixture ($\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Ag}_2\text{Cr}_2\text{O}_7$, and concentrated H_2SO_4) directly to a water sample placed into a special apparatus in the ratio of 1:1. When the liquids mix, the silver that bonds most of Cl^- precipitates from the solution. Further combustion is carried out at 130°C . The final step is visual back titration of the $\text{Ba}(\text{OH})_2$ solution. Disadvantages of the method are as follows: long analysis time (about 3.5 h), uncertainty, complexity of the apparatus

design, imperfection of visual titration, necessity of making a blank test correction.

Kay's method was developed in the work by Duursma¹³ who increased sample volume up to 50 ml, used a new version of the apparatus and replaced visual titration for manual coulometric one. This resulted in a simplification of some operations; however, the major drawbacks remained, i.e., brittleness and complexity of the apparatus, necessity of oxygen gas-bag use, coulometric manual titration, possibility of CO₂ bubbles discharge through the absorbing solution, long analysis time, necessity of making a blank test. According to the author the method reproducibility is 0.03 mg C/l.

In 1959 Beisova and Kryukov¹⁴ studied the capabilities of conductometric analysis in a carrier gas for the determination of DOC in natural waters. The authors used two "wet" combustion procedures, i.e., persulfate oxidation of the initial or a partially evaporated sample and oxidation of the dry residue that is left after sample evaporation in iodic, chromic, sulfuric, and phosphoric acid mixture. Purified carrier gas together with the oxidation products gets into a spiral absorber with platinum electrodes. The absorber is filled with Ba(OH)₂ solution whose electrical conductivity varies due to CO₂ absorption. Measurements were carried out manually with a precision conductometric apparatus. This method's sensitivity is 1 ... 3 µg C; it is limited by the instability of the blank experiment. The reproducibility is equal on the average to 2.5%.

The final conductometric step of analysis of sea water for DOC was used in the work of Krey and co-workers.¹⁵ The authors adopted Kay's method, but they simplified the apparatus for sample combustion and gas purification. As the oxidation catalyst AgMnO₄ was used. The conductometric cell was filled with NaOH solution. Automatic titration enabled monitoring of the combustion process and termination of the analysis at a proper moment. These improvements resulted in shorter analysis time (20 min), the reproducibility of results for standard solutions of oxalic acid being 2 µg C.

Among the existing sensitive physical methods for CO₂ determination, IR spectroscopy, flame ionization, and thermal conductivity measurement techniques are in a wide use. An interesting method has been proposed in Ref. 16. The authors used a commercial gas chromatograph for CO₂ and CO determination in the oxidation products of water suspension samples. In principle, the method can be used for DOC determination in sea water; however, it was not widely adopted.

Wilson¹⁷ has proposed a simple version of DOC analysis of sea water following "wet" combustion of a sample with the aid of K₂S₂O₈, the final CO₂ determination being carried out with a nondispersive infrared gas analyzer. The method's reproducibility is about 7%.

A substantial improvement of the method was proposed by Van Hall and co-workers.¹⁸ An 0.02-ml water sample is injected into a quartz tube containing a platinum catalyst heated up to 950°C. The water vapor and oxidation products are swept off by oxygen. On cooling down and condensation of water, the gas comes into the cell of an infrared gas analyzer. The analysis duration is about 2 min. Later on the method was improved. Today the apparatus based on this principle is commercially available.

A version of the "wet" combustion method for DOC determination using infrared gas analyzer is described by Menzel.¹⁹ The oxidation of a 5-ml sample is carried out in a sealed ampul made from pyrex and filled with K₂S₂O₈ solution at 130°C during 30 min. The final determination is

performed at a shore laboratory where the ampul is opened and blown with nitrogen in a special apparatus and where the CO₂ quantity is measured using an infrared gas analyzer. To allow for a blank test correction, analysis is made of "carbon-free" water sample into which a known quantity of standard organic matter is added. According to the authors, a blank test for samples having carbon concentration of 4 mg C/l gave 0.5 mg C/l. The reproducibility of the method is 0.1 mg C/l.

This method has been widely adopted by researchers abroad for analysis of ocean waters. A vast material on DOC distribution in the world ocean has been obtained using this method. Unfortunately recent investigations have shown that the sea water organic matter is oxidized only partially in this technique.

Coming back to the problem on DOC analysis, it is worth noting that many researches abroad pay too much attention to the techniques and instrumentation capable of providing rapid analysis owing to the use of automated operations and calculations that seems to be not critical to a careful development of all stages of the analysis. This might be the reason why geochemists took for granted all the data on DOC concentration in sea water. Such is the idea of a homogeneous DOC distribution in the abyssal depth of the ocean and of comparatively low DOC concentration in surface waters.

Recently Sugimura and Suzuki²⁰ reported on the application of their own apparatus for carrying out dry high-temperature oxidation of microsamples over a platinum catalyst. This study arose a problem on incomplete oxidation of the organic matter of sea water samples. The authors presume the oxidation of colloidal forms of organic matter with the aid of persulfate or hydrogen peroxide solutions or by irradiation of samples with short-wave ultraviolet light to be inefficient. A study of sea water samples obtained from the western part of the Pacific Ocean revealed that DOC concentrations in surface water samples amounted up to 3 mg C/l and those in abyssal depth water samples did up to 1.5 mg C/l. These values are twice as high as those reported earlier by foreign oceanologists. Further publications cast doubt on all the calculated values for carbon distribution in the ocean.²¹

The necessity of substantially revising already established concepts led to the organization of the above mentioned conference which was held in 1993 in the USA. The problems concerning the techniques of high temperature oxidation were the main subject of discussions at this conference. Several types of commercially available apparatuses were also compared. It turned out so that different apparatuses and different methods yielded results for one and the same samples that showed a significant disagreement. It became clear that a substantial improvement of sample preparation and analytical procedures for DOC determination in natural water samples (including sea water samples) is called for. The report of the organizing group together with the reports of subgroups outlined the main avenues of future research aimed at assessing method reproducibility, blank test corrections, oxidation catalyst's efficacy, conditions of sample injection into the heated zone of evaporating furnaces, etc.²

It is noteworthy that most devices for DOC determination that are commercially available in other countries are extremely expensive (they cost tens of thousands of dollars), therefore, only big research institutes and laboratories can purchase them. In Russia there are only few such instruments.

One of the authors of the present paper, who was involved in DOC analysis carried out in the ocean, has proposed a substantially improved apparatus for

accomplishing the "wet" oxidation method using automated coulometric titration.²²

The automation of the coulometric CO₂ determination (the final step of the procedure of organic carbon measurements) allowed us to significantly extend the capabilities of the method as a whole. To confirm this, we would like to describe an original method and an apparatus for organic carbon determination we used long ago. For clarity, it is desirable to formulate the main principles of coulometric titration.

Coulometric titration is a strictly dosed-out electrolysis resulting in a substance which reacts with the matter under study. If the quantity of the electrogenerated substance is equivalent to the quantity of electricity that has passed through the electrodes (current output is about 100%), then such a reaction may be used for a coulometric detection. Modern instrumentation of electrochemical research permits high precision measurements of the quantity of electricity thus allowing one to measure precisely the amount of the reagent-titrant that has formed in the solution under study. The accuracy of measurements of some coulometric titration procedures is comparable to that of volumetric and gravimetric methods of chemical analysis. Easy-to-work feature of coulometric titrimeters well compensates for a certain complexity of the electrochemical instrumentation, especially when making routine standard analysis. The coulometric method possesses an important advantage of being easily automated.

Coulometric analysis is generally subdivided into "constant potential" and "constant current" coulometry. The former assumes the electrolysis to be carried out under the conditions of constant voltage at the generator electrodes. The voltage applied depends on the potential of the ion under study. This method is applicable to the analysis of complex mixtures and offers high selectivity. However, implementation of this method presupposes the availability of special devices, i.e., variable current integrators. The latter method assumes the electrolysis to be carried out at constant current at the generator electrodes. In this case, the quantity of electricity consumed during the electrolysis turns out to be directly proportional to the electrolysis time. Consequently, when the titration is on, one should measure accurately the electrolysis time alone. Time-measuring instruments are reliable and easy to operate. It is this version of coulometric analysis that we used in our device, the Lyutsarev carbon analyzer (LCA).

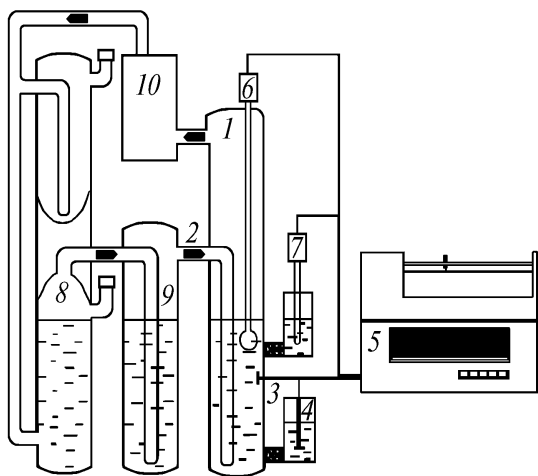


FIG. 1. Block-diagram of an LCA device for determination of organic carbon content in water.

Block-diagram of an LCA device is shown in Fig. 1. This device uses acid-base titration of CO₂ that comes to the absorption vessel 1 together with the carrier gas flow passing through the tubing 2. The cathode 3 is in the absorption vessel, while the anode 4 and the anode solution are placed into a separate vessel connected with the cathode solution of the absorption vessel by means of an electrochemical bridge filled with agar-agar gel. A solution of KJ having concentration about 50 g/l is used as an anolyte. The catholyte contains BaCl₂ solution having concentration about 50 g/l. Both electrodes are connected to the direct current generator 5.

When the current is on, the iodide-ion oxidizes at the anode to give elemental iodine which is bound with potassium iodine excess. A decrease in the quantity of iodide-ions is compensated for with chloride-ions which diffuse through the electrolytic bridge from the catholyte. Simultaneously, the electrolysis of water takes place at the cathode to give hydroxyl-ions and hydrogen. As a result, the solution in the absorption vessel (catholyte) becomes alkaline.

The electrolysis goes on until *pH* becomes equal to nine. At this *pH* value the catholyte is able to absorb CO₂ from the gas bubbles getting out from the tubing 2. The *pH* value is recorded with a *pH*-meter 5 equipped with the glass electrode 6 and the reference electrode 7. Before starting the analysis, *pH* adjustment to the required value of 9 is carried out using electrolysis. In the absence of CO₂ in the carrier-gas flow passing through the absorbing solution, the *pH* value of the solution remains constant. When the organic matter of a sample undergoes oxidation in the carrier-gas flow, CO₂ evolves and reacts with Ba(OH)₂ to give poorly soluble BaCO₃. As a result the *pH* value of the absorbing solution decreases; therefore, in order to compensate for these changes, additional electrolysis is carried out to maintain *pH* = 9. The device measures the time required for additional electrolysis which is related to the quantity of CO₂ absorbed. The calculations are performed using the following formula: $C = 0.0623 It$, where *C* is the quantity of carbon in a sample (mg); *I* is the specified strength of current (A); *t* is the electrolysis time (s). The above process of *pH* compensation is repeated and the evolution of CO₂ occurring in the course of sample oxidation is simultaneously recorded on a digital display and on a chart recorder. This method is of direct continuous coulometric titration in contrast to a simple periodic titration.

The sample oxidation is carried out in a special reactor (8) using the mixture of Ag₂Cr₂O₇, K₂Cr₂O₇, and concentrated H₂SO₄ at 130°C. The CO₂ evolved as well as the carrier-gas flow are purified to remove extraneous impurities, in the gas purification system 9 in Na(H₂PO₂)₂ + KJ solution which absorbs nitrogen and sulfur oxides from the carrier-gas flow. The purified gas passes through the tubing 2 into the absorption vessel of the coulometric cell and is recycled with the aid of the micropump 10 into the reactor of the device. Heating of the reactor and heat setting are carried out with the help of a halogen-cycle incandescent lamp with a special heat setting control circuit.

Figure 2 shows the block-diagram of the LCA electronics. The input of the mini-*pH*-meter having high input impedance (> 100 GOhm) is connected to the measuring electrode. In the course of the electrolysis when the required potential in the coulometric cell is attained, the commutator is put into operation, it switches on the

direct-current generator. As this compensation current flows through the cell, the opto-electronic commutator is put into operation and, in its turn, starts the crystal oscillator.

The control unit forms the required pulses with the aid of the frequency divider onto the counters that control the light-emitting diode displays via the decoding circuits. If necessary, the control unit gives out information onto the outer connector assembly for reading it into a microcomputer. In principle the circuit design of the device is an analog-to-digital charge-to-time converter, since the digital readout on the counter displays Σ is proportional to the compensation charge of the steady-state current generator. The compensation charge, in its turn, corresponds to the quantity of carbon in the sample analyzed.

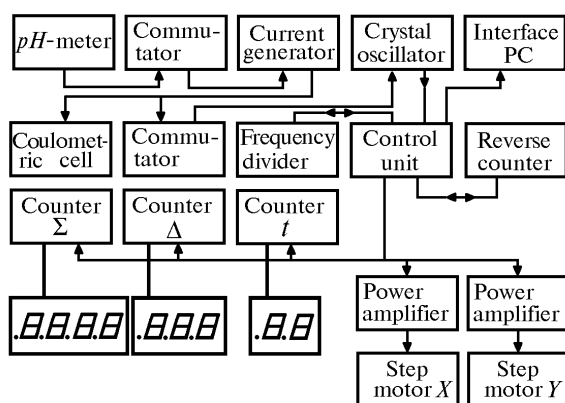


FIG. 2. Block-diagram of the LCA electronics.

The t counter calibrated against the crystal oscillator frequency records the current time of analysis, which is necessary for accurate calculation of carbon concentration in the sample analyzed. The Δ counter gives information about the differential increment in the charge in the cell, which is necessary for determining the moment when the measurements are to be stopped.

Numerical readout is duplicated on a chart recorder of original design with step motors operated by the control unit. The recorder allows one to obtain hard copies of measurement data on an A4 format at a scale of $1 \mu\text{g C/mm}$ which is convenient for handling graphic data. When time-consuming (up to 90 min) analysis or analysis of samples having high carbon concentrations is carried out, the reverse counter changes the direction of the recorder's pen via the control unit. Thus, the device operates in a semi-automatic mode, therefore, it is only at the initial stage of sample preparation that the operator's presence is required.

The LCA device is designed for the determination of absolute total concentrations of solid, soluble, colloidal, and emulsified organic matter including anthropogenic impurities (petroleum, industrial, and domestic sewage) as well as for environmental monitoring and expertise. The device is of small size, highly reliable, what makes it useful not only for industrial and research laboratories but also for extremely tough field conditions of geological survey and marine expeditions. The range of measurement is $3 \dots 1500 \text{ mg C}$ per sample for solids and $0.5 \dots 300 \text{ mg C/l}$ for solutions. Measurement error is 3% at a concentration of 10 mg C/l ($150 \mu\text{g C}$ per sample) and 5% at a concentration of 2 mg C/l ($30 \mu\text{g C}$ per sample). Measurement time is less than 90 min.

A great bulk of data on DOC contents in various regions of the ocean have been collected with the aid of the

LCA device at a shipborne laboratory.²³ Surface waters were found to contain $2 \dots 4 \text{ mg C/l}$ and abyssal depth waters — $1 \dots 1.5 \text{ mg C/l}$.

The data obtained were summarized and a mathematical model of the vertical DOC distribution vs logarithm of the depth of the layer investigated was proposed.²⁴

We used the LCA device during an expedition onboard "Il'ya Repin" ship down Volga river in the summer of 1993. Samples were taken at a depth of 20 cm from water surface. Analysis was performed within an hour following sampling. The results obtained are shown in the Table I.

The average concentration of DOC in the Volga water was 14.1 mg C/l for the area investigated, the variance of measurement data being equal to 2.1. Water samples collected on June 30, 1993 near the town of Ples turned out to be the most pure (10.4 mg C/l), while those obtained on July 4 and 5, 1993 near the village Podosyoenovo and Novookatovo turned out to be the most contaminated (18.3 and 17.1 mg C/l , respectively).

TABLE I. Results of total organic carbon measurements (mg C/l) during an expedition onboard the "Ilya Repin" ship (June–July, 1993).

Sample No.	Date	Time	Distance from Moscow, km	Reference point	C_{org} , mg C/l
1	30.06	19.15	555	Kostroma	13.0
2	30.06	21.40		Ples	10.4
3	01.07	8.00	806	Gorodets	13.7 12.5*
4	01.07	10.40		Balakhna	12.1
5	02.07	19.15	861	Nizhny Novgorod	14.6
6	02.07	23.40		Lock	—
7	03.07	17.00	614	Ples	—
8	03.07	21.15	614	Ples	13.4
9	03.07	22.15	—	Ples	13.8 13.7**
10	04.07	18.40	—	Yaroslavl	14.9
11	04.07	19.50	—	Podosyoenovo	18.3
12	05.07	18.30	190	Novookatovo	17.1
13	06.07	10.30	233	Tver	14.5
14	06.07	18.15	—	Tver	13.9
15	30.06 (Sample from the boat water-supply)				10.6

* Analysis of Sample No. 3 24 h after sample collection (without conservation).

** Repeated measurement of Sample No. 9.

Analysis of Sample No. 3 was duplicated after storage for 24 h in darkness without conservation. The DOC content in this sample was found to be decreased by 9% as a result of bacterial microflora activity, which is proof of the need for performing analysis upon sample collection without any delay. Repeat measurement carried out using Sample No. 9 that was collected on July 3, 1993 near the town of Ples revealed satisfactory reproducibility of the results obtained with the LCA device.

It should be kept in mind, when considering the data obtained, that the water samples were not filtered prior to DOC determination, therefore, the total organic matter content was measured. The major portion of DOC is represented by humus-like substances of natural origin (fulvic acids), by metabolism products of bacteria, phyto- and zooplankton, by water-soluble and emulsated anthropogenic impurities (e.g., petroleum, detergents, etc.) of industrial and domestic origin, by organic matter of colloidal particles and water suspension.

For comparison purposes, the results of measurements with the LCA device are presented for Neva river obtained near the city of Leningrad (Strelka of Vasilievsky Island) – 12.1 mg C/l; Don river near Rostov-on-Don – 14.2 mg C/l; water samples obtained near the town of Norilsk – 2 ... 4 mg C/l; melted ice of the Elbrus glassier – 0.9 ... 1.9 mg C/l.

The results obtained during our expedition reveal the fact that the lowest contamination level is in the Volga water samples collected near the town of Ples. However, in order to make a reliable assessment of pollutants level of the river water, multiple season measurements should be conducted at representative points of any particular aquatorium.

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