BIOXHMEIA. - **Contribution to the knowledge of dissolved organic matter in sea water,** *by A. Christomanos, Aphr. Dimitriadi and Demetr. Giannitsis* [*]. Ἀνεκοινώθη ὑπὸ τοῦ κ. Γεωργ. Ἰωακείμογλου [**].

Samples of sea water from different Greek sea areas were examined about their oxidation by KMnO4.

The organic matter 1) in sea water is due, about 90 %, to dissolved organic substances of unknown concistency, to Plancton and to detritus. The amount of organic matter in sea water lies in average 2 mg C per Liter.

A correct direct routine method of determination of C in sea water does not exist and therefore we are obliged to express the amount of dissolved or ganic matter by the amount of KMnO4 which was used for oxidation of a definite quantity of sea water.

The technique used in our experimental work was first published by M. Gilbricht (2) from the «Biologische Anstalt Helgoland» and is based upon the previous work of Ruppin (3) who used for the oxydation of the organic matter in sea water, KMnO4 in alkalin medium.

It should be pointed out that the values obtained in this way represent the amount of KMnO4 used for oxydation, and consequently they represent only indirectly the quantity of C (4).

Gilbricht sustains in his paper that the KMnO4 values could be brought to close connection with the quantity of KMnO4 needed to oxidize Saccharose or Starch to Oxalic acid.

Nevertheless it should be emphasized that we do not know the real nature of the organic substances dissolved in sea water (5 - 6), and therefore we are not sure about the end products of oxydation of these substances by KMnO4. On account of this doubt we preferred to express the total quantity of organic matter (dissolved C + Plancton + Detritus) in different sea samples collected during the cruise «Tithys», as refered in a previous paper, in mg. KMnO4 used for their oxydation.

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[*] Α. ΧΡΗΣΤΟΜΑΝΟΥ, ΑΦΡ. ΔΗΜΗΤΡΙΑΔΟΥ καὶ ΔΗΜ. ΓΙΑΝΝΙΤΣΗ, Συμβολὴ εἰς τὴν γνῶσιν τῶν διαλυομένων εἰς τὸ θαλάσσιον ὕδωρ ὀργανικῶν ἑνώσεων.

[**] Ἀνεκοινώθη εἰς τὴν συνεδρίαν τῆς 8 Φεβρουαρίου ἐ.ἔ. (βλ. ἀνωτ., σ. 63).

A. Theoretical principles of oxydation by KMnO4.

By boiling in alcaline solution of KMnO4 with organic substances, the Permanganate ions are transformed to Manganate ions and MnO2.

$$[MnO_4]' + e = [MnO_4]''$$
$$[MnO_4]'' + 4H + 2e = MnO_2 + 2H_2O$$
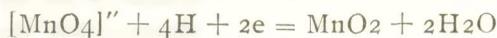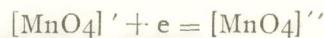
The minute quantity of oxydation products of NaCl, are instantaneously oxydized by the hot alcaline medium to chlorates, whereas organic substances are accordingly to Ruppin oxydized to oxalic acid. By acidifying the alcaline medium, the Manganate ions and Manganoxyde are transformed in Permanganate ions

$$5[MnO_4]'' + 8H^+ = 4[MnO_4]' + Mn^{++} + 4H_2O$$
$$5[MnO_2] + 4H^+ = 2[MnO_4]' + 3Mn^{++} + 2H_2O$$
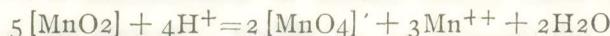
which in turn oxydizes the remaining oxalic acid, accordingly to Gilbricht.

$$[MnO_4]' + 8H^+ + 5e = Mn^{++} + 4H_2O$$
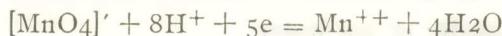
B. Experimental method.

To 15 ml. of the sample of sea water to be examined, 2.5 ml. of a 40 % NaOH solution, and in continuation 7 ml. of N/50 KMnO4 were added. The flask containing the mixture is then placed, for 1 hour, in a boiling water bath with the glass stopper half open. In the meantime the colour of the liquid changes from violet to dark green, accordingly to the formation of Manganate ions (MnO4).

After that, 30 ml. of diluted H_2SO_4 ($3H_2O : 1/H_2SO_4$) were added, and the flask is stirred gently.

Because of the addition of Sulfuric acid and the changing pH to 2-3, the green coloured reduction products of Permanganate change to Mangane and violet coloured Permanganate ions. After addition of exactly 1 ml. 5 % KJ solution, the flask is tightly stopped, stirred, and left for 10 minutes in dark. During this time, the remaining Permanganate liberates the equivalent amount of Jodine from KJ. The free Jodine is now titrated by N/100 Na2S2O3, after addition of 1 ml. 1 % Starch solution, until colourless.

For each double determination, a blank determination with twice destilled water was carried out.

The calculation of the quantity of KMnO4 used for oxydation of the

Number Locality	Depth in m.	mg. $Na_2S_2O_3$ used for the sample	mg. $Na_2S_2O_3$ used for the titr. of dest. H_2O	mg. $Na_2S_2O_3$ used for the titr. of KJ	mg. $KMnO_4$ used for oxydation of organ. substances
Euboean Gulf 38°43′ N 22°22′ E	0 10	25.9904 29.8096	32.1408 »	41.3184 »	73.78 ? 29.70
Euboean Gulf 38°42.2 N 23° 16.2 E	0 50	27.4536 29.0904	32.1408 »	41.3184 »	59.55 38.47
Euboean Gulf 38°42, N 23°14.3 E	0 15	30.0576 29.9088	31.3452 »	41.3184 »	16.33 17.91
Gulf of Corinth 38°20.9 N 21°50 E	0 50	28.4704 28.3668	31.3452 »	41.3184 »	36.36 37.94
Gulf of Patras 38°14.2 N 21°19.8 E	0 50	27.3668 28.2720	31.3452 »	41.3184 »	50.59 38.99
Montagu Reei, Ionian Sea 37°54.4 N 20.59 E	0 50	29.6360 29.7600	32.0992 »	41.3184 »	31.09 29.51
Islands of Strophades, 21°01 E 37°15 N	0 50	31.4376 29.1152	32.0992 »	41.3184 »	7.90 37.94
Gulf of Kyparissia 37°14.8 N 21°36.5 E	0 50	28.9416 27.1560	31.4464 »	41.3184 »	31.62 54.28
Gulf of Kalamata 36°50.7 N 21°57.8 E	0 50	29.0656 28.9664	31.4464 »	41.3184 »	30.03 31.62
Gulf of Kalamata 36°47.6 N 22°09.3 E	0 50	30.3304 28.3960	32.1408 »	41.3184 »	22.66 47.43
Cape Tenaron 36°22.8 N 22°29.0 E	0 50	29.4872 28.4704	32.1408 »	41.3184 »	33.72 46.37
Cape Malleas 36°26.8 N 23°15.0 E	0 50	30.6648 30.6528	32.1904 »	41.3184 »	18.97 19.49
Island Parapolla 36°46.5 N 23.29.0 E	0 50	30.9008 30.0080	32.1904 »	41.3184 »	16.33 27.40
Gulf of Thessaloniki	0	30.5784	31.5024	41.3184	11.54
Harbour of Thessaloniki	0	29.1648	31.5024	41.3184	29.51

organic substances is based on the formula published by Gilbricht in his paper:

$$\text{mg. } KMnO_4/\text{Liter} = \frac{527 \text{ mg. } Na_2S_2O_3 \text{ for sample} - \text{mg. } Na_2S_2O_2 \text{ for dest. } H_2O}{\text{mg. } Na_2S_2O_3 \text{ for 1 ml. } 5\%\text{ KI}}$$

C. Results.

The results of 27 sea water analyses are listed in the table below, each listed value being the average of two or three analyses.

The oxydation of a known quantity of oxalic acid by alcaline Permanganate solution, according to the method cited above, can be titrimentricaly determined. Accordingly to our experiments, 1 mg. $Na_2S_2O_3$ corresponds to 0.23 mg. oxalic acid, or to 0.061 mg. C, consequently we can deduce from the difference between the amount of thiosulfate used for the titration of destilled water after oxydation, and the amount of thiosulfate used for the titration of the sample of sea water oxydized by $KMnO_4$, the amount of C present.

DISCUSSION

It is obvious from the foregoing cited values of $KMnO_4$, that the deeper layers of the sea, show a greater content of oxydized substances by $KMnO_4$, than the water of surface, in eleven of the fifteen stations. This fact is due perhaps not to the greater content of dissolved unoxydized organic matter, but most probably to the denser presence of planctonic organisms. This question can only be solved by further investigations.

We should like to point out that with reference to the analytical method employed in our investigation, the values of the by $KMnO_4$ oxydized substances are not absolute, because of the simultaneous oxydation of the chlorates ions to free Cl_2 wkich in turn liberates Jodine from KJ. The oxydation of chlorates to Chlorine occurs by MnO_4 ions, after acidification of the alcaline $KMnO_4$ solution.

Although this represents a deficiency of the method, we can not deny that the method of Gilbricht. has a great comparative value, inasmuch as the differences of NaCl content of the sea water samples, are negligible.

ΠΕΡΙΛΗΨΙΣ

Αἱ εἰς τὸ θαλάσσιον ὕδωρ ἀνευρισκόμεναι ὀργανικαὶ ἑνώσεις ὀφείλονται κατὰ 90 % εἰς διαλελυμένας ἑνώσεις ἀγνώστου συστάσεως, ὡς καὶ εἰς τὸ μικροπλαγκτὸν καὶ ὑπολείμματα ὀργανικῶν ἑνώσεων καταπιπτουσῶν ἐκ τῆς ἐπιφανείας.

Διὰ τῆς μεθόδου τοῦ Gilbricht, διὰ τῆς ὁποίας ὀξειδοῦνται αἱ ὀργανικαὶ ἑνώσεις εἰς διὰ NaOH ἀλκαλικὸν περιβάλλον διὰ KMNO₄, καὶ ὀγκομετρήσεως κατόπιν τοῦ μὴ ἀναχθέντος ὑπερμαγγανικοῦ καλίου δι' ὑποθειώδους νατρίου, διεπιστώθη εἰς ἕνδεκα ἐκ τῶν ἐξετασθεισῶν δεκαπέντε περιπτώσεων, ὅτι τὸ ὕδωρ τῆς ἐπιφανείας ἐνεῖχε μικροτέραν ποσότητα ἀναγουσῶν ἑνώσεων ἢ εἰς βάθος 50 μέτρων. Ἡ διαφορὰ αὕτη ἀναμφιβόλως ὀφείλεται μᾶλλον εἰς μικροπλαγκτονικοὺς ὀργανισμοὺς παρὰ εἰς τὴν παρουσίαν μεγαλυτέρας ποσότητος ἀνοξειδώτων ὀργανικῶν ἑνώσεων.

Ἂν καὶ ἡ μέθοδος ἥτις ἠκολουθήθη εἰς τὴν παροῦσαν ἐργασίαν περιλαμβάνει ὡρισμένα ἀσθενῆ σημεῖα, οὐχ ἧττον ὅμως δύναται νὰ χρησιμοποιηθῇ μὲ ἐπαρκῆ ἀκρίβειαν διὰ συγκριτικὰς μελέτας, αἵτινες ἀναμφιβόλως δύνανται νὰ ἔχουν ἀξίαν διὰ τὴν πιστοποίησιν τῆς ὑπάρξεως πλουσίων ἢ μὴ πλαγκτονικῶν στρωμάτων εἰς τὰς θαλάσσας.

Ἡ παροῦσα ἐργασία ἔχει σημασίαν προκαταρκτικῆς κατατοπιστικῆς μελέτης, θέλει δὲ ἐπεκταθῇ κατὰ τὸ προσεχὲς μέλλον εἰς τὴν ἐξέτασιν τῶν βαθυτέρων στρωμάτων τῶν Ἑλληνικῶν θαλασσῶν.

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Ὁ Ἀκαδημαϊκὸς κ. **Γεώργ. Ἰωακείμογλου** ἀνακοινῶν τὴν ἀνωτέρω μελέτην εἶπε τὰ ἑξῆς.

Οἱ ἐρευνηταὶ Ἀ. Δημητριάδου καὶ Δ. Γιαννίτσης διεπίστωσαν ὅτι αἱ ἐν τῷ θαλασσίῳ ὕδατι εὑρισκόμεναι ὀργανικαὶ ἑνώσεις ὀφείλονται κατὰ 90 % εἰς διαλελυμέ

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ΓΕΩΛΟΓΙΑ.— **Über den «Thessalischen See»**, *von Horst E. Schneider*[*].

Ἀνεκοινώθη ὑπὸ τοῦ Ἀκαδημαϊκοῦ κ. Μαξ. Μητσοπούλου[**].

Bereits in der Literatur der Antike findet sich die Vermutung, dass das Innere Thessaliens von einem grossen See erfüllt gewesen sei, der schliesslich einen Abfluss zum Meer durch das Tempetal gefunden habe (z. B. Herodot, Strabon). Auch später findet sich diese Darstellung in mehreren geographischen und geologischen Abhandlungen (z. B. Krause 1865, Fallmerayer 1845, Déprat 1904), ohne dass bisher ein wirklicher Beweis für die Existenz einer früheren Seebedeckung der gesamten innerthessalischen Ebene erbracht worden wäre (worauf übrigens Philippson bereits mit Recht hinwies).

Es ist allerdings nicht erstaunlich, dass es zu der Annahme eines ehemaligen Sees kam, wenn man sich das Landschaftsbild Innerthessaliens vor Augen hält. Die grossen Ebenen von Larissa (ostthessalische Ebene)

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[*] H. E. SCHNEIDER, Περὶ τῆς «Θεσσαλικῆς λίμνης».

[**] Ἀνεκοινώθη εἰς τὴν συνεδρίαν τῆς 8 Φεβρουαρίου ἑ.ἔ. (βλ. ἀνωτ., σ.63).