Natural Radiocarbon Measurements on Surface Water from the North Atlantic and the Arctic Sea

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Abstract

An apparatus for the extraction of carbon dioxide from 100 liters of sea-water using carbonate-free sodium hydroxide solution as absorbant liquid and its performance is described. A test series of 6 sea water samples is presented, on which natural C14 determinations are made and the results obtained are briefly discussed in relation to other age measurements on similar waters. The correlation between salinity and C14 activity is shown.

Introduction

Various methods for the recovery of carbon dioxide from sea-water for C14 analysis have been used during the last years. Thus solutions of 8-N potassium hydroxide purified with barium hydroxide (BROECKER 1957), hot barium hydroxide solution (RAFTER 1955) have been used, as well as freezing out the CO_2 by means of liquid air (RAFTER and FERGUSSON 1957). We prefer to use 2-N carbonate free sodium hydroxide solution, which is easy to prepare and to handle. A simple apparatus has been constructed, in which liberation of the carbon dioxide from sea-water and absorption in the sodium hydroxide runs fast and smoothly.

Description of the apparatus

Fig. 1 shows schematically the absorption apparatus. A is a nitrogen gas cylinder with a pressure gauge connected to a 50 liter polyethylene vessel B by a thick rubber tubing (vacuum) fitted to a glass tube C supported by the rubber stopper D and ending in the glass filter E near the bottom. The stopper also supports a drop funnel F (500 ml) containing concentrated sulphuric acid. The funnel ends about 20 cm below the stopper. Through a third hole in D a short glass tube G is inserted ending just under the stopper. G is connected by a thick vacuum rubber tubing to the side tube J_1 in the absorption apparatus consisting of two similar glass vessels L_1 and L_2 connected in series. Each vessel is equipped with a glass filter I_1 and I_2 (Pyrex "Coarse"). Under the filter a tube leads through a rubber stopper into the vessel K_1 ending about 5 mm from the bottom. K_1 and K_2 have bottom taps, H_1 and H_2. The vessels L are closed by rubber stoppers M with a glass tube connected to the second absorption vessel. N is an ordinary 250 ml Jena glass bottle with rubber stopper. P and Q are clamps.

The absorption liquid

2-N carbonate free NaOH is prepared in advance ashore by diluting a 50 % solution using Sörensens method, according to textbooks in quantitative inorganic analysis (e.g. VOGEL). The 2-N solution is transferred into the 250 ml Jena bottles which are tightly closed by rubber stoppers (bottle *N* in the figure). The bottles may be stored for a long time.

Description of the operation

For a C14 analysis 100 liters of sea water, corresponding to about 4 liters of CO_2 gas, are necessary. We have used two 50 liter polyethylene bottles for the samples. They are easy to handle on board and can not be broken. For surface samples, the bottles are simply filled with sea water. On board *s/s Anton Dohrn* we used a sea water tap going directly through the ships side 1 meter below the water line. On board *m/s Aranda* a big sea water sampler was used. Pumps which might mix air into the water have to be avoided. The absorption equipment has to be well fastened and secured in the ship laboratory or on some sheltered place. The liberation and absorption of the CO_2 gas is carried out in the following way. (Fig. 1.) The polyethylene vessel *B* is filled with sea water, leaving a space of about 250 ml under the rubber stopper *D*, which is fastened air tight and secured with cords. Now *C* is connected to the gas cylinder *A*, and *G* to the side tube J_1. The absorption liquid is filled from the bottle N_1 through the neck M_1 of the absorption vessel, the tap of course being closed. The second vessel is filled in the same way from a second bottle and connected to the first one. All connections have to be pressure tight. The clamps *P* and *Q* are opened and a part of the liquid flows down into the vessels K_1 and K_2. Now 250 ml of conc. sulphuric acid is introduced into the water sample. It is suitable to connect a rubber bulb, O, to the funnel and squeeze in order to force the acid down. The acid sets free CO_2 and this will give a small pressure in *B*, raising the absorption liquid into the vessel *L*, and forcing some gas through the glass filter. When the bubbling stops, nitrogen from the gas cylinder is carefully started. The flow rate is adjusted to about 150 liters/hour. After two hours, the vessel *B* is changed to a new one and the second part of the sample is treated in the same manner. Finally, the nitrogen flow is stopped and by opening the stopper at *M* and the tap *H*, the absorption liquid is poured into the bottle *N*, which is then well closed, sealed and labelled for further processing ashore.

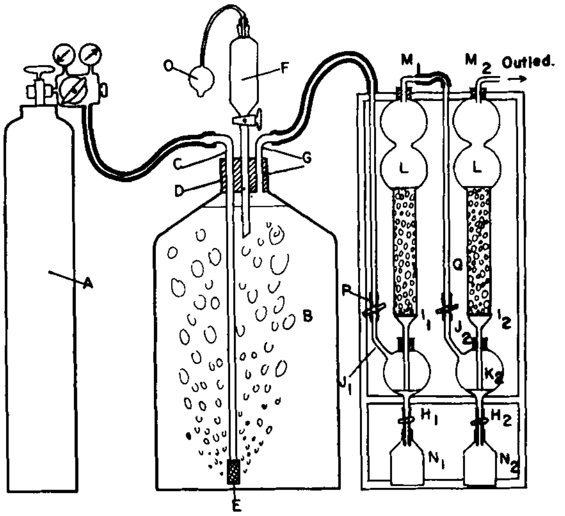

Fig. 1. CO_2 absorption apparatus.

Determination of the quantity of carbon dioxide obtained in the liquid is easily made by titrating a small aliquot portion with 0,1-N hydrochloric acid. The first end point, about pH 9, indicated by phenolphtalein, gives the sum of sodium hydroxide and carbondioxide. After further addition of bromcresol green or methyl red, the titration is continued to about pH 5. The difference in acid consumption between these two end points gives the quantity of carbon dioxide in the sodium hydroxide solution.

Radiometric Analysis

The bulk of the hydroxide-carbonate solution is transferred to a half liter bottle, a few drops of methyl red is added, and while running a slow stream of oxygen through the solution, sulphuric acid is slowly added until the whole solution becomes acid. The liquid is then boiled a few minutes, still in the oxygen stream, until all carbon dioxide has been driven out. The mixture of carbon dioxide and oxygen is led to the combustion train of the radiocarbon dating apparatus already described by one of us (Östlund, 1957). The radiocarbon proportional counting tube requires 1.82 l of carbon dioxide measured at 0° C and 760 mm Hg. It has an effective volume of about 0.5 l, a working pressure of 3 atm, exhibits a background of 1.8 counts per min (cpm) and a net counting rate from modern carbon of 9.5 cpm. In one case, the quantity of carbon dioxide obtained was large enough to be used in our 1 liter counter, thus giving a more accurate value of the relative activity.

Results obtained

First, a test was made to see if the sodium hydroxide solution might be poured from one bottle to another and back again, without being appreciably contaminated with atmospheric carbon dioxide. Thus, 250 ml 2-N solution was poured from the bottle to an empty, ordinarily washed 1 liter flask and back again to the bottle. After this operation titration showed the carbonate content to be about 0.04 % of the NaOH. After 10 such rough treatments back and forth again between the bottle and the flask, not more than 0.15 % of the NaOH had been converted to carbonate. It is thus established that no error of importance is introduced by pouring sodium hydroxide solution from the bottle to the absorption vessel and back to the bottle again.

The entire process was tested by collecting six surface water samples from the North Atlantic and the Arctic Sea. Four samples were collected on cruise with *s/s Anton Dohrn* (St 322, 331, 332, and 334) and two on board the Finnish research vessel *m/s Aranda* (St 335, and 336). The yields of purified carbon dioxide ready for C14-counting are given in Table 1. In all these cases, two absorption vessels were used, connected in series with 250 ml of NaOH solution in each. Titration showed, however, that the second of these bottles never contained more than 2 %, and generally only about 1 % of the total carbonate quantity. Thus this second absorption flask has later been omitted. This also indicates that the efficiency of the absorption is very high.

Result of the C14 measurements

In Table 2 are given the results obtained for the isotopic composition of the inorganic carbon of sea water. The standard used is so called pre-industrial wood, in this case tree-rings from 1850 AD of an oak having grown in the vicinity of Stockholm, and the disintegration rate is corrected for decay up

TABLE 1

Yields of Carbon Dioxide from Sea Water

Sample No.	Working name	Quantity of water, liters	Quantity of nitrogen used, liters	Quantity of pure CO_2 obtained	
				moles	liters at 0° 760 mm
St 322	Gulf Stream	100	600	0.13	2.9
St 331	Denmark Strait I....	100	600	0.12	2.7
St 332	Denmark Strait II...	100	600	0.11	2.5
St 334	Denmark Strait III...	100	1200	0.16	3.6
St 335	Barents Sea I.	115	1500	0.19	4.2
St 336	Barents Sea II	115	1500	0.18	4.1

In a later series of samples, not yet having been measured for C14, the average yield using 100 l of water and 600 l of nitrogen was 0.17 moles, with smaller variation than among these first six samples.

TABLE 2

C14 and C13 values for North Atlantic and Arctic Sea water

No	Sample from	Date y/m/d	Pos.		Depth m	Salinity ‰	Temp. °C	Relative C14-activity $\Delta R'$%	C13 fractionation factor Δr %	Relative C14 activity corrected for C13 ΔR %	"Ag yrs (B for pre ent
			Lat.	Long.							
	1850 AD wood, corrected for decay until 1958 AD							0 ± 0.5	0*	0	
	NBS Radiocarbon standard**	—	—	—	—	—	—	$+4.5 \pm 0.5$	—	—	-
St 322	Gulf Stream	1957/03/30	62.6°N	8.0°W	0	35.37	+7.8	$+0.7_4 \pm 0.7$	$+2.4_3$	—4.1	33
St 331	Denmark Strait I .	1957/04/02	67.8°N	25.1°W	0	32.72	—1.6	$-1.8_3 \pm 0.7$	$+2.4_3$	—6.7	54
St 332	Denmark Strait III	1957/04/10	65.5°N	26.6°W	0	33.17	+6.0	-0.3 ± 0.7	$+2.5_0$	—5.3	42
St 334	Denmark Strait III	1957/04/17	64.8°N	35.5°W	0	34.97	+0.7	$+0.6 \pm 0.9$	$+2.4_5$	—4.3	34
St 335	Barents Sea I	1957/07/03	72.9°N	41.8°E	337	34.98	—0.7	$+0.4 \pm 0.6$	$+2.4_5$	—4.5	36
St 336	Barents Sea II....	1957/07/04	73.9°N	33.6°E	0	35.08	+4.9	$+0.9 \pm 0.6$	$+2.4_5$	—4.0	32
	Weighted mean of all							$+0.3 \pm 0.5$	$+2.4_5$	—4.6	37

* This value is 2.46 % lower than the Chigaco PDB C13 standard used by e.g. *Craig* (1957).

** U.S. National Bureau of Standards, Contemporary Standard for C14-Dating Laboratories.

to 1958 AD. If m is the net count rate of the standard oak, corrected for decay, and x the actual net count rate of the sample, $\Delta R'$ is defined by

$$\Delta R' = \frac{x}{m} - 1 \tag{1}$$

The C13/C12 ratios, r_x, of the samples with respect to the same ratio for our standard wood, r_m, was measured mass-spectrometrically. We define

$$\Delta r = \frac{r_x}{r_m} - 1 \tag{2}$$

To bring all measurements up to the same "standardized" isotopic composition we use

$$\Delta R = \Delta R' - 2\Delta r$$

The apparent "age" of the sample's carbon dioxide may be derived from

$$A = -\frac{5568}{\ln 2} \cdot \ln R \tag{3}$$

or, with sufficient accuracy,

$$A = -8033 \cdot \Delta R \tag{4}$$

In the table are also given the standard deviations, σ:s, of the values, taking into account the statistical uncertainties of the measurement of the sample itself and related measurements of background. The uncertainty of the standard measurements is given separately. Thus, comparison between two measurements within this series should be made calculating with only the two actual σ:s. If comparison is made by samples made at another laboratory, the σ:s of the standard figure must also be included.

Discussion

The C13 values of the samples listed in Table 2 exhibit a very marked constancy, since the uncertainty of those determinations is about ± 0.1 %.

The C14 values are more variable. If, however, the sample St 331 is excluded it is not possible to state with a high grade of reliability that any of them is statistically different from the mean value. On the other hand, it is seen from figure 2 that a slight relation between salinity and relative activity appears. Of these values the sample of the highest salinity, St 322, represents Atlantic water in the branch of the Gulf Stream that enters the Norwegian Sea.

The other extreme, St 331, with a low acitivity, represents Arctic water from the East Greenland Current emerging from under the ice pack. From its C14 content it appears to be about 200 years older than the Atlantic water. This is interesting in view of the estimate by SVEDRUP ET AL (1942) of 165 years for the complete renewal time for the Arctic Mediterranian water. If the sea water entering the Arctic basin was shielded from the atmosphere, no C14 would be added during the time the water spends in this basin. One can therefore expect this water to show an apparent age of that magnitude relative to the Atlantic water. Another possible explanation of the low activity could be that the average C14 activity level of sea water has been raised since 1954, due to the hydrogen bomb tests (e.g. RAFTER and FERGUSSON loc. cit.). Owing to the magnitude of that increase any lower residence time might be reasonable. If the industrial effect (SUESS 1955 and others) also should have affected the sea water, the problem becomes still more complex. At present there is, however, no reliable indication that such variations should have been detected in open sea surface waters. Cf. table 3 below.

As to the samples St 332 and 334, their activity suggests that they are mixtures of Atlantic and Arctic water which have been exposed to the atmosphere for some time, thus aquiring extra C14.

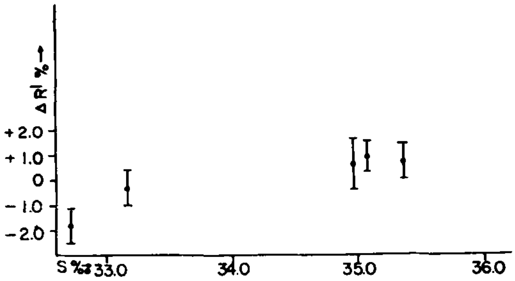

Fig. 2. Relation between salinity and relative activity.

The sample St 332 is taken near the west coast of Iceland, and the water has a higher salinity and temperature. The relative activity is — 0.3 % and all values indicate that this

TABLE 3

Comparison between various C14 measurements on sea surface water

Sample from	Sample No	*R'* %	*r* %	*R* %
Broecker				
Lamont Oak 1890 AD		0	0	0
Average North Atlantic Surface water 1956 19—38°N 51—75°W		+ 1.0	+ 2.5	— 4.0
Rafter and Fergusson				
New Zealand Wood Standard corrected for industrial effect		0		
Makara, Wellington, N.Z. Shallow water				
Nov. 1954	AA3678	— 0.2		
Dec. 1954	AB1192	— 0.4		
17 Jan. 1957	R 216	+ 0.9		
3 May 1957	R 259	+ 1.6		
Open sea, South Pacific 37°S 170°E 14 Febr. 1957	R 228/1	— 0.5		
This paper				
Stockholm 1850 AD Oak standard		0 ± 0.5	0	0
NBS Radiocarbon standard		+ 4.5 ± 0.5		
North Atlantic Gulf Stream 62°N 8.0°W	St 322	+ 0.7 ± 0.7	+ 2.4	— 4.1
Average Irminger Current 65°N 26—36°W	St 332	+ 0.1 ± 0.6	$+ 2.4_6$	— 5.4
Apr. 1957	St 334			
Barents Sea 73,9°N 33,5°E	St 336	+ 0.9 ± 0.6	$+ 2.4_6$	— 4.0
Jul. 1957				
East Greenland Current	St 331	— 1.8 ± 0.7	$+ 2.4_3$	— 6.7

sample is a mixture of Arctic water and water from the north bound salter and warmer Irminger Stream.

A part of water of the Irminger Stream turns to the left and streams southwards, parallel to the East Greenland Stream near the coast of Greenland. St 334 is taken in this part of the Irminger Sea, and the salinity and the temperature show that this sample is also a mixture of Atlantic and Arctic water. The relative activity is + 0.6 %.

The Barent Sea sample 336 is surface water of Gulf Stream origin, i.e. water from the Norwegian Current. The sample 335, on the other hand, is bottom water and considerably colder than 336, and possibly formed during the winter in the Norwegian Sea or in the Barents Sea. Still this deep water most likely is of Atlantic origin. Also the salinity and activity of both samples are in accordance with their Atlantic origin.

The present lack of measurements on the international C14 standard is a serious source of uncertainty when comparing geophysical radiocarbon measurements, made by different laboratories. Nevertheless, we have made an attempt to compare our values with those by LAMONT (BROECKER loc. cit.) and the New Zealand (RAFTER and FERGUSSON 1957) C14 laboratories. Broecker's primary standard is Lamont oak wood grown 1890 AD. Our own measurements refer to 1850 AD oak, and Rafter's figures can be recalculated from 1954 New Zealand wood over to pre-industrial N.Z.-wood using the correction of 1.5 % (FERGUSSON 1958). Thus all figures in Table 3 refer to pre-industrial wood.

Broecker's (loc. cit.) wood standard and ours have the C13-values of — 2.40 % and — 2.46 % respectively in the scale of the Chicago PDB standard. This source of error is thus eliminated when using the Lamont and Stockholm values together. The C13 value of the N.Z. standard was not known to us. Further differences of standards (e.g. *de Vries* 1958) could not be regarded.

If the assumptions above are made, one finds that there are no really significant differences in the C14-age of open sea surface water from South Pacific, and North Atlantic, except for the sample at the ice border, which is Arctic water. The shallow Makara water, on the other hand, tends to exhibit an excess of C14 in comparison with open sea in the spring of 1957.

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