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PERCHLORATE IN SEA WATER

By R. Greenhalgh and J. P. Riley

Department of Oceanography, The University, Liverpool, 3

(Text-figs. 1–5)

In the perchlorate ion four oxygen atoms are arranged tetrahedrally about a central chlorine atom. The symmetry of this configuration and the fact that the chlorine atom has all its valency electrons shared, and is surrounded on all sides by oxygen atoms, confers great stability on the perchlorates compared with the much less stable chlorates. Many perchlorates are stable at temperatures of up to 500° C. The oxidizing properties exhibited by hot concentrated perchloric acid have been attributed to the undissociated acid. When cold, or in its dilute solutions it is completely dissociated and free from oxidizing properties. Under these conditions the perchlorate ion is only reduced by the strongest reducing agents such as Cr^{2+} and Mo^{3+}.

Not only are perchlorates difficult to reduce but they are also only formed in comparatively few reactions. The only recorded modes of formation are based on the action of heat on chlorates, electrolytic oxidation of chloride, probably via chlorate, and chemical or photochemical oxidation of chlorate.

Perchlorates are known to occur naturally only in the nitrate beds of Chile, which average 0·5 % ClO_4^- but may contain up to 6 % ClO_4^-. In these beds perchlorate is associated with ions of high redox potential such as iodate, chromate and selenate. The mode of formation of these ions is not known, but it is believed that they were not formed *in situ*.

Recently Baas Becking, Haldane & Izard (1958) claimed to have detected up to 150 p.p.m. of perchlorate in ocean water, even more in some estuarine waters, and up to 10,000 p.p.m. in brines. They consider that this perchlorate is formed from chloride by an unspecified oxidation mechanism involving iodate. They further state that sea-water samples should be stored under conditions of high redox potential to prevent reduction of perchlorate to chloride. Complete reduction of 150 p.p.m. of ClO_4^- in a sea water would increase its chlorinity by *ca.* 0·053 ‰. Perchlorate formation and reduction would thus have a serious effect on the use of chlorinity as a conservative property of sea water and on its use for computing σ_t values.

In view of these facts it seemed important to have an independent check on the amount of perchlorate present in sea water; particularly because of the inherent improbability that the perchlorate ion would be reduced to chloride under conditions normally used for the storage of sea water samples.

Baas Becking *et al.* (1958) describe five methods for the detection and determination of traces of perchlorate in water. They themselves apparently used a method based on the precipitation of methylene blue perchlorate. The precipitated perchlorate was separated by filtration or centrifugation, and the excess methylene blue was determined colorimetrically in the clear liquid. They state that the sensitivity of this method is 100 p.p.m. ClO_4^-. Such a technique tends to give high results owing to chloride interference and to the ease with which methylene blue is adsorbed by glass. In a further method which they describe, methylene blue perchlorate was extracted with *iso*-propyl methyl ketone and then determined colorimetrically in the organic phase. They claim a sensitivity of 1 p.p.m. for this procedure. Unfortunately, although they do not state this, chloride is also extracted, and erroneously high results are obtained if appreciable amounts of chloride are present.

It is thus evident that the use of methylene blue should be avoided in any confirmatory work on perchlorate in sea water. A review of the literature revealed that, although the perchlorate ion exhibits very few specific reactions, it does form comparatively insoluble perchlorates with a number of organic compounds, such as strychnine (Denigès, 1917), the ferrous sulphate complex of *o*-phenanthroline (Smith & Richter, 1944), nitron (Loebich, 1926), tetraphenylarsonium chloride (Willard & Smith, 1939).

The perchlorates of strychnine and of ferrous *o*-phenanthroline are rather too soluble to be used for the detection of traces of perchlorate and were not investigated. Experiments were made using nitron and good recoveries of 100 p.p.m. of perchlorate from distilled water were obtained. In solutions containing chloride a gelatinous precipitate of nitron chloride was formed and this method was not studied further.

The use of tetraphenylarsonium chloride, $(C_6H_5)_4As\,Cl$, was next investigated. It was found that this reagent gave no precipitate with distilled water, perchlorate-free sodium chloride solution or filtered sea water. In the presence of 5 p.p.m. of added ClO_4^-, each gave a visible precipitate of tetraphenylarsonium perchlorate within 10 min. of the addition of the reagent. It therefore appeared that if perchlorate was present in sea water its concentration must be below 5 p.p.m.

Since 5 p.p.m. of perchlorate is the lowest concentration that can be directly detected with this reagent, it was necessary to concentrate the perchlorate before lower concentrations than this could be determined. This was achieved by adding a known amount of potassium perrhenate to the water before addition of the reagent. The precipitate of the analogous tetraphenylarsonium perrhenate co-precipitated tetraphenylarsonium perchlorate quantitatively.

The concentration of the perchlorate in the mixed precipitate was determined by infra-red spectrophotometry. The two compounds have similar absorption characteristics over most of the spectrum from 5·5 μ to 15 μ (Fig. 1), since the organic moiety is the same in both. Their Cl-O and Re-O vibrations give rise to strong widely separated absorption bands, at 9·13 and 11·0 μ,

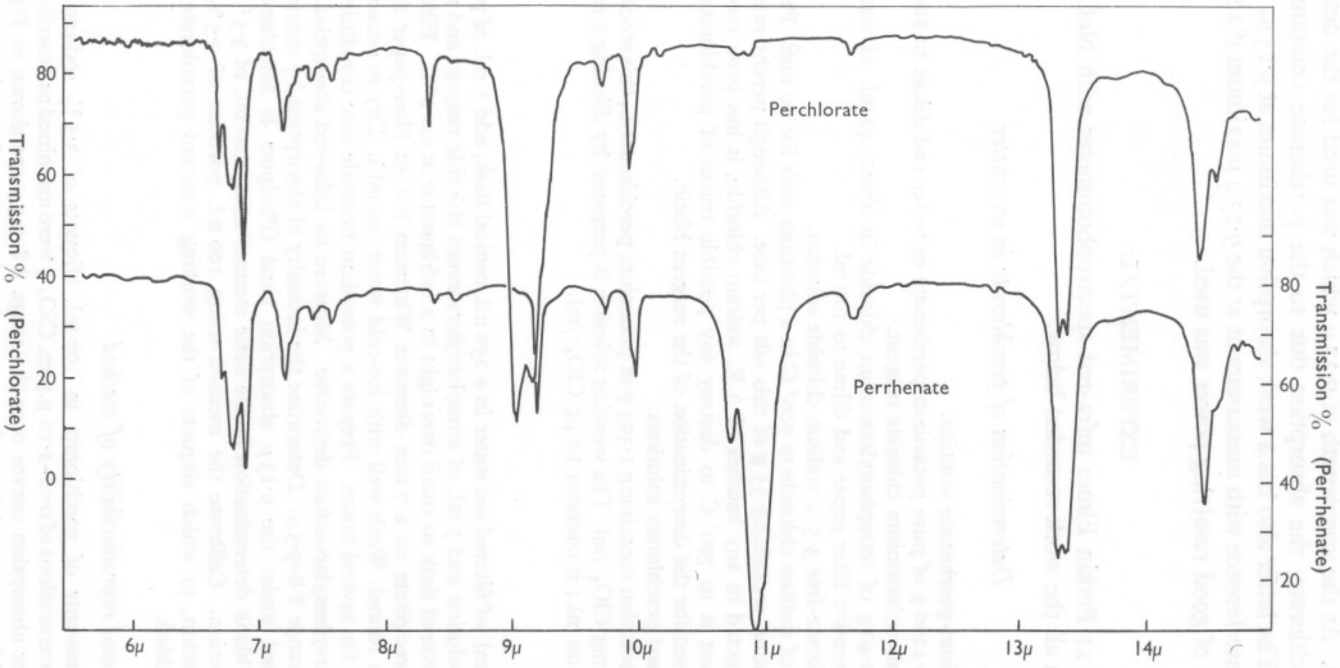

Fig. 1. Transmission-wavelength curves of tetraphenylarsonium compounds (Nujol mull).

respectively. At the wavelength of 9·13 μ which was used for the determination of perchlorate, the absorption due to the perrhenate compound was negligible. The latter also has a weak absorption maximum at 9·25 μ, but this caused no interference with measurement at the 9·13 μ maximum if a spectrophotometer of good resolving power was used.

EXPERIMENTAL

A model 21 Perkin Elmer infra-red spectrophotometer with NaCl optics was used in all the work recorded below.

Determination of perchlorate in sea water

Reagents

(1) Potassium-perrhenate solution.

Dissolve 0·1200 g of pure potassium perrhenate in water and dilute to 100 ml.

(2) Tetraphenylarsonium chloride reagent.

Dissolve 0·40 g of tetraphenylarsonium chloride in about 40 ml. of water, filter through a retentive filter paper and dilute to 100 ml.

(3) Perchlorate-free 3·5 % sodium chloride solution.

Heat 40 g of sodium chloride to 700° C in a platinum dish for 30 min. Prepare an aqueous solution containing 35 g of this salt per litre. Although perchlorate has not yet been detected in any batches of A.R. sodium chloride, it has been thought advisable to heat it to 700° C to destroy any possible traces of perchlorate, as this solution is used for the determination of the reagent blank.

(4) Standard perchlorate solutions.

Prepare a solution containing 1·393 g of potassium perchlorate/l., this stock solution contains 1·0 mg ClO_4^-/ml. The working solution is prepared by diluting 1 ml. of this solution to 100 ml.; it contains 10 μg ClO_4^-/ml.

Method

Place 100 ml. of filtered sea water in a 250 ml. conical flask, add 5 ml. of potassium perrhenate solution and 5 ml. of tetraphenylarsonium chloride reagent and mix well. Allow the covered flask to stand overnight in a refrigerator at *ca.* 2° C. Filter off the crystalline precipitate on a 7 mm diameter Whatman No. 52 filter-paper fitted in a small Hirsch funnel. Wash well with ice-cold water (20 ml.). Dry *in vacuo* at room temperature for several hours. Prepare a potassium bromide disc containing 4 % of the dried tetraphenylarsonium derivative. Measure its infra-red absorption over the wavelength range 8·8–9·5 μ. Determine the intensity of absorption by measuring the area contained under the 9·13 μ absorption band (Phillpots & Maddams, 1960). Carry out a blank determination in the same manner using 100 ml. of 3·5 % sodium chloride solution. Calibrate the method using 100 ml. portions of 3·5 % sodium chloride solution, to which aliquots of the working standard perchlorate solution have been added.

Sensitivity and reproducibility of method

Various amounts of perchlorate in 100 ml. aliquots of 3·5 % sodium chloride solution (concentrations of 0·02–2·16 p.p.m. ClO_4^-) were examined as described above. The resultant absorption curves over the range 8·8–9·5 μ are shown in Fig. 2. The optical densities computed from the area under the 9·13 μ absorption band show a

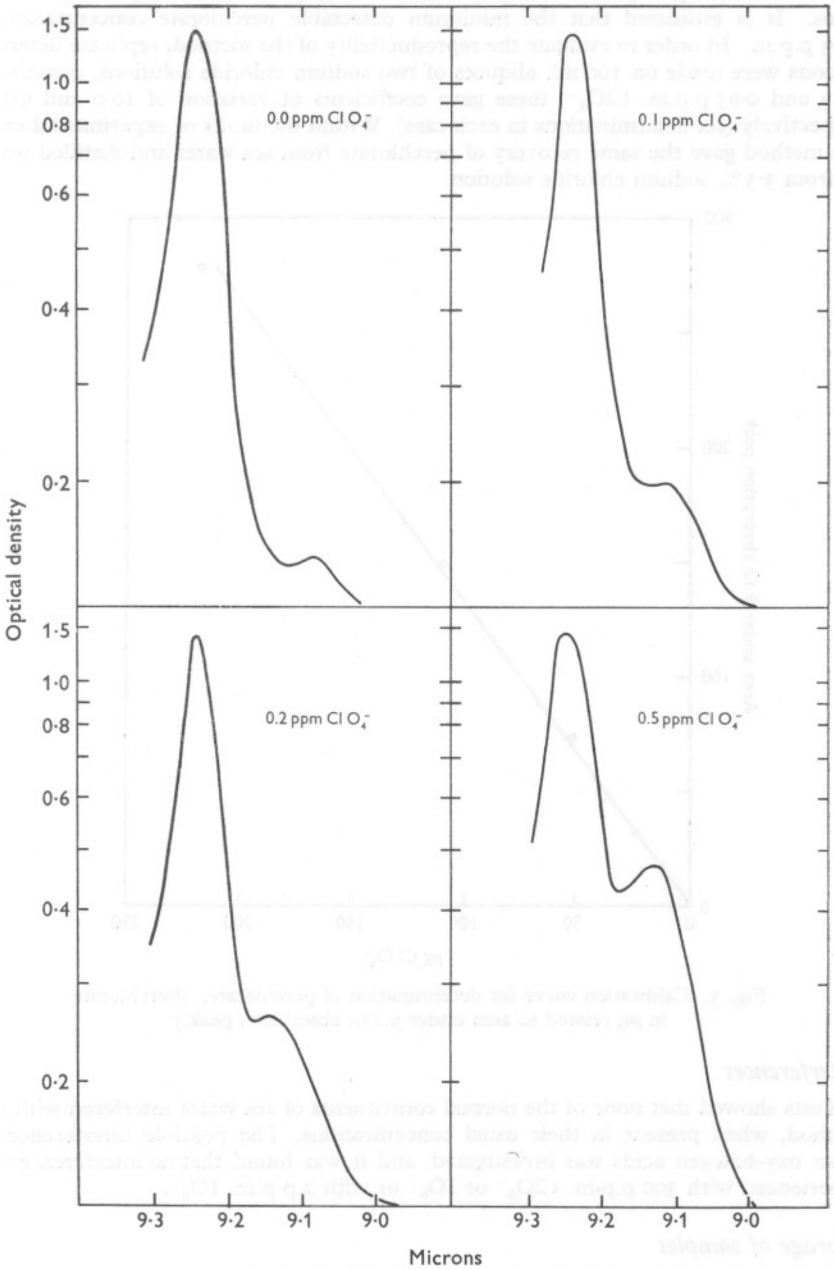

Fig. 2. Absorbance-wavelength curves of tetraphenylarsonium perrhenate, precipitated from sea water containing various concentrations of perchlorate ion.

linear relationship to perchlorate concentration (Fig. 3) over this range of concentrations. It is estimated that the minimum detectable perchlorate concentration is 0·03 p.p.m. In order to evaluate the reproducibility of the method, replicate determinations were made on 100 ml. aliquots of two sodium chloride solutions, containing 0·13 and 0·65 p.p.m. ClO_4^-, these gave coefficients of variation of 10·0 and 9·1 % respectively (six determinations in each case). Within the limits of experimental error the method gave the same recovery of perchlorate from sea water and distilled water as from 3·5 % sodium chloride solution.

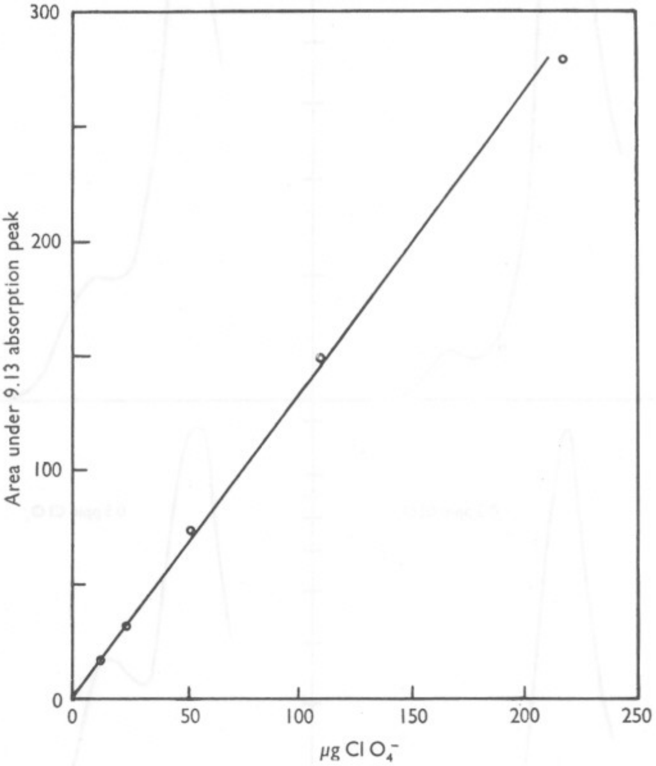

Fig. 3. Calibration curve for determination of perchlorate. (Perchlorate in μg related to area under 9.13μ absorption peak.)

Interferences

Tests showed that none of the normal constituents of sea water interfered with the method, when present in their usual concentrations. The possible interference of other oxy-halogen acids was investigated, and it was found that no interference was experienced with 300 p.p.m. ClO_3^- or IO_3^- or with 2 p.p.m. IO_4^-.

Storage of samples

There was no detectable change in the perchlorate content of sea water samples, which had been enriched with 1 p.p.m. of perchlorate, on storage for about 1 month in full glass or polythene bottles. Furthermore no bio-reduction of perchlorate occurred in perchlorate-enriched sea waters in which cultures of micro-organisms were growing freely. These findings which agree with what is known about the difficulty of reducing the perchlorate ion, directly confute the statement of Baas Becking *et al.* (1958) that perchlorate is reduced to chloride under conditions of slightly low redox potential.

Solubility of tetraphenylarsonium perchlorate and perrhenate

The solubilities of the tetraphenylarsonium derivatives in water, 3·5 % sodium chloride solution and sea water were determined. The optical densities of saturated solutions, prepared from the purified salts, were measured at 264 mμ* and compared with those of solutions of the two compounds of known strength. The results are shown in Table 1.

TABLE 1. SOLUBILITIES OF TETRAPHENYLARSONIUM COMPOUNDS IN WATER, 3·5 % SODIUM CHLORIDE SOLUTION, AND SEA WATER

	Solubility (mg/l.)					
	Water		3·5 % sodium chloride		Sea water (Cl = 18·97 ‰)	
Temperature (°C) ...	21·0	2·5	21·0	2·5	21·0	2·5
$(C_6H_5)_4AsClO_4$	20·2	16·3	32·1	22·0	37·0	27·8
$(C_6H_5)_4AsReO_4$	24·9	19·6	35·7	23·0	36·1	25·9

RESULTS

Analyses for perchlorate were made on samples of surface waters from twenty-six stations in the North Atlantic, English Channel, Irish Sea, Barents Sea, Mediterranean Sea, Red Sea, Arabian Sea, Persian Gulf and Indian Ocean (Table 2). In addition analyses were made of the deep waters at seven of these stations.

Although the analytical method will detect 0·03 p.p.m. of perchlorate in sea water, in no case was any found. These negative results are supported by the observation of Klemperer (1957) that the addition of as little as 0·05 p.p.m. of perchlorate to sea water reduced the rate of uptake of ^{131}I by *Fucus ceranoides* by 60 %. Shaw & Klemperer (private communication) have found a similar effect with *F. serratus*.

It appears therefore that the high concentrations of perchlorate found in sea water by Baas Becking *et al.* are completely erroneous. It is likely that this error was caused by the interference of chloride in their analytical method (*vide supra*), and it seems significant that the amount of perchlorate allegedly present in their samples is generally roughly in proportion to their chloride content.

It was thought that if there was any perchlorate present in sea water, it might have been formed, *in situ*, by photochemical oxidation by hydroxyl

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* Aqueous solutions of both derivatives have their absorption maxima at 220 mμ with a lesser maximum at 264 mμ.

radicals formed by the catalytic action of traces of transition metals. Experiments were therefore carried out in which 100 ml. aliquots of 3·5 % sodium chloride solutions, buffered to pH 8·1 with sodium carbonate–bicarbonate buffer, and containing 0·1 p.p.m. of Fe^{3+}, Ni^{2+}, Co^{2+}, Tl^{+} or Cu^{2+}, were irradiated at 30° C in silica flasks for 48 h, close to a mercury vapour lamp with quartz burner. In no case was any detectable perchlorate formed. Since the extremely energetic 2536 Å mercury radiation does not produce any

TABLE 2. SAMPLING STATIONS FOR DETERMINATION OF PERCHLORATE

Stn. no.	Lat.	Long.	Sampling depths (m)	Cl ‰
Barents Sea				
F3	74° 00′ N.	20° 00′ E.	0	18·674
F4	74° 25′ N.	14° 15′ E.	0	19·479
North Atlantic				
F1	65° 00′ N.	05° 00′ E.	0	19·537
H219	62° 30′ N.	14° 30′ W.	400, 1000	19·556, 19·580
30	48° 40′ N.	06° 45′ W.	0	19·614
26	46° 41′ N.	10° 20′ W.	0	19·766
25	44° 01′ N.	07° 48′ W.	0	19·710
23	40° 33′ N.	09° 35′ W.	0	19·619
20	36° 56′ N.	00° 05′ W.	0	19·853
Cavall	46° 30′ N.	08° 00′ W.	0, 511, 956	19·399, 19·347, 19·354
Cavall	46° 30′ N.	08° 00′ W.	2082, 2987, 3855	19·738, 19·808, 19·702
South Atlantic				
B1	36° 49′ S.	21° 18′ E.	0	19·572
Irish Sea				
Kish	53° 20′ N.	05° 17′ W.	0	19·069
Mediterranean				
16	36° 31′ N.	00° 40′ E.	0	20·465
M1	42° 00′ N.	06° 00′ E.	1, 200, 1000	21·233, 21·302, 21·256
M3	42° 58′ N.	08° 14′ E.	0, 2500	21·126, 21·266
13	38° 08′ N.	09° 54′ E.	0	20·965
12	33° 01′ N.	28° 38′ E.	0	21·382
E9	33° 01′ N.	28° 32′ E.	0	21·361
Red Sea				
E6	20° 00′ N.	38° 25′ E.	0, 1000	21·464, 22·487
Arabian Sea				
7	17° 00′ N.	57° 02′ E.	0	19·993
2	23° 06′ N.	64° 02′ E.	0	19·979
E3	22° 31′ N.	61° 55′ E.	3000	19·246
Persian Gulf				
1	26° 00′ N.	55° 00′ E.	0	20·597
Indian Ocean				
B2	50° 02′ S.	35° 12′ E.	0	18·757
B4 (1)	30° 07′ S.	64° 14′ E.	0	19·745
B4 (2)	30° 21′ S.	67° 15′ E.	4720	19·221
B6 (1)	33° 31′ S.	101° 08′ E.	0	19·843
B6 (2)	36° 08′ S.	106° 13′ E.	998	19·038
B6 (3)	33° 31′ S.	101° 07′ E.	6510	19·209

detectable amount of perchlorate from chloride ion, it is unlikely that any will be formed naturally by the action of sunlight, as this contains very little radiation of wavelength shorter than 3200 Å.

Investigation of the effect of perchlorate on marine organisms

Before it was realized that the perchlorate content of sea water was much less than that claimed by Baas Becking *et al.*, experiments were initiated to investigate the effect of the ion on marine organisms. The organisms selected were various unicellular planktonic algae, which are usually quite sensitive to the presence of toxic substances.

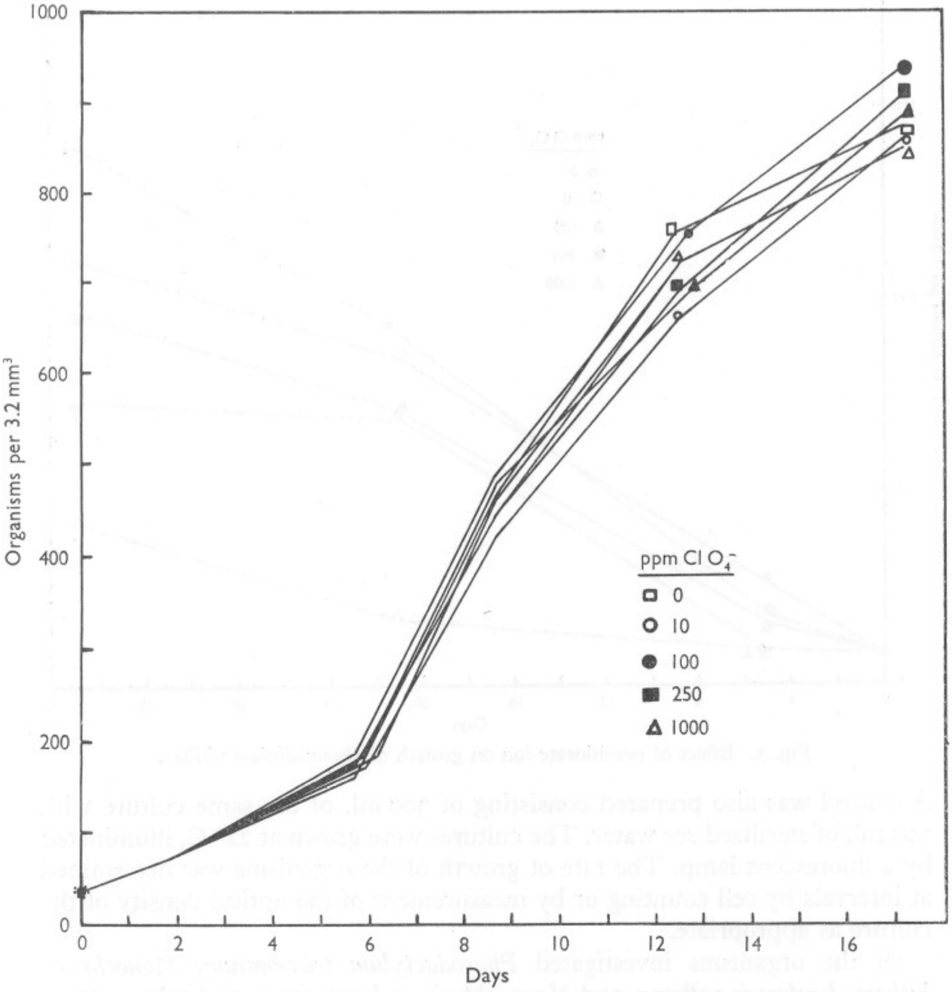

Fig. 4 Effect of perchlorate ion on growth of bacteria-free *Phaeodactylum tricornutum.*

Bulk cultures (2 l.) of the organisms (mainly bacteria-free) were prepared under sterile conditions in the medium described by Droop (1958). After several days, when the organisms were growing freely, aliquots (300 ml.) of these cultures were placed in sterilized conical flasks, containing varying volumes of a solution of chlorate-free sodium perchlorate in sterilized sea water. Sterilized sea water was added to bring the final volume to 400 ml. The final perchlorate concentrations were 10, 100, 250 and 1000 p.p.m. ClO_4^-.

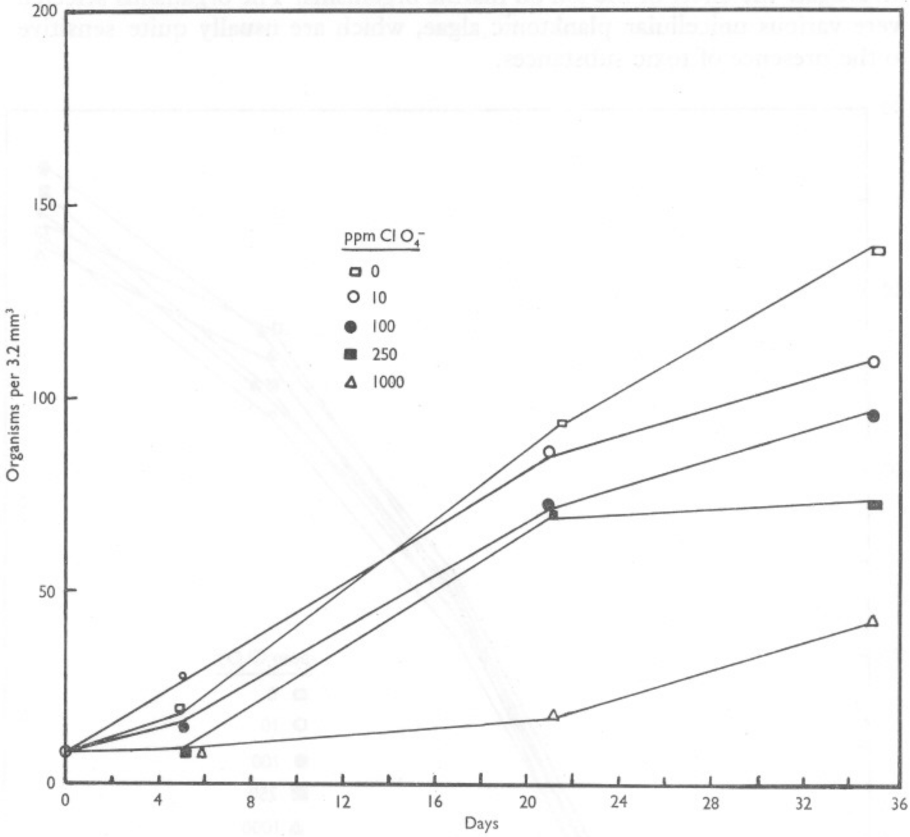

Fig. 5. Effect of perchlorate ion on growth of *Gymnodinium vitiligo*.

A control was also prepared consisting of 300 ml. of the same culture with 100 ml. of sterilized sea water. The cultures were grown at 22° C, illuminated by a fluorescent lamp. The rate of growth of the organisms was determined at intervals by cell counting or by measurement of the optical density of the culture as appropriate.

Of the organisms investigated *Phaeodactylum tricornutum*, *Monochrysis lutheri*, *Isochrysis galbana*, and *Nannochloris oculata* were completely resistant to even 1000 p.p.m. of perchlorate, as typified by *P. tricornutum* (Fig. 4). Some organisms (viz. *Prorocentrum micans* (St German's strain), *Gymnodinium vitiligo*, and *Peridinium trochoideum*) were more sensitive, and with 1000 p.p.m. ClO_4^- exhibited a reduced rate of growth. Certain of these at this perchlorate level also showed an induction period before growth commenced (*P. trochoideum* and *G. vitiligo*) (Fig. 5).

These observations show that the toxicity of the perchlorate ion is very slight, compared with the chlorate ion which is toxic to plant life at a level of a few parts per million. This is probably due to its great chemical stability and its resistance to bio-reduction.

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SUMMARY

The use of tetraphenylarsonium chloride for the detection and determination of perchlorate in sea water has been investigated. An aqueous solution of this reagent gives a visible precipitate of tetraphenylarsonium perchlorate with sea water containing 5 μg ClO_4^-/ml. within 10 min. For the quantitative determination of traces of perchlorate, potassium perrhenate is added to the water sample, and the tetraphenylarsonium perrhenate, which is precipitated by addition of the reagent, co-precipitates tetraphenylarsonium perchlorate. Perchlorate is determined in the mixed precipitate by infra-red absorption spectrophotometry. Using 100 ml. of sea water, a sensitivity of 0·03 μg ClO_4^-/ml. can be attained, with a coefficient of variation of *ca.* 10%. No interference is caused by the ions normally present in sea water.

Over thirty surface and deep water samples from the seas of both the northern and southern hemispheres have been examined for perchlorates, in all cases with negative results. The finding of up to 100 p.p.m. of ClO_4^- in sea water by Baas Becking *et al.* is attributed to the interference of chloride in their analytical method. Contrary to their statement, perchlorate added to sea water is not reduced under normal conditions of storage, nor does it seem to be reduced by biological processes.

The action of perchlorate on the growth of seven unicellular algae has been examined and it has been found that even 1000 p.p.m. of the ion was without action on most of them.

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