

The Phosphorus and Arsenic Compounds of Sea-Water.

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THE first estimations of phosphate in sea-water, in which sufficiently accurate analytical methods were adopted, were carried out more or less simultaneously by Matthews (1916, 1917) and by Raben (1916-20) working independently. Matthews used the colorimetric method of Pouget and Chouchak (1909, 1911), and precipitated the phosphate from 500 c.c. of sea-water by means of ferric chloride. Pouget and Chouchak checked their method using the gravimetric method of Posternak, weighing the barium phosphomolybdate obtained. Values similar to those obtained by Matthews were obtained in the Government Chemist's Laboratory, London, upon samples sent from Plymouth, and the seasonal variation in the phosphate content of sea-water as found by one of us (1923) is in close agreement with the analyses recorded by Matthews—although an entirely different method was used, that of Denigès, which is colorimetric.

Raben analysed sea-water from many sources and from various depths, but his results and those of his co-workers are uniformly much higher than those of Matthews and Atkins (1925, 1926) for surface water; moreover, these results as plotted by Brandt (1920) never indicate that lack of phosphate may set a limit to the algal plankton, for the minimum value found was close to 50 mg. of phosphate, as P_2O_5 per m.³, whereas Matthews and Atkins found the surface water to be almost entirely devoid of phosphate in summer. As has previously been pointed out by one of us (1926) a serious discrepancy exists, though Raben tested his analytical methods upon known minute amounts of phosphate in the presence of the salts of sea-water, and his results leave nothing to be desired so far as their accuracy is concerned and within the limits of the conditions of his test.

Matthews, however, found that with the ammonium phosphomolybdate precipitate a little molybdic acid was liable to be thrown down, and he considered the colorimetric method to be the preferable. He also found

that after oxidising with permanganate or nitric acid larger yields were obtained. He arrived at the conclusion that "the analyses as a whole, however, do not allow more to be stated with certainty than that there is a soluble phosphorus compound present other than phosphoric acid, that it is probably not a lower acid of phosphorus, owing to the comparative difficulty with which it is oxidised, and that it is probably an organic compound." Now Raben's ordinary routine involved evaporation with nitric acid, so the results obtained are comparable rather with Matthews' results for phosphate plus phosphate from organically combined phosphorus than for his values for phosphate alone. The writers do not wish to deny that a portion of the phosphorus present in sea-water may exist in an organic combination, since it is built up into such compounds as lecithin (choline distearyl-glycerophosphate) and others of similar or greater complexity. Such a body as lecithin* is, however, hydrolysed, and not oxidised to phosphate.

While not denying that some of the phosphorus of sea-water may be in solution as a complex phosphate, or as some other complex phosphorus compound, the writers are of the opinion that the results obtained by Matthews can be equally well explained, on a qualitative basis, by taking into account the presence of arsenic in sea-water. The quantitative analyses available show, moreover, that arsenic, calculated as As_2O_3 , may be present in amount equal to, or greater than, that of phosphate, as P_2O_5 . The suggestion is also put forward that Raben's high values for phosphate are due to his method of analysis (though reliable for phosphate alone) including arsenate; the latter would be produced from arsenite originally present, by oxidation with nitric acid as carried out in the course of his method of analysis.

With the object of testing these points, a study of the behaviour of various methods of analysis of phosphate, arsenate and arsenite, was undertaken, the results being published elsewhere (1926). It was found that Denigès reaction for phosphates is given by arsenates also, but not by arsenites. Values for phosphate in sea-water, thus obtained, will accordingly include arsenate, if any; both these radicles would therefore be quantitatively removed from surface waters in early summer. Now algæ are known to contain small amounts of arsenic, as will be mentioned later, so it is possible that a little arsenate is present in sea-water, and is removed by the plankton simultaneously with the removal of phosphate. Arsenic up to 25 mg. As_2O_3 per m^3 is, however, present in water of the English Channel in November (Orton, 1924). This was ascertained by the electrolytic modification of Marsh's apparatus in the Government Chemist's Laboratory, London. It accordingly records

* Stoklasa (1896) showed by a culture experiment with *Avena sativa* in a sterile solution, to which lecithin was added as the only source of phosphorus, that the plant was able to take up lecithin and utilise it.

only the presence of arsenic, without indicating its state of combination. The arsenic, if present as arsenite, would therefore only be detected by Denigès reaction after oxidation. Similarly it was found that Bell and Doisy's method for phosphates was applicable to arsenates also, but arsenites behaved irregularly. This method is, however, less sensitive than that of Denigès, and was not used for sea-water.

Pouget and Chouchak's method, used by Matthews, was also examined; it gives with phosphates either an immediate opalescence in the cold or, if very dilute, on standing; with arsenates in equimolecular quantities no opalescence is obtained in the cold—or at most a very faint opalescence, though on warming the normal opalescence and yellow colour appear; with arsenites only a very faint opalescence appears on warming, due probably to slight oxidation to arsenate. Matthews' results obtained after oxidation appear therefore to be, in part at least, due to the oxidation of arsenite, present in sea-water, to arsenate; the irregularity of the figures obtained, upon which Matthews comments specially, seems to have been due to the uncertain amount of arsenate yielding the opalescence in a solution, not actually warmed, but probably warm from its previous treatment, and to the difficulty of oxidising the arsenite quantitatively to arsenate by either nitric acid or permanganate.

Again, in Raben's work the phosphate was precipitated as ammonium phosphomolybdate, and by using an artificial sea-water made up from pure chemicals Raben demonstrated that the accuracy was not impaired by the presence of the salts. Such a mixture would, however, contain little arsenic, though minute traces must have been present. In sea-water, however, arsenic and phosphorus are, in winter, present in amounts which are roughly equal or of the same order of magnitude. Arsenite present in sea-water would certainly have been converted almost entirely into arsenate by the prolonged evaporation with nitric acid which forms a part of Raben's method, and the ammonium arsenomolybdate produced would have been precipitated and weighed with the phosphomolybdate.

Nevertheless according to Kuhn (1923) it is impossible to base a method for quantitative estimation of arsenic upon the separation of ammonium arsenomolybdate. Under the usual conditions for the precipitation of phosphate, Kuhn states that only a small fraction of the arsenic will be precipitated at 75°, and even at 90° precipitation is incomplete, while at the higher temperatures varying amounts of molybdic acid are precipitated according to the period of heating. Kuhn, however, has overlooked Maderna's (1910) method for the quantitative precipitation of ammonium arsenomolybdate. Raben's analyses appear accordingly to have been vitiated by the weighing of a certain proportion of arsenomolybdate with the phosphomolybdate. This explains why he never obtained results indicating the complete removal of phosphate from the

surface waters, since arsenite remained in the sea-water and was recorded as phosphate.

Pending a study of the arsenic content of sea-water throughout the year it is of interest to note that Gautier and Clausmann (1904) record the presence of 11 mg. per m.³ of arsenic—given as element, not oxide—for surface water 40 kilometres from the coast of Brittany. Near the Azores they found 25 mg. per m.³ at 10 m. depth, and note that the arsenic showed much increase at greater depths. The season is not recorded. The results were obtained by precipitation with a ferric salt and estimation with Marsh's apparatus—and it may be pointed out that Gautier and Clausmann's results afford direct evidence that the phosphate precipitated by Raben also contained arsenic. The values obtained for arsenic are quite in keeping with that found by the Government Chemist, London, 25 mg. per m.³ of arsenic, recorded as As₂O₃, for water near the bottom, 70 m. depth, in the English Channel in November. Since Orton (1924) records a considerable amount of arsenic in oysters, more, in fact, than the amount allowed by law to be sold in foodstuffs, and since oysters feed largely upon diatoms, it is clearly indicated that diatoms must contain a certain amount of arsenic. The increase of arsenic with depth also suggests that in the upper layers its amount has been diminished through absorption by plants. The analyses of Jones (1922) are direct evidence on this point, for he found that the arsenic content of eleven species of algæ varied from seven parts per million of As₂O₃ in *Chondrus crispus* to 125 p.p.m. in *Laminaria digitata*; most of the arsenic is soluble in cold water, and the arsenic content seems to run roughly parallel to that of iodine. Comère (1909), too, has shown that potassium arsenate can be substituted, though apparently not entirely, for phosphate as a nutrient salt for the cultivation of *Stichococcus flaccidus* and *Spirogyra crassa*; of these the former resists the action of various solutions better than the latter, and can take up much more arsenate. Similar experiments showed that *Edogonium capillare* could not thrive on arsenate.

SUMMARY.

1. Much of what was formerly considered to be phosphorus in organic combination, in sea-water, is in reality arsenic.
2. Certain analyses giving high values for phosphate in sea-water and a June minimum very far from complete exhaustion of phosphate are vitiated by the inclusion of arsenate, as arsenomolybdate, in the phosphomolybdate precipitate.
3. Arsenic in sea-water exists mainly in the form of arsenite. The arsenate present, if any, has hitherto been included in the results obtained for phosphate.

4. Since arsenic is found in algæ and has been recorded as increasing in quantity with increase of depth it seems that the arsenic present in sea-water must undergo seasonal changes.

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