

## A SOURCE OF ERROR IN THE ABSORPTIOMETRIC DETERMINATION OF INORGANIC AND TOTAL PHOSPHORUS IN SEA WATER

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In the course of phosphate determinations by the Denigès method it has been noticed that use of stannous chloride solutions containing some stannic tin and a low concentration of hydrochloric acid may give misleadingly high values for the reagent blank in distilled water, when the extinctions<sup>1</sup> of the solutions are measured with a photoelectric absorptiometer in red light (Harvey, 1948). In daylight the solutions may show a perceptible yellow colour, or even, in extreme cases, a turbidity.

The magnitude of the effect has now been measured in reagent blank determinations with distilled water and in phosphate determinations with sea water. In sea water it is smaller or non-existent, so that the reagent blank value is inappropriate and causes over-correction of the measured phosphate content of the samples, leading to fictitiously low results.

The error may be from 1 to 2 mg./m.<sup>3</sup> of phosphate-phosphorus, or even higher when a turbidity is to be seen. It may be eliminated by ensuring that the stannous chloride solution contains about 5% by volume of concentrated hydrochloric acid.

The effect was first observed when an aged stock solution of stannous chloride was diluted with water to give a working solution which contained the required 0.3–0.45 mg. of stannous tin in three drops. When this was added to blank solutions these became faintly yellow in colour and the measured extinctions were greater than was expected. The stock solution had been prepared by dissolving 16 g. of Analar stannous chloride in 40 ml. of a solution containing equal volumes of concentrated hydrochloric acid and water. It had undergone aerial oxidation in the course of 11 months, and a test showed that only 53% of its tin content was in the stannous form. It seemed likely that the presence of stannic tin in this solution had caused the high extinction values found, by producing a colloidal suspension of basic stannic compounds which absorbed or scattered light. Since the production of these compounds is known to be hindered in presence of hydrochloric acid, the experiment of diluting this aged stock solution with 5% v/v hydrochloric acid

<sup>1</sup> The term 'extinction' is here used to denote the function  $\log_{10} I_0/I$ , where  $I_0$  and  $I$  are the intensities of the light entering and leaving the coloured solution. In the concentrations used, the molybdenum blue colour obeys the Beer-Lambert law so that extinction is proportional to the amount of blue compound present. All measurements were made in a 15 cm. cell.

instead of water was tried. (When diluted with water only, the resulting solution contains about 0.8% by volume of concentrated hydrochloric acid.) When the more acid solution was used for reagent blank determinations the extinction measured was found to be about one-third of that given by the stock solution diluted with water, and no yellow colour was apparent.

Other concentrations of hydrochloric acid were tried with the results shown in Table I. The reagent blank solution contained 67 ml. of distilled water and 3 ml. of a reagent containing 18% by volume concentrated sulphuric acid and 10.7% ammonium molybdate. The dilute stannous chloride solutions were adjusted so that each contained 0.45 mg. stannous tin in the 3 drops used. The best concentration appears to be 5% by volume.

TABLE I. INCREASE IN EXTINCTION (MEASURED IN RED LIGHT) OF A REAGENT BLANK SOLUTION UPON ADDITION OF STANNOUS CHLORIDE

Stock stannous chloride diluted with	Increase in extinction (in 15 cm. cell)	Calculated reagent blank (mg. phosphate-P/m. <sup>3</sup> )
Water	0.024	2.9
	0.024	2.9
1 % v/v HCl	0.020	2.4
	0.022	2.6
2 % v/v HCl	0.010	1.2
	0.009	1.1
5 % v/v HCl	0.009	1.1
	0.009	1.1
10 % v/v HCl	0.012	1.4
	0.012	1.4

To see how the reagent blank was affected by varying stannic tin content of the stannous chloride solution, three solutions were made as follows:

(1) By dissolving 16 g. of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 40 ml. of 1:1 HCl, the salt being about 10 years old and badly oxidized. The solution was found to contain 68% of stannous and 32% of stannic tin.

(2) By preparing a similar solution from fresh stannous chloride of good appearance. This contained 93% of stannous and 7% of stannic tin.

(3) By dissolving 8.4 g. of tin in 32 ml. of conc. HCl and 8 ml. of water, adding two drops of 5% copper sulphate to assist solution. On test, this preparation was found to contain 100% stannous tin.

From each of these, diluted solutions of the same stannous tin content were made, in water and in 5% v/v HCl, and were used for reagent blank determinations. The results are shown in Table II.

From these it appears that in solutions diluted with water, high stannic tin content is accompanied by high reagent blank values. When hydrochloric acid is used the blanks appear to be independent of the stannic tin concentration. It is notable that even in the case of the reagent prepared by diluting the 100% stannous chloride with water there is an enhanced extinction, which may be due to the production of sufficient stannic tin in the diluted solution to cause some scattering of light.

After this demonstration that the reagent blank is increased in distilled water if the stannous chloride reagent has a low HCl content and high stannic tin concentration, the effect in sea water was measured. The experiments were carried out under the same conditions as are used when phosphate in sea water

TABLE II. EFFECT OF VARYING STANNIC TIN CONTENT OF STANNOUS CHLORIDE REAGENT UPON REAGENT BLANK

Fraction of total tin content of stock solution in		Stock solution diluted with water		Stock solution diluted with 5% v/v HCl	
Stannous form (%)	Stannic form (%)	Extinction	Reagent blank (mg./m. <sup>3</sup> )	Extinction	Reagent blank (mg./m. <sup>3</sup> )
68	32	0.023	2.7	0.009	1.1
		0.029	3.4	0.008	1.0
93	7	0.024	2.8	0.007	0.8
		0.022	2.6	0.008	1.0
100	Nil	0.018	2.1	0.009	1.1
		0.019	2.3	0.008	1.0

is determined, viz. to 67 ml. of sea water 3 ml. of a reagent containing 18% v/v H<sub>2</sub>SO<sub>4</sub> and 10.7% ammonium molybdate were added. The extinction of the resulting solution was measured. Three drops of stannous chloride were added, and the extinction again measured when it had attained its maximum. To the solution 0.3 ml. of a standard phosphate solution was then added, increasing the phosphorus concentration by 20 mg. per m.<sup>3</sup>, followed by a further two drops of stannous chloride. The extinction was measured again when it had reached its maximum. The difference between the first two readings was a measure of the phosphate-phosphorus content of the sea water, together with the blank contributed by the reagents. The difference between the second and third readings measured the extinction produced by unit quantity of phosphorus under the experimental conditions. A separate determination of the reagent blank allowed the phosphate-phosphorus content of the sea water to be calculated.

Table III shows results obtained with a sample of sea water of low phosphate content which had been filtered to remove any particulate matter which might contain phosphate (Cooper, 1948, p. 298).

Although in absence of sufficient hydrochloric acid it is seen that the increase in extinction is enhanced by the presence of stannic tin, this enhancement is less in sea water than in distilled water; it has led in the extreme case to a negative value for the calculated phosphate-phosphorus. No significant alteration is seen in the extinction recorded after addition of phosphate subsequent to the first measurement.

The experiment was duplicated with the same sea water enriched with 8.9 mg./m.<sup>3</sup> of phosphate-phosphorus. The stannous chloride solutions in this experiment were different preparations. The results are shown in Table IV.

The difference in extinction values for the addition of 20 mg./m.<sup>3</sup> phosphate-phosphorus between Tables III and IV can be accounted for by the temperature difference.

TABLE III. ESTIMATION OF PHOSPHATE IN SEA WATER USING STANNOUS CHLORIDE REAGENTS CONTAINING EQUAL QUANTITIES OF STANNOUS, AND VARYING AMOUNTS OF STANNIC TIN. TEMPERATURE OF SOLUTIONS, 22° C.

Stannic tin content of stock solution as fraction of total tin present (%)	Stock solution diluted with water					Stock solution diluted with 5% v/v HCl				
	Extinction in		Further increase in extinction in sea water after subsequent addition of 20 mg./m. <sup>3</sup> phosphate-P	Calculated PO <sub>4</sub> -P (mg./m. <sup>3</sup> )	Extinction in		Further increase in extinction in sea water after subsequent addition of 20 mg./m. <sup>3</sup> phosphate-P	Calculated PO <sub>4</sub> -P mg./m. <sup>3</sup>		
	Distilled water	Sea water			Distilled water	Sea water				
67	0.068, 0.069	0.037 0.039	0.168 0.172	-3.8 -3.4	0.011, 0.010	0.031 0.033	0.170 0.168	2.4 2.6		
32	0.030, 0.030	0.043 0.040	0.170 0.172	1.5 1.2	0.010, 0.009	0.030 0.030	0.171 0.169	2.4 2.4		
Nil	0.016, 0.015	0.031 0.033	0.167 0.169	1.9 1.9	0.010, 0.010	0.031 0.033	0.170 0.168	2.5 2.6		

TABLE IV. ESTIMATION OF PHOSPHATE IN SEA WATER ENRICHED WITH 8.9 MG. PHOSPHATE-P PER M.<sup>3</sup> USING STANNOUS CHLORIDE REAGENTS CONTAINING EQUAL QUANTITIES OF STANNOUS, AND VARYING AMOUNTS OF STANNIC TIN. TEMPERATURE OF SOLUTIONS, 20° C.

Stannic tin content of stock solution as fraction of total tin present (%)	Stock solution diluted with water					Stock solution diluted with 5% v/v HCl				
	Extinction in		Further increase in extinction in sea water after subsequent addition of 20 mg./m. <sup>3</sup> phosphate-P	Calculated PO <sub>4</sub> -P mg./m. <sup>3</sup>	Extinction in		Further increase in extinction in sea water after subsequent addition of 20 mg./m. <sup>3</sup> phosphate-P	Calculated PO <sub>4</sub> -P mg./m. <sup>3</sup>		
	Distilled water	Sea water			Distilled water	Sea water				
59	0.042, 0.032	0.107 0.108	0.166 0.167	8.4 8.5	0.010, 0.010	0.107 0.107	0.167 0.168	11.6 11.6		
32	0.030, 0.030	0.111 0.116	0.167 0.168	9.7 10.2	0.011, 0.011	0.109 0.109	0.167 0.168	11.7 11.7		
Nil	0.014, 0.013	0.108 0.107	0.167 0.167	11.2 11.1	0.009, 0.009	0.107 0.107	0.168 0.168	11.7 11.7		

The last columns of these tables, showing the calculated phosphorus in the sea water without and with the addition of 8.9 mg./m.<sup>3</sup>, show a mean difference of 9.18 mg./m.<sup>3</sup> with a maximum difference of 9.3 and a minimum difference of 9.0. This estimated difference is considered to be in reasonable agreement with the known addition of phosphate, and indicates that the technique of 'subsequent addition' is valid (Harvey, 1948, p. 351).

It is therefore recommended that the stannous chloride used in this method should contain at least 5% by volume of concentrated hydrochloric acid.

This condition, it should be noted, is complied with in the original visual method of Atkins (1923, p. 144), in which the freshly prepared stannous chloride contains 10 to 20% by volume of acid. In any event the presence of stannic tin with a low acid concentration is less likely to upset the visual estimation of the reagent blank, as its effect is to discolour, not augment, any blue colour formed.

## SUMMARY

The results of phosphate determinations in sea water by the Denigès method, using red light, in an absorptiometer, may be in error if the stannous chloride reagent has low HCl concentration, and contains stannic tin.

The error is in the reagent blank determination, and seems to be caused by colloidal stannic compounds which increase the opacity of the solution. In sea water the effect may be smaller or immeasurable so that results are over-corrected.

When the stannous chloride solution contains about 5% hydrochloric acid, reagent blank figures are low, and independent of stannic tin concentration. This acidity is recommended.

## REFERENCES

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