

This Week's Citation Classic®

CC/NUMBER 12
MARCH 24, 1986

Murphy J & Riley J P. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27:31-6, 1962.
[Department of Oceanography, University of Liverpool, England]

This paper presents a simple and reproducible photometric procedure for the determination of parts per billion concentrations of phosphate in natural waters. It is adaptable to many other types of sample because of its freedom from interelement interferences. [The SC/® indicates that this paper has been cited in over 1,520 publications, making it the most-cited paper ever published in this journal.]

James Murphy and John P. Riley
Department of Oceanography
University of Liverpool
Liverpool L69 3BX
England

January 28, 1986

In the late 1950s, we had been carrying out work at the Department of Oceanography, University of Liverpool, on the cycle of phosphate in the sea. Our work was held back by the lack of a suitable method for determination of the very low levels present ($< 1\text{-}160\mu\text{g l}^{-1}$). Photometric methods depending on the formation of phosphomolybdenum blue complexes had been in use since the 1920s. However, the intensity of the colour that was obtained with a given amount of phosphate very much depended on the reductant used to reduce the intermediate phosphomolybdic acid.¹

Tin (II) chloride had been used for this purpose, as it gave a very intense blue colour and hence a very high sensitivity. It had the disadvantages that the colour was only stable for a very few minutes and that in seawater the formation of the colour was delayed and its intensity decreased by the presence of the major ions of the seawater. We set about trying to find a reducing agent free from these defects.

After testing a number of compounds, we found that ascorbic acid (vitamin C) was satisfactory and

allowed the analysis to be carried out with a single reagent rather than by adding the reducing agent after the acid molybdate as had been done before.² It had the disadvantage that the colour development required 12 hours, leading to the possibility that organic phosphorus compounds might be hydrolysed and their phosphorus included in the analysis. Ascorbic acid had been used as a reductant in the analysis before,³ but the conditions employed were not optimal, and maximum colour was not, therefore, developed.

We decided, therefore, to see if the rate of colour development could be increased. I had read that the incorporation of bismuth in the reagent did speed up the reaction.⁴ When we tried this, we found that this was the case but that hydrolysis of the bismuth led to a turbidity that made the technique useless for the determination of low levels of phosphate. Consideration of the periodic table suggested that it might be worthwhile substituting antimony—its immediate neighbour in Group Va—for bismuth. Immediate success was achieved when this was done, colour development being complete in two to three minutes. Once formed, the colour, which was due to a complex containing antimony, phosphorus, and molybdenum, was stable for many days. Furthermore, the technique gave a sensitivity slightly superior to that obtained with tin (II) chloride, was free from interference from most other elements, and was not affected by seawater salts.

I suppose that the reason this paper has been so extensively cited is that it provides a simple, highly reproducible technique for the determination of microgram amounts of phosphate. Almost 25 years later, the method is still basically the recommended standard procedure for the analysis of fresh and potable waters,^{5,6} as well as seawater.^{7,8} Although it was originally developed for the analysis of phosphate in natural waters, it has been widely adopted in many other fields, including, for example, botany, zoology, biochemistry, geochemistry, metallurgy, and clinical medicine. Indeed, kits for the determination are available commercially for use in physiological investigations and water analysis.

1. Burton J D & Riley J P. The determination of soluble phosphate and total phosphorus in sea waters and of total phosphorus in marine muds. *Mikrochim. Acta* 9:1350-7, 1956.
2. Murphy J & Riley J P. A single solution method for the determination of soluble phosphate in sea water. *J. Mar. Biol. Assn. UK* 37:9-14, 1958. (Cited 60 times.)
3. Greenfield L J & Kalber F A. Inorganic phosphate measurement in seawater. *Bull. Mar. Sci. Gulf Caribb.* 4:323-35, 1954.
4. Jean M. Étude du dosage du phosphore et de l'arsenic dans les aciers par colorimétrie. *Anal. Chim. Acta* 14:172-82, 1956.
5. Her Majesty's Stationery Office. *Methods for the examination of waters and associated materials: phosphorus in waters, effluents and sewages.* London: HMSO, 1981. 31 p.
6. American Public Health Association. *Standard methods for the examination of water and wastewater.* Washington, DC: American Public Health Association, 1984.
7. Koroleff K. Determination of nutrients. (Grasshoff K, Ehrhardt M & Kremling K, eds.) *Methods of seawater analysis.* Weinheim, FRG: Verlag Chemie, 1983. 419 p.
8. Parsons T R, Malta Y & Lalli C M. *A manual of chemical and biological methods for seawater analysis.* Oxford: Pergamon Press, 1984. 173 p.