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Review

The molybdenum blue reaction for the determination of orthophosphate revisited: Opening the black box

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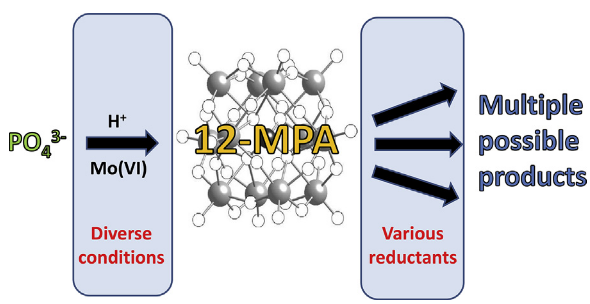
HIGHLIGHTS

- Molybdenum blue chemistry for orthophosphate determination is discussed.
- The choice of reductant determines the blue product(s) obtained.
- Mechanisms are described for various additive and subtractive interferents.
- The choice of strong mineral acid for the reaction should be considered.
- Detailed recommendations are made for method optimisation.

GRAPHICAL ABSTRACT



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ABSTRACT

The molybdenum blue reaction, used predominantly for the determination of orthophosphate in environmental waters, has been perpetually modified and re-optimised over the years, but this important reaction in analytical chemistry is usually treated as something of a 'black box' in the analytical literature. A large number of papers describe a wide variety of reaction conditions and apparently different products (as determined by UV–visible spectroscopy) but a discussion of the chemistry underlying this behaviour is often addressed superficially or not at all. This review aims to rationalise the findings of the many 'optimised' molybdenum blue methods in the literature, mainly for environmental waters, in terms of the underlying polyoxometallate chemistry and offers suggestions for the further enhancement of this time-honoured analytical reaction.

List of abbreviations: (br), Broad absorption band; (sh), Absorption shoulder; 12-MPA, 12-Molybdophosphoric acid ($H_3PMo_{12}O_{40}$); 11-MPA, 11-Molybdophosphoric acid ($H_3PMo_{11}O_{37}$); 12-MSA, 12-Molybdosilicic acid ($H_4SiMo_{12}O_{40}$); AA, Ascorbic acid; ANS, 1-Amino-2-naphthol-4-sulfonic acid; AsMB, Arsenomolybdenum blue; DA, Discrete analyser; DAPH, 2,4-Diaminophenol dihydrochloride; DOP, Dissolved organic phosphorus; MB, Molybdenum blue; DRP, Dissolved reactive phosphorus; ESI-MS, Electrospray ionisation mass spectrometry; FIA, Flow injection analysis; HQ, Hydroquinone; HS, Hydrazine sulfate; IVCT, Intervalence charge transfer; LMCT, Ligand-metal charge transfer; Metol, 4-(Methylamino)phenol sulfate; MRP, Molybdate reactive phosphorus; PMB, Phosphomolybdenum blue; rFIA, Reverse flow injection analysis; SFA, Segmented continuous flow analysis; SIA, Sequential injection analysis; SiMB, Silicomolybdenum blue; TDP, Total dissolved phosphorus.

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Contents

1. Introduction

Orthophosphate concentration is a key water quality parameter and spectrophotometric detection using the molybdenum blue (MB) reaction is the most common means of determination [1]. It can also be used for the spectrophotometric determination of silicate, arsenate and germanate. Strictly, this reaction determines the 'molybdate reactive phosphorus' (MRP) fraction which includes other labile phosphorus species in addition to orthophosphate [2] as discussed in Section 4.1.

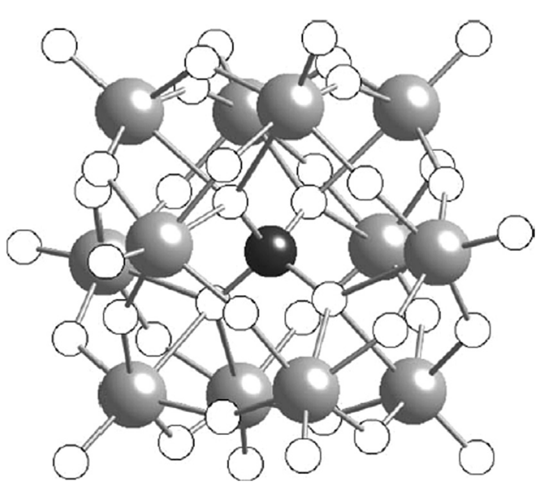

Fig. 1. Structure of the Keggin ion $[PW_{12}O_{40}]^{3-}$, analogous to that of $[PMo_{12}O_{40}]^{3-}$. The black, grey and white spheres represent P, W and O respectively. Reproduced from Ref. [5] with permission from The Royal Society of Chemistry.

The reaction involves the formation of a polyoxometallate species, a heteropoly acid, from orthophosphate and molybdate under acidic conditions, which is then reduced to form an intensely coloured phosphomolybdenum blue (PMB) species. This reaction was mentioned by Scheele in 1783, but its discovery is widely attributed to Berzelius (1826) [3]. It was not until 1934, however, that Keggin proposed the structures of a range of 12-heteropoly acids [4] (Fig. 1). 'Molybdenum blue' refers not to a single species, but rather to a family of reduced molybdate compounds, which may or may not contain a heteroatom, e.g. phosphorus. Distinction between heteropoly (containing a hetero-atom) and isopoly (containing no hetero-atom) molybdenum blue species is made in this review where necessary.

A fundamental understanding of the inorganic chemistry of the MB reaction is important for optimising its analytical application for the determination of orthophosphate. In particular, the concentrations of the reagents can be optimised to maximise the degree of product formation and product stability (for batch methods)