

**HIGHLY SENSITIVE SIMULTANEOUS SPECTROPHOTOMETRIC
DETERMINATION OF PHOSPHATE AND SILICATE BASED ON FORMATION
OF ION ASSOCIATION COMPLEXES BETWEEN ASTRA PHLOXINE AND
12-HETEROPOLYMOLYBDATE ANIONS**

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Nowadays the highly sensitive determination of phosphate and silicate ions is necessary for the analysis of high purity chemicals and water, including water used as cooling water in thermal and nuclear power plants. According to the standards, their concentration should be less than 10^{-7} mol L⁻¹.

The most serious problem in the analytical chemistry of heteropoly molybdate is the mutual interfere in the determination of phosphorus (V), silicon (IV), arsenic (V), and germanium (IV). To avoid these interferences in applying spectrophotometric methods there is a need to develop a method that can determine one element by the elimination of the interference of other elements.

In the present study, a green, rapid, highly sensitive, selective, and non-extractive spectrophotometric method has been developed for individual and simultaneous determination of trace amounts of phosphate and silicate in aquatic samples and high purity chemicals. These methods are based on the formation of ion association complexes (IA) between 12- heteropoly molybdate of the indicated elements with polymethine dye Astra Phloxine FF (AP) to form a red-violet color-specific IA, Which has the maximum absorption in the difference spectrum at 574 nm. Ion associates formed between heteropolyanions (HPAs) and cationic dyes are stable for several hours. There is no need to use surfactant for the solubilization of the finely dispersed precipitate. The molar absorptivities of corresponding IAs are 1.54×10^5 and 2×10^5 L mol⁻¹ cm⁻¹ for P(V) and Si(IV), respectively. The calibration curves were linear over a concentration range of 4×10^{-8} – 8×10^{-7} and 2×10^{-8} – 8×10^{-7} mol L⁻¹ for phosphate and silicate, respectively. The corresponding limits of detection were calculated to be as low as 7 nmol L⁻¹ for both phosphate and silicate.

The interfering effect of Si(IV) on P(V) determination and vice versa can be minimized using a specific order of acidification or by applying masking agents. Silicate requires lower acidity than phosphate to form heteropoly acids but has greater stability and is not destructed even in 1 M H₂SO₄. The optimal concentration of acid used in this work for the reaction with phosphate was unsuitable for the formation of complexes with silicate. This allowed determining orthophosphate in presence of up to 20-fold excess of silicate without masking. Using masking with 6×10^{-3} mol L⁻¹ of NaF the permissible concentration of silicate ions was increased to 10^{-3} M (more than 1000-fold excess). The interference of phosphate in the determination of silicate was avoided by adding a 2×10^{-3} mol L⁻¹ of an oxalic acid solution or 2 mL of concentrated hydrochloric acid to destroy the molybdophosphoric acid complex. In the first case, permissible phosphate concentration was equal to 5×10^{-4} mol L⁻¹.

The proposed method was successfully applied to the simultaneous determination of phosphorus and silicon in steels immediately after dissolution, in distilled and bidistilled water, in hydrochloric and nitric acids, in samples of natural waters, and salts.

The content of P(V) and Si(IV) in distilled water was equal to 5.65 and 9 µg L⁻¹, respectively. Sodium chloride of «chemically pure» quality contained 1.047×10^{-5} % of Si(IV) and 6.28×10^{-6} % of P(V).