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Review

Ion chromatographic separations of phosphorus species: a review

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Abstract

The aim of this paper is to review recent literature regarding the determination of phosphorus species by ion chromatography (IC), and describe the implementation of new developments in sample treatment and ion chromatography methodology for the analysis of these compounds. Ion-exchange methods using both carbonate/hydrogencarbonate and hydroxide selective columns in combination with self-regenerating membrane and solid-phase-based suppressors enable determination of phosphate down to ppb levels. New technology, particularly on-line electrolytic hydroxide generators and electrolytic self-regenerating suppressor devices, has allowed the use of elution gradients in both carbonate/hydrogencarbonate and hydroxide selective systems, improving sensitivity and reducing total analysis time for samples containing phosphate together with other inorganic anions. In addition to a review of these developments, optimization and application of chromatographic methods using reversed stationary phases and cationic and/or zwitterionic surfactants is also discussed.

The objective of most of the IC methods developed for phosphorus species is the determination of phosphate and total phosphorus. Therefore, sample treatment and separation conditions specifically developed for this purpose are also described. In addition, application of IC to the analysis of other inorganic (reduced and condensed) and organic (phytates, alkyl phosphate, and phosphonates) phosphorus species is discussed along with methodology and relevant applications in water analysis and other miscellaneous fields.

Keywords: Ion chromatography; Phosphorus; Phosphate determination

Contents

Abbreviations: AES, anion electrolytic suppressor; AMMS, anion micromembrane suppressor; ANN, artificial neural network; ASRS, anion self-regenerating suppressor; CTA, cetyltrimethylammonium; DBP, dibutyl phosphate; DDA, didodecyldimethylammonium; EIC, electrostatic ion chromatography; ERIS, electrochemically-regenerated ion suppressor; ESI-MS, electrospray ionization-mass spectrometry; EVB/DBV, ethylvinylbenzene/divinylbenzene; FIA, flow injection analysis; FID-IC, flow injection dialysis-ion chromatography; IC, ion chromatography; ICP-MS, inductively coupled plasma-mass spectrometry; InsP6, phytate; InsP6–InsP1; IP, inositol hexakis- to mono-phosphates; LOD, limit of detection; LOQ, limit of quantitation; MBP, monobutyl phosphate; MES, 2-(*N*-morpholino)ethanesulfonic acid; MFP, monofluorophosphate; MOPS, 3-(*N*-morpholino)-2-hydroxypropanesulfonic acid; MPA, molybdophosphoric acid; MTA, myristyltrimethylammonium; PGC, porous graphitized carbon; SCAN, sample concentration and neutralization processor; SPME, solid phase microextraction; TBA, tetrabutylammonium; TBP, tributyl phosphate; TRIS, tris(hydroxymethyl)aminomethane; TTA, tetradecyltrimethylammonium; VPD, vapour phase digestion

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1. Introduction

Phosphorus, a key nutrient in certain living organisms, such as plants and microorganisms, is involved in several biological and environmental processes. Phosphates [P(V)], the most abundant form of phosphorus in the environment, are readily available for assimilation, and for this reason, they have traditionally been used as fertilisers. In addition, phosphate and other phosphorus compounds are widely employed as detergents and food additives, among other uses [1,2]. Extensive input of phosphorus by overfertilization, and by industrial and domestic wastewater pollution result in overabundance in aquatic media [3]. Consequently, monitoring of phosphorus content in natural and wastewaters is essential to control and avoid eutrophication of the aquatic environment. Although, in addition to orthophosphate, several phosphorus species, such as polymeric inorganic and organic phosphorus compounds, can be found in the environment, analysis is commonly performed as phosphate [4,5]. Acid hydrolysis using sulfuric-nitric acid mixtures and digestion procedures, mainly by means of persulfate oxidation, transform condensed and organic phosphorus species to orthophosphate, allowing determination of total phosphorus content. The final step, which involves determination of orthophosphate, may be performed using various techniques, commonly by spectrometry and ion chromatography (IC). In addition to environmental studies, determination of phosphates and total phosphorus content is also important in other areas, including food and plants analysis. For this purpose, ion chromatography has been extensively applied [6–9].

Since its introduction by Small et al. [10], ion chromatography has become the method of choice for the analysis of anions in a wide variety of samples. Since then, the term ‘ion chromatography’, which was initially used to define a chromatographic method for ion analysis using ion-exchange columns and suppressed conductivity detection, has evolved substantially. Nowadays, ion chromatography is also performed using non-suppressed conductivity detection. Non-suppressed IC was developed by Gjerde et al. as an alternative approach to ion analysis using low conductivity eluents [11]. Currently, in addition to ion-exchange, ‘ion chromatography’ encompasses various chromatographic systems for ion determination, such as ion-exclusion, ion-interaction, and the novel electrostatic ion chromatography (EIC). Moreover, in addition to conductimetry, which is by far the most common detection technique in IC, other techniques, such as UV (indirect or post-column), refractive index, evaporative laser light scattering, and inductively coupled plasma and atmospheric pressure ionisation mass spectrometry, have also been combined with IC separations [12].

Although IC methodology for routine phosphate determination is well established, and has even been included in regulatory and standard methods, research in this field remains active [13,14]. The implementation of recent advances, such as the development of new suppressors, on-line eluent generators, and special columns, to the development of new IC methods for the determination of phosphate and other common anions has been directed towards the improvement of sensitivity and selectivity in ion chromatography. Thus, various papers deal with the optimization and comparison of anion separations using new technology, and its further application to complex samples, enabling the resolution of compromised separations with enhanced detection limits. Recent technical advances and applications of ion chromatography in various analytical fields have been periodically reviewed. Most of these reviews have been published in the yearly special issues of the *Journal of Chromatography* devoted to the International Ion Chromatography Congress. In particular, reviews focused on new developments in ion chromatography [12,15], particularly in suppressor [16] and column technology [17], and applications in different fields [6–9] are highly recommended.

This review surveys ion chromatography methods for the determination of phosphorus species, addressing methods and applications published since 1997. The focus of the revision is centered on the determination of phosphate and total phosphorus, which is the objective of most of the IC methods developed for phosphorus species. However, IC applications