Analytica Chimica Acta 647 (2009) 137–148

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Review

Determination of phosphorus, sulfur and the halogens using high-temperature molecular absorption spectrometry in flames and furnaces—A review

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ARTICLE INFO

Article history:
Received 27 April 2009
Received in revised form 4 June 2009
Accepted 11 June 2009
Available online 21 June 2009

Keywords:
Molecular absorption spectrometry
Non-metals determination
Phosphorus
Sulfur
Halogens

ABSTRACT

The literature about the investigation of molecular spectra of phosphorus, sulfur and the halogens in flames and furnaces, and the use of these spectra for the determination of these non-metals has been reviewed. Most of the investigations were carried out using conventional atomic absorption spectrometers, and there were in essence two different approaches. In the first one, dual-channel spectrometers with a hydrogen or deuterium lamp were used, applying the two-line method for background correction; in the second one, a line source was used that emitted an atomic line, which overlapped with the molecular spectrum. The first approach had the advantage that any spectral interval could be accessed, but it was susceptible to spectral interference; the second one had the advantage that the conventional background correction systems could be used to minimize spectral interferences, but had the problem that an atomic line had to be found, which was overlapping sufficiently well with the maximum of the molecular absorption spectrum. More recently a variety of molecular absorption spectra were investigated using a low-resolution polychromator with a CCD array detector, but no attempt was made to use this approach for quantitative determination of non-metals. The recent introduction and commercial availability of high-resolution continuum source atomic absorption spectrometers is offering completely new possibilities for molecular absorption spectrometry and its use for the determination of non-metals. The use of a high-intensity continuum source together with a high-resolution spectrometer and a CCD array detector makes possible selecting the optimum wavelength for the determination and to exclude most spectral interferences.

Contents

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0003-2670/$ – see front matter
doi:10.1016/j.aca.2009.06.029

1. Introduction

1.1. Importance of the non-metals

Phosphorus, sulfur and the halogens are of great importance for a number of reasons: firstly, all of them, maybe with the exception of bromine, are essential elements for humans, animals and many plants, and have therefore to be determined in body fluids and tissues, but also in food and feed, soils and plants in order to avoid deficiency or an over-dose of these elements in our diet. Secondly, all of these elements are highly toxic in elemental form and/or in certain compounds; hence, all of them are of environmental concern and have to be determined in air, water, soils and sediments, and in plants and animals of exposed areas. Thirdly, all the above elements are of great importance in chemical industry, and are contained in many intermediate and final products, either as essential components or as (unwanted) residues from the manufacturing process.

Phosphorus is with a content of about 0.1% the 12th most abundant element of our earth's crust. All living organisms store energy in a process called phosphorylation, where adenosine-5′-diphosphate (ADP) is converted to adenosine-5′-triphosphate (ATP) by the uptake of inorganic phosphate. In humans and vertebrate phosphorus is found as calcium phosphate in bones, and as building block of nucleic acids in the form of esters of phosphoric acid. Phosphates are essential for animals and plants, but a high concentration of phosphate in lakes and oceans can cause excessive growth of algae.

Sulfur is with a content of about 0.048% the 15th most abundant element of our earth's crust. It is an essential element for plants and animals; it makes part of various amino acids, co-enzymes and vitamins. The gaseous compounds H_2S and SO_2, however, are highly toxic; the latter one is liberated in great quantities by combustion of fossil fuel, and it has contributed significantly to acid rain. The reduction of sulfur in diesel fuel is currently one of the greatest international projects in order to improve air quality and reduce the environmental impact of SO_2.

Fluorine is with a content of about 0.07% the 13th most abundant element of our earth's crust; it is an essential element for humans, although fluorides are pronounced poisons that are blocking various enzymes. The benefits of fluorides in the prevention of dental caries has been discussed controversially for many years, but is generally accepted nowadays. The World Health Organization (WHO) recommends supplementation of 1.0–1.5 mg F per day, preferably by fluoridization of drinking water; fluoride has also been used successfully in the treatment of osteoporosis. Because of its importance for human health, fluorine is often determined in food, drinks and water [1–4], whereas its determination in coal is necessary because of its possible harmful ecological effects [5].

Chlorine is with a content of about 0.0314% one of the 20 most abundant elements of our earth's crust. The greatest reserve of chloride is in the oceans; sea water contains in average about 2% of chloride. Chloride is one of the major ions in living organisms. The human organism contains about 0.12% Cl. Chlorine is also one of the most important base products of chemical industry, for example for the production of vinyl chloride, PVC and many others. Because of its omnipresence, chlorine has to be determined in a wide variety of matrices, such as water [3,6], food and drinks [6], body fluids [7], soils and sediments [6], airborne dust [8], and also in crude oil and petroleum products [9].

Bromine is only contained to 0.00078% in our earth's crust; the biggest reserves of bromide, similar to chloride, are the oceans; sea water contains an average of 0.0065% Br. Bromine has no known biological function, but bromium compounds are used as tranquilizers. Bromium compounds are widely used in photographic chemicals, as flame retardants in plastic materials and for hydraulic fluids in crude oil extraction. Methyl bromide has high insecticidal and fungicidal properties and is used for the fumigation of plant products in storage, which necessitates a determination of bromine in crops [10].

Iodine is a typical trace element with an abundance of only 0.000061% in our earth's crust, but it is an essential element for all vertebrate; it is a component of the thyroid hormones thyroxine and tri-iodothyronine. The human body contains about 10–30 mg iodine, 99% of which is in the thyroids. Iodine deficiency results in hypothyrosis and formation of goiter in adult or cretinism in children. The WHO recommends a daily intake of 150–200 μg of iodine, and in many countries iodide-enriched table salt is used for that purpose. An excess of iodine can cause hyperthyroidism and allergies. The main reservoirs of iodine are the oceans; sea water contains an average of 50 mg t^{-1}, and organisms, such as algae, seaweed and sponges can accumulate iodine up to a concentration of 19 g kg^{-1} dry weight.

1.2. Methods for the determination of non-metals

The variety of methods and instrumental techniques that have been used for the determination of the non-metals is so great that it is impossible to mention all of them. They reach from classical wet chemical procedures, which are still widely used, over ion-selective electrodes, chromatographic procedures to sophisticated spectrometric techniques, such as high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). It should be mentioned, however, that there is not a single instrumental technique that could be used for the determination of all the non-metals treated in this review, maybe except for HR-ICP-MS. In the following we only want to discuss briefly selected techniques with special emphasis on spectrometric techniques, their advantages and limitations.