Analytica Chimica Acta 854 (2015) 13–19

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

Fast sequential multi-element determination of major and minor elements in environmental samples and drinking waters by high-resolution continuum source flame atomic absorption spectrometry

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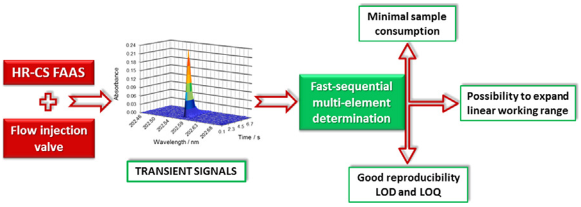
HIGHLIGHTS

- We develop a HR CS FAAS method for fast sequential multi-elemental analysis.
- Major and minor elements are determined in a single run using the same solution.
- Less than 10 mL of sample are necessary to determine in triplicate eleven elements.
- The method is successfully applied in environmental samples and drinking waters.
- The sample consumption is minimal compared to multi-elemental analysis by LS FAAS.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 July 2014
Received in revised form 16 October 2014
Accepted 30 October 2014
Available online 31 October 2014

Keywords:
High-resolution continuum source flame AAS
Multi-element determination
Side pixel registration
Low sample consumption
Metal analysis in environmental samples and drinking waters

ABSTRACT

The fast sequential multi-element determination of 11 elements present at different concentration levels in environmental samples and drinking waters has been investigated using high-resolution continuum source flame atomic absorption spectrometry. The main lines for Cu (324.754 nm), Zn (213.857 nm), Cd (228.802 nm), Ni (232.003 nm) and Pb (217.001 nm), main and secondary absorption lines for Mn (279.482 and 279.827 nm), Fe (248.327, 248.514 and 302.064 nm) and Ca (422.673 and 239.856 nm), secondary lines with different sensitivities for Na (589.592 and 330.237 nm) and K (769.897 and 404.414 nm) and a secondary line for Mg (202.582 nm) have been chosen to perform the analysis. A flow injection system has been used for sample introduction so sample consumption has been reduced up to less than 1 mL per element, measured in triplicate. Furthermore, the use of multiplets for Fe and the side pixel registration approach for Mg have been studied in order to reduce sensitivity and extend the linear working range. The figures of merit have been calculated and the proposed method was applied to determine these elements in a pine needles reference material (SRM 1575a), drinking and natural waters and soil extracts. Recoveries of analytes added at different concentration levels to water samples and extracts of soils were within 88–115% interval. In this way, the fast sequential multi-element determination of major and minor elements can be carried out, in triplicate, with successful results

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http://dx.doi.org/10.1016/j.aca.2014.10.051

without requiring additional dilutions of samples or several different strategies for sample preparation using about 8–9 mL of sample.

1. Introduction

Determination of trace, minor and major elements in environmental samples such as natural waters, soils or sediments is necessary for characterization of samples and monitoring in pollution processes [1]. For example, a soil used for agricultural purposes must be fertilized with adequate nutrients to optimize crop production, as a function of its physical–chemical characteristics and the grown crop [2,3]. In this way, there is an increase in the number of environmental samples and elements that must be analyzed and determined. Besides, a quality control of drinking waters (tap or bottled water samples) must be also performed to ensure these samples meet the legislative requirements. Development and implementation of screening and fast multi-element methods are of great interest for routine laboratories devoted to large scale analysis in order to reduce significantly time and analytical cost. Furthermore, if the sample consumption as well as the use of toxic or hazardous reagents can be diminished analytical methods achieve additional economic and environmental benefits and so they can be considered environmental-friendly [4,5].

Most common techniques usually employed to determine metals are based on spectrometric techniques, such as atomic absorption spectroscopy (AAS) with flame or graphite furnace atomizers and inductively coupled plasma-optical emission or mass spectrometry (ICP-OES or ICP-MS) [6–8]. Analytical methodologies based on AAS techniques are used to perform numerous routine tasks in the laboratory ranging from the determination of trace contents through to major constituents. The main drawbacks of these methodologies are narrow ranges of calibration and single-element determinations [9,10]. Plasma techniques show high sensitivity and permit multi-elemental analysis, so in many laboratories the well-established AAS methodologies is being replaced by ICP-OES or ICP-MS if multi-element analysis is required [8,9]. However, AAS has gained its place alongside ICP-OES and ICP-MS due to the adequate sensitivity, reasonable cost, and relatively simple operation of classical AAS methods.

The introduction of high-resolution continuum source atomic absorption spectrometry (HR-CS AAS) in the last decade has further expanded the applicability of AAS methods [11,12]. Using this approach simultaneous determination of more than one element at the same time if absorption lines or the elements appear within spectral interval that reaches the detector can be performed [13,14]. Moreover, it is possible to use the main and secondary analytical lines and the choice of the line wings to enhance sensitivity and/or extend the linear working range of elements [15–18]. In addition, methods based on HR-CS AAS with flame atomizer (HR-CS FAAS) for a fast sequential multi-element determination in a single run have been reported [9,15,16,19,20].

The aim of this work has been the development of a simple and reliable methodology for fast multi-element determination of Cd, Ni, Cu, Pb, Zn, Mn, Fe, Mg, Na, K and Ca with minimal sample consumption by HR-CS FAAS in different environmental samples and drinking waters. For this purpose, absorption lines were selected, and burner height and flame composition were optimized for each element. A flow injection valve was used to obtain a transient analytical signal and reduce the sample consumption. In order to achieve an almost Gaussian peak, injection conditions such as measurement time and injection time were studied. The use of different secondary lines and the side pixel registration approach were investigated to extend the linear working range. The principal analytical parameters were calculated and the methodology was employed to determine the metals in environmental samples and drinking waters. In our opinion, this new methodology based on HR-CS AAS, a technique that has been introduced in the last decade, coupled with a flow injection valve could be considered an interesting and novel approach and a reliable alternative to methods based on ICP-OES.

2. Materials and methods

2.1. Instrumentation

All measurements were carried out using a ContrAA 700 high-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) equipped with both flame and graphite furnace atomizers in two separate sample compartments and the autosampler module AS 52S for flame mode (Analytik Jena AG, Jena, Germany). Air-acetylene flame was used for atomization. High-purity acetylene 99.6% (Carburos Metálicos, Madrid, Spain) was employed as fuel gas and the air flow rate was fixed at 470 L h^{-1}. The aspiration rate was fixed at 10 mL min^{-1}, and all measurements were carried out in triplicate. A model SFS 6 injection module (Analytik Jena AG, Jena, Germany), controlled by computer, was used for aspiration of blank, standard and sample solutions. This module comprises a two-way flow injection valve with two inlets and one outlet to the nebulizer. The carrier solution, ultrapure water or blank solutions, is continuously aspirated. Injection of sample or standard solutions is performed by automatic commutation of the valve from carrier solution inlet to sample inlet for an established period of time and then back to carrier solution. In this way, aspiration of air is avoided when the switch of the valve is performed. Discrete sample volumes are introduced by controlling the injection time with the software.

A PerkinElmer-Anton PAAR Multiwave microwave sample preparation system (Graz, Austria), using perfluoroalkoxy (PFA) model MF 100 digestion vessels was used to carry out acid treatment of the solid samples.

2.2. Reagents and standard solutions

All reagents used in this work were of analytical or for trace analysis grade, and used as received without further purification. Ultrapure water with resistivity not less than 18.2 MΩ cm obtained from an Ultra Clear^{TM} TWF UV EDI water purification system (Siemens, Barsbüttel, Germany) was used throughout. Cadmium, nickel, lead, copper, zinc, manganese, magnesium, iron, calcium, sodium and potassium commercial stock solutions for atomic absorption spectrometry of 1.000 g L^{-1} (Scharlau, Barcelona, Spain) were used to prepare standard solutions. A 100 g L^{-1} cesium chloride – 100 g L^{-1} lanthanum chloride commercial buffer for flame atomic absorption spectrometry (Fluka, St. Gallen, Switzerland) was added to all measurement solutions to avoid ionization and chemical interferences. Hydrochloric acid (37%) and nitric acid (65%) of trace analysis grade (Fluka, St. Gallen, Switzerland) were used to mineralize solid samples and prepare standard solutions. Multi-element standard solutions were prepared daily by adequate