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Solid sampling determination of lithium and sodium additives in microsamples of yttrium oxyorthosilicate by high-resolution continuum source graphite furnace atomic absorption spectrometry

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ABSTRACT

Solid sampling high resolution continuum source graphite furnace atomic absorption spectrometry (SS-HR-CS-GFAAS) methods were developed and studied for the fast and sensitive quantitation of Li and Na additives in microsamples of cerium-doped yttrium oxyorthosilicate (Y_2SiO_5:Ce) scintillator materials. The methods were optimized for solid samples by studying a set of GFAAS conditions (i.e., the sample mass, sensitivity of the analytical lines, and graphite furnace heating programs). Powdered samples in the mass range of 0.099–0.422 mg were dispensed onto graphite sample insertion boats, weighed and analyzed. Pyrolysis and atomization temperatures were optimized by the use of single-element standard solutions of Li and Na (acidified with 0.144 mol/L HNO_3) at the Li I 610.353 nm and Na I 285.3013 nm analytical lines. For calibration purposes, the method of standard addition with Li and Na solutions was applied. The correlation coefficients (R values) of the calibration graphs were not worse than 0.9678. The limit of detection for oxyorthosilicate samples was 20 μg/g and 80 μg/g for Li and Na, respectively. The alkaline content of the solid samples were found to be in the range of 0.89 and 8.4 mg/g, respectively. The accuracy of the results was verified by means of analyzing certified reference samples, using methods of standard (solution) addition calibration.

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1. Introduction

Yttrium oxyorthosilicate crystals doped with cerium (Y_2SiO_5:Ce) are important blue phosphors with high intensity scintillation response to X-ray irradiation, which has been applied in medical imaging devices [1]. These optical materials are usually fabricated by means of flux-assisted high temperature (>1200 °C) fusion. Li^+/Na^+ co-doping is a widely applied method to enhance optical efficiency of oxide-based materials [2]. Dopants (e.g. Ce) as well as flux elements, such as Li and Na applied as fluorides, can efficiently build into the lattice of the host crystal, which can modify the luminescence intensity [3]. Consequently, the accurate determination of these components is of high importance for the optimization of the synthesis procedure, and to provide supporting information for crystal-physical/chemical studies.

Since the Y_2SiO_5:Ce crystals are prepared in small amounts (~250 mg per batch) for research purposes in the authors' laboratory, the sample mass available for chemical analysis is limited to some milligrams only. Therefore, for quantitative composition analysis, instrumental methods of high sensitivity and selectivity are necessary to be applied. Liquid dosing analytical methods require digestion/

dissolution of the sample, thus they are labor-intense and handicapped by the risk of sample contamination, while sample dilution deteriorates the limit of detection (LOD). Thus, solid sample dosing is preferred for performing such microanalytical tasks. High resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS-GFAAS) is a fairly novel, highly selective and sensitive technique, which offers the option for liquid and direct solid (powdered) sample analysis as reviewed in detail in Refs. [4-6]. Thus it has been selected for the current microanalytical task too.

Several direct solid sampling (SS) GFAAS methods have been reported in the literature for the analysis of various advanced materials [7–19], geological samples [20,21], and certified reference materials (CRMs) [20,22]; for instance, Cu, Zn, alkali- and alkaline-earth elements in powdered molybdenum [7,8], and in powdered molybdenum silicide [8], Al, Co, Cr, Cu, Fe, K, Mg, Na, Ni and Zn in high-purity niobium pentoxide [9], Si in titanium pieces [10], and in high-purity cellulose [11], As, Cd, Hg, Pb, Sb and Zn in high-purity TiO_2 [12], P [13] and Hg [14] in plastic materials, Cr, Fe and Mn in high-purity lithium niobate optical crystals [15], As, Cd, Cr, Cu, Pb and Sb in silica [16], Pb in glasses [17], Cr and Sb in polymers from electrical and electronic equipment [18], Co, Fe, Ni and Pb in carbon nanotubes [19], Cd, Cr and Pb in cement, river sediment and CRMs [20], As, Cd, Cr, Cu, Pb, Ni and V in commercial barites [21], and Cd, Cr, Cu, Pb and Zn in soil CRMs [22]. These methods realized LODs around the ng/g, or even lower levels.

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Most of the studies have reported on various analytical difficulties, spectral and non-spectral interferences hampering the SS-GFAAS determinations, for instance, co-vaporization of refractory matrix components causing high background (BG) absorption [8,23], decreased lifetime of the graphite tubes/sample insertion boats caused by the high reactivity of the matrix [12], under- and overcompensation errors for the BG absorption [23], effects of the particle size and homogeneity of powdered samples on accuracy [21], and method calibration problems [23]. These difficulties were overcome by means of using deuterium [13,20,22] and Zeeman BG correction systems [16, 20], occasionally with 3-magnetic-field arrangement [12], the transversally heated graphite atomizer (THGA) [10,12–14,16–21], the graphite rod [8] and the two-step atomizers [23], various (T- and fork-shaped) graphite platforms [20] and graphite boat designs [8], the cup-in-tube technique [7,23], alternative (methane) atmosphere in the furnace during sample atomization [9], chemical modifiers (e.g., Pd [19], Pd-Mg(NO$_3$)$_2$ [10,11,16,17,19,21,22], Pd-ascorbic acid [13], HNO$_3$ [19], NH$_4$F [22], carbon powder [10,12,19]), mechanical/compressed air-assisted removal of the sample residues [12], medium or maximum internal furnace gas flows during atomization [14–16], matrix-matched [23], and external and standard addition calibrations [15,20,21].

The selection of the proper methods/standards of calibration as well as the sample mass introduced into a graphite furnace is a keystone to accurate quantitation in SS-GFAAS [24]. For instance, Eames and Matousek [25] determine Ag in silicate rocks by SS-GFAAS, based on weighing different amounts of samples, followed by adding a standard solution of the same concentration. Although a linear relationship was established between the absorbance and the sample mass, the analytical results significantly varied, responding to small changes in the slope of the absorbance *versus* sample mass curve. In order to overcome this drawback, Minami et al. [26] suggested the three-point-estimation standard addition method for the solid sampling determination of Cr in biological samples, which utilizes addition of standards at various concentrations. This calibration method was also applied in the analysis of optical crystals [15]. Solution-based calibration was reported to be suitable for the direct SS-GFAAS and electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) determination of Cr in various CRMs (milk powder, lobster hepatopancreas, polyethylene, and sewage sludge) [27]. The GFAAS method offered a lower LOD (2 ng/g) than ETV-ICP-MS (30 ng/g). Regarding the sample mass, too small or too large sample amounts led to inaccurate results in the determination of Cu in a vitamin complex, even when the analyte content was within the linear range of calibration [24]. Dosing too high and too low sample masses results in underestimated and overestimated analytical data, respectively [13].

The determination of Li and Na has scarcely been reported in the GFAAS literature [28–32]. In addition, these methods are based on solution sample introduction, involving in digestion/decomposition of the sample matrix (e.g., serum [28], photoresist [29], gallium arsenide [30], and high-purity alumina [31]), or dispension of slurry [31], or hot water assisted extraction/leaching of the analyte from solid samples (e.g., tea and herbal infusions) [32], prior to introduction into the graphite atomizer.

In this study, solid sampling HR-CS-GFAAS methods were developed and applied to the determination of Li and Na additive (flux) elements in Y$_2$SiO$_5$:Ce polycrystalline materials. The amount of the solid sample, decomposition of the matrix, alternative analytical lines, application of various chemical modifiers and calibration procedures (external and standard addition) were studied for method optimization. The accuracy of the method was verified with the analysis of CRM samples by applying solid sampling HR-CS-GFAAS and solution introduction high-resolution continuum source flame atomic absorption spectrometry (HR-CS-FAAS).

2. Experimental

2.1. Instrumentation

All the experiments were performed on an Analytik Jena Model ContrAA-700 tandem HR-CS-AAS spectrometer (Analytik Jena AG, Jena, Germany) equipped with a THGA, a furnace video-camera, and Analytik Jena Model SSA-600L and MPE-60 autosamplers for solid (powder) and liquid samples, respectively. The SSA-600L has a built-in electronic microbalance (precision: ± 1 μg), and fitted with a liquid sample dosing accessory (LDA) for dispensing solutions of additives/chemical modifiers and/or standards onto the graphite boats, applied for solid sample insertion. The spectrometer's optics contain a high-pressure, xenon short-arc lamp used as a primary radiation (light) source, operating in optimized hot-spot mode, a high resolution monochromator optics, and a charge coupled device (CCD) array detector with 588 pixels. The 200 pixels of the CCD are only applied for detection of the concerned spectral range, while the others are utilized for internal spectral correction. The monochromator of the optics consists of a pre-dispersing prism monochromator and a high-resolution echelle grating monochromator, which are arranged in the Littrow mounting. The working point current of the xenon lamp was set to 13 A. Spectral lines of Na I 285.3013 nm, Na I 268.034 nm, Li I 610.353 nm and Li I 670.7845 nm were selected for the analysis.

Peak volume selected absorbance (PVSA) [33], i.e., the integrated absorbance (A$_{int}$) signal of the central pixel (CP) plus the adjacent ones (CP ± 1), corresponding to a spectral range of ~4.6 pm has been utilized for signal evaluation. An iterative background correction (IBC) method was applied for compensation of the non-specific absorption. The assignment of analytical lines and molecular bands were mostly based on the application of the spectral database in the spectrometer's ASpect Software® (version: 2.1.1.1., Analytik Jena AG), but the Spectral Tables of Zaidel et al. [34], the NIST Spectral Database [35], and the Tables of Pearse and Gaydon [36] were utilized as well.

Pyrolytic graphite coated graphite IC-tubes without dosing hole (Analytik Jena) and pyrolytic graphite IC-platforms (Analytik Jena) were applied for solid sampling. For the optimization of the solid sampling method with the assistance of standard solutions, regular pyrolytic THGA graphite tubes with PIN-platforms (Analytik Jena) were applied. The graphite tubes were formatted each day before first analysis using the manufacturer's furnace heating program. This is also important for true-temperature calibration/measurement of the graphite atomizer. High-purity (4N6) argon purchased from Messer-Hungary (Budapest) was applied as the graphite furnace sheath gas. The lifetime of the graphite tubes was in the range of 250–300 analytical cycles, while that of the graphite boats was between 30 and 50 firings. This reduced lifetime was due to the corrosive nature of the matrix components of the oxyorthosilicate samples, which accelerated the deterioration of the pyrolytic graphite surface. The optimized graphite furnace heating programs are listed in Table 1.

Table 1
Graphite furnace heating program optimized for the solid sampling determination of Li and Na in oxyorthosilicate and CRM samples.

Step	Temperature (°C)	Ramp Time (°C/s)	Hold Time (s)	Internal furnace gas flow rate (dm^3 min^{-1})
Drying 1	80	6	20	2
Drying 2	90	3	20	2
Drying 3	110	5	10	2
Pyrolysis 1	350	50	20	2
Pyrolysis 2	800	300	10	2
Gas adaption	800	0	5	0
Atomization	2400	2000	10/5[a]/3[b]	0
Cleaning	2450	500	4	2

[a] Optimal value for solution analysis of Li and Na (as nitrate).
[b] Optimal time for solid sampling analysis of powdered krill reference samples.