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Spectrometer system using a modular echelle spectrograph and a laser-driven continuum source for simultaneous multi-element determination by graphite furnace absorption spectrometry

Sebastian Geisler, Michael Okruss, Helmut Becker-Ross, Mao Dong Huang *, Norbert Esser, Stefan Florek

Leibniz-Institut für Analytische Wissenschaften — ISAS — e.V., Department Berlin, Schwarzschildstr. 8, 12489 Berlin, Germany

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ABSTRACT

A multi-element absorption spectrometer system has been developed based on a laser-driven xenon continuum source and a modular simultaneous echelle spectrograph (MOSES), which is characterized by a minimized number of optical components resulting in high optical throughput, high transmittance and high image quality. The main feature of the new optical design is the multifunction usage of a Littrow prism, which is attached on a rotation stage. It operates as an order-sorter for the echelle grating in a double-pass mode, as a fine positioning device moving the echelle spectrum on the detector, and as a forwarder to address different optical components, e.g., echelle gratings, in the setup. Using different prisms, which are mounted back to back on the rotation stage, a multitude of different spectroscopic modes like broad-range panorama observations, specific UV–VIS and NIR studies or high resolution zoom investigations of variable spectral channels can be realized. In the UV panorama mode applied in this work, MOSES has simultaneously detectable wavelength coverage from 193 nm to 390 nm with a spectral resolution $\lambda/\Delta\lambda$ of 55,000 (3-pixel criterion). In the zoom mode the latter can be further increased by a factor of about two for a selectable section of the full wavelength range. The applicability and the analytical performance of the system were tested by simultaneous element determination in a graphite furnace, using eight different elements. Compared to an instrument operating in the optimized single line mode, the achieved analytical sensitivity using the panorama mode was typically a factor of two lower. Using the zoom mode for selected elements, comparable sensitivities were obtained. The results confirm the influence of the different spectral resolutions.

1. Introduction

Graphite furnace atomic absorption spectrometry (GF AAS) is a widespread method for trace elemental analysis [1–3]. It provides excellent sensitivity and specificity, combined with high tolerance for complex sample matrices, and even slurries and solid samples can be analyzed directly [4–6]. An additional advantage over flame-AAS or ICP-based methods is the low requirements concerning sample amounts, which are normally in the range of 10 to 20 μL. Recently it was shown that even sample volumes down to the nanoliter level can be analyzed reliably with increased sensitivity [7].

Despite the advantageous features of the method, there is a basic inherent constraint. Owing to line source based operation, the conventional AAS is a single-element method. A specific lamp for each element is required and only a single element can be determined by one sample measurement. Multi-element determination requires multiple sample runs, which result in slow sample throughput and long analysis time. Therefore, there has been urgent need to encourage physicists and analytical scientists to extend the AAS, especially GF AAS, to a simultaneous multi-element method.

On the way towards the realization of the multi-element feature, those flagship specifications of classic GF AAS, such as high specificity and high sensitivity should be maintained as far as possible. Ideally, the concept of a multi-element GF AAS system should fulfill the following requirements: (i) Full wavelength coverage from 190 nm (arsenic) to 860 nm (cesium); (ii) flexibility regarding the number and the combination of elements determinable; (iii) high spectral resolution for the prevention of spectral interferences and, in case of using continuum source, for achieving high sensitivity; (iv) flexible and effective background correction; (v) large dynamic range; and (vi) simple and compact design, combined with reasonable acquisition and operation cost.

A number of systems with multi-element abilities have been developed and tested. Some of them are introduced to market [8]. The first attempt in 1965 was based on the substitution of a single-element lamp by a multi-element line source [9]. Later on concepts based on the combination of several single- and/or multi-element line sources [10–12] as well as the diode laser [13] were tested. Because of certain limitations, convincing success could not be achieved by any of those systems. First, there was no true simultaneous multi-element feature for an

* Corresponding author.
E-mail address: huang@isas.de (M.D. Huang).

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arbitrary number of elements. The concepts were restricted to simultaneous determination of two to six elements with applicability only to certain suitable element combinations. Second, the use of beam-combining optics resulted in a marked loss of intensity, which increased with the number of elements determined [14,15].

Obviously, the assembling of several line sources is not an adequate way for achieving full wavelength coverage and flexible element combination. Promising progress has then been accomplished in 1979 by Harnly et al. They developed a multi-element system using a xenon arc continuum source and an echelle polychromator, which has been named SIMAAC (simultaneous multi-element atomic absorption with continuum source). The xenon arc lamp provided a continuum spectrum over a broad wavelength range from 190 to 1500 nm and the high-resolution echelle polychromator ensured characteristic concentrations, curve linearity, and elemental specificities comparable to line source AAS. Mechanical wavelength modulation was used for eliminating instability of the continuum source and for correction of background absorption. The system was capable of determining up to 16 elements at one time using photomultiplier tubes (PMTs) as detectors. A major drawback of that system was the poor detection limits in the far UV (below 280 nm) because of the lack of intensity of the xenon arc lamp and the restricted slit height of the echelle spectrometer [16,17]. The analytical performance was then improved by substitution of the single-channel PMT detectors by a multi-wavelength solid state array detector, such as a linear photodiode array (LPDA) [18] or a linear charge coupled device (CCD) [19]. Because, in the case of the PDA having 2048 pixels, the wavelength range for simultaneous recording was only about 10 nm, the measurement procedure actually was more or less sequential-like, since only in few cases sensitive lines of different elements collectively appear in such a small spectral window [20].

Harnly also showed the possibility to use the Optima 3000 echelle spectrograph featuring a segmented array CCD (SCD-type) detector [19]. This system has been optimized by Perkin Elmer Inc. (USA) for ICP applications and covered two-thirds of the elements determinable by AAS. The results proved the potential of the system for true simultaneous multi-element CS AAS measurements.

Meanwhile, high-resolution continuum source AAS (HR-CS AAS) based on a high-pressure xenon lamp operating in a hot-spot mode as continuum source, an echelle-monochromator, and a CCD array as detector is commercially available and is gaining increasing credence [21,22]. Although the instrument was designed for single-element application, because only 200 pixels of the CCD detector are used for simultaneously registering the absorption at the analytical line and its vicinity, it provides potential for a few practical applications in simultaneous multi-element analysis, which has been reviewed recently by Resano et al. [23].

True simultaneous multi-element determination can be accomplished by means of echelle-spectrographs equipped with megapixel array detectors. Within a study using a flame atomizer, a CCD detector with 1024×1024 pixels was applied to simultaneously record the spectral range between 200 nm and 465 nm with a relatively high spectral resolution of $R = \lambda/\Delta\lambda \approx 25{,}000$ (3-pixel criterion) [24]. Atomic and molecular absorption spectra were recorded with a deuterium lamp as continuum source using a long integration time around 15 s.

For the capture of the transient absorption signal produced in a graphite furnace, a frame rate of at least 10 s^{-1} is required. On the other hand, for the simultaneous recording of the whole wavelength range from 190 nm to 860 nm with adequate analytical performance a two-dimensional array with approximately four megapixels is required. Detectors with such capabilities are not available yet, at least not at acceptable expenses. A compromise has to be made between achievable spectral resolution and wavelength coverage. The system described by Katskov and Khanye [25] is exemplary for such a tradeoff. By covering a relatively large wavelength range from 190 nm to 410 nm, the simultaneous determination of 18 elements was performed. Due to the low spectral resolution the system is inappropriate for analysis of samples with complex matrix, and the achievable limits of detection for individual elements were between one and a half and two orders of magnitude higher compared to those found in the single element mode.

In this work, a spectrometer system for simultaneous multi-element determination by graphite furnace absorption spectrometry is described and evaluated. It consists of a laser-driven xenon lamp as continuum source, a CCD detector, and a unique modular simultaneous echelle spectrograph (MOSES). The spectrograph design is characterized by the ability to implement a multitude of different spectroscopic modes like broad-range "panorama" observation and high-resolution "zoom" operation of arbitrary spectral intervals. In this way the tradeoff between spectral resolution and wavelength coverage can be properly adjusted to meet various analytical requirements.

2. Experimental

2.1. Instrumentation

A schematic diagram of the optical system is shown in Fig. 1. The atomizer and the associated illumination optics are similar to the single-element high-resolution CS AAS measuring arrangement developed at ISAS (Berlin, Germany) [26,27]. The earlier set-up was based on a conventional AA system model AAS 6 Vario from Analytik Jena (Analytik Jena AG, Jena, Germany), equipped with a transversely heated graphite furnace and a MPE 60 autosampler. It featured a xenon arc continuum source (XBO 300, GLE, Berlin, Germany) and two off axis ellipsoids to replace the hollow cathode lamp and the related beam guide, as well as the double echelle monochromator DEMON to replace the original Czerny–Turner monochromator.

For the current investigation two main modifications of the previous arrangement were made. The XBO continuum source was exchanged by a laser-driven light source (LDLS 1500, Energetiq Technology Inc., Woburn, MA, USA) and the DEMON monochromator was substituted by the new MOSES echelle spectrograph. As shown in Fig. 1, the image transfer optics consists of two elliptical mirrors. The first one creates a threefold magnified image of the light source in the atomizer. Then the image is downscaled by a factor of two by the second elliptical mirror and projected onto the entrance slit to fill the aperture of the spectrograph. The laser-driven light source was chosen because of its nearly unlimited lifetime and the high spatial and temporal stability of its plasma spherule.

The main goal for the MOSES design was the combination of the broad-range capability of an echelle spectrograph with the high spectral resolution and the high optical throughput of an optimized echelle monochromator. This should be realized by a single optical system featuring only one entrance slit with adjustable size, one detector, and a minimum of optical components and moveable parts. The design is based on the classical Littrow-mounting, which is characterized by using only one concave mirror or a lens system to collimate the radiation from the entrance slit and to pass it to a reflective dispersion element and similarly to focus the spectrum backwards on the detector located close to the entrance slit. In the specific MOSES optical design the parallel beam from an off-axis parabola is guided through a reflective prism to a subsequent echelle grating, which spreads the multitude of diffraction orders perpendicular to the prism refraction. After diffraction at the grating the wavelength-sorted bundles pass the prism again and are focused by the same parabola as a two-dimensional spectrum pattern on the image detector.

The Littrow prism as the key component of MOSES is mounted on a rotation stage and operates as a multifunctional tool. Primarily it operates as an order-sorter in a double-pass mode for the echelle grating, and by rotating the stage it selects a set of echelle orders, which are actually focused on the detector. In the same way the prism rotation enables the fine positioning of the echelle spectrum to assure a precise wavelength adjustment. Furthermore, a second prism of possibly different material and prism angel is mounted back to back on the rotation