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A NEW TECHNIQUE OF SOLID MATERIAL SAMPLING FOR ANALYTICAL ATOMIC SPECTROMETRY WITH INDUCTIVELY COUPLED PLASMA

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Abstract. A new rapid method of direct spectrochemical analysis of solid-state materials is proposed on the basis of a tandem technique of pulsed laser ablation of a sample in deionised water with on-line transportation of a suspension of nanoparticles in analytical volume of inductively-coupled plasma of optical emission spectrometer. In result, all instrumentation and methodical advantages of the standard equipment in combination with calibration procedure by standard aqueous solutions are provided.

1. INTRODUCTION

Such widespread and well-known technique as optical emission spectroscopy with inductively coupled plasma (OES-ICP) has the routine application at the analysis of liquid samples. The simplest way of the analysis of solid-state materials is based on a direct dissolution of an analyzed sample or its fragment. Unfortunately, often this approach requires additional time and expenditures of labour, frequently significant, uses a sealed pressure vessels for holding strong mineral acids or alkalis at temperatures well above normal boiling points, does not allow carrying out microanalysis of analyzed samples.

For the analysis of solid and especially powder materials without their dissolution there are various variants of their direct input in analytical volume of ICP or preliminary evaporation in electrothermal atomizer with the subsequent transportation to analytical volume of ICP. OES with a sample atomization in ICP combined with preliminary laser ablation (LA) of a solid sample in a carrier gas (LA-ICP-OES) is at present the most conventional and suitable direct method for the elemental spectrochemical microanalysis of any solids with minimum or no sample preparation as well as of materials that are difficult to dissolve. Nevertheless, this high-sensitive technique is till now very limited by the availability of solid-state certificated reference materials with necessary matrixes and chemical elements.

There are successful attempts to realize really calibration-free laser-induced breakdown spectroscopy (LIBS) (see e.g. Burakov et al. 2007). However, it is true that the LIBS technique, having some important advantages, still suffers from relatively poor sensitivity with respect to more standard technique such as OES-ICP (see e.g.

Fichet et al. 2006). The detection limits of LIBS are about 3-4 orders of magnitude higher compared with those of OES-ICP even when double-pulse lasers are used in LIBS for sample ablation.

To replace calibration procedure with the help of the solid-state reference materials by the standard aqueous solutions spark ablation of conducting metallic samples in deionised water was offered originally for atomic absorption with thermal atomization (see e.g. Ghiglione et al. 1976), and subsequently for OES-ICP (see e.g. Aziz et al. 1984). However, such approach has a number of restrictions, therefore, in analytical practice it is not used except for not numerous research works.

We have realized the tandem technique of a direct laser sampling of any solid material in deionised water with on-line analysis of prepared by such way aqueous solution with the help of conventional OES-ICP. Such approach makes it possible to achieve a combination of all advantages of LA-ICP-OES with routine calibration by standard reference aqueous solutions usually available for any element of interest. On the other hand, laser ablation of a solid material in a liquid medium (see e.g. Iida et al. 1991) is at present a well established technique for nanoparticle production for various purposes. Generally speaking, the main problem in the described approach consists in revealing and discrimination of possible specific features of evaporation and atomization in ICP of such specific solutions (suspensions) containing nanoparticles in comparison with the real aqueous solutions.

2. EXPERIMENTAL

The instrumentation employed in our work is at present quite standard and maximally suitable for a routine practice (Fig. 1).

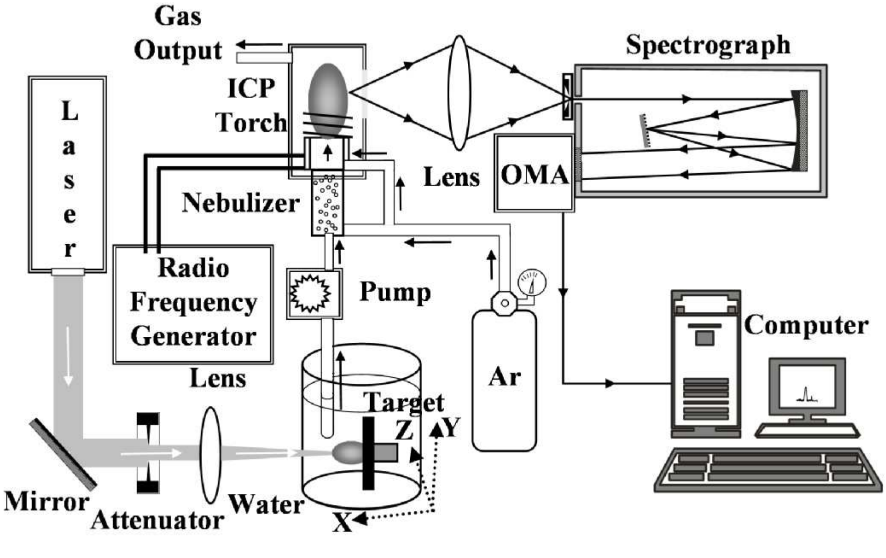

Figure 1: Schematic outline of OES-ICP with LA of a solid in a liquid.

The fundamental (1.06 μm) in the most cases or the second harmonic (0.53 μm) of a nanosecond Q-switched Nd:YAG laser (LS-2134 U, Lotis, Belarus) with a pulse duration of 6-8 ns (depending on wavelength and energy) and 10-Hz pulse repetition rate is employed for ablation of solids immersed in a cell with deionised water. The laser used is an improved version with variable reflectivity mirrors (VRM). This model provides high stability of the emitted radiation. The VRM resonator gives excellent harmonic conversion efficiency due to an increased spatial uniformity of the output beam, a low divergence and a short pulse duration. The laser beam, with an aperture of $\leq$ 6 mm and a beam divergence of $\leq$ 0.8 mrad, is sharply focused on the sample surface by a 50 mm focal length plano-convex quartz lens. The laser spot diameter on a target surface is about 50 μm. A sample is fixed at a X, Y, Z translation holder, which enables precise adjustment of focusing on sample surface. The laser pulse energy can be varied from 10 to 270 mJ with an energy stability of ± 3%. Thorough optimization of laser output parameters, mainly pulse power density on a target surface and a number of pulses (usually 50) were carried out at the microanalysis of bronze, glass and gold reference samples with known compositions. Comparatively small amounts of prepared aqueous suspensions (usually 10-15 cm^3) were on-line (to avoid possible nanoparticle agglomeration) analyzed by OES-ICP (IRIS Intrepid II, Thermo-Electron) in accordance with a conventional reliably fulfilled procedure of analysis of liquid samples and calibration by aqueous standards.

3. RESULTS AND DISCUSSION

Fig. 2 shows the TEM images (LEO 906E) of the trapped products of LA of a glass sample in a water.

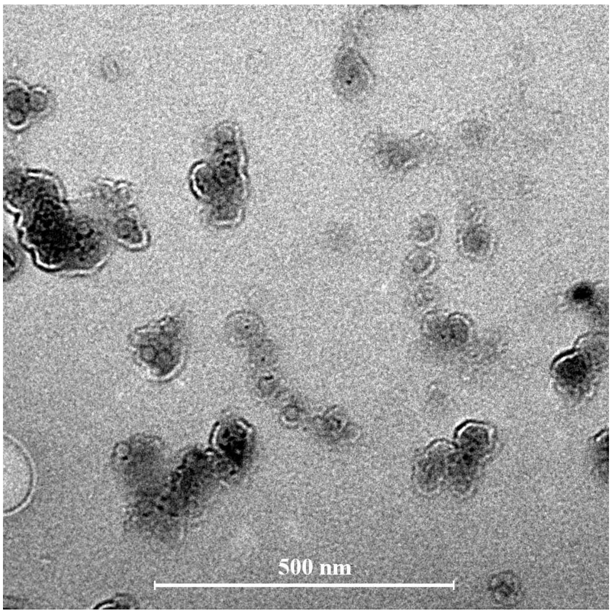

Figure 2: TEM photograph of nanoparticles produced by LA in deionised water.

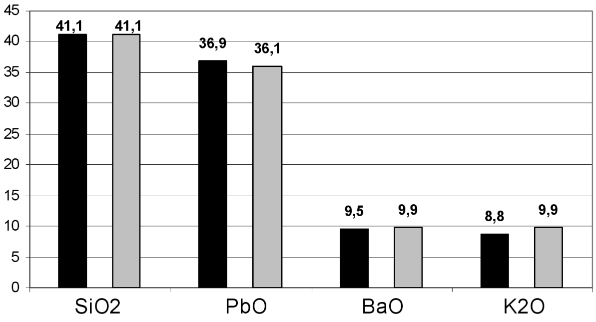

Figure 3: Composition of glass, % (black – reference data; grey – measured data).

As a whole, the satisfactory quantitative conformity of measured and reference data for all analyzed materials (bronze, glass and gold reference samples) has been received. Nevertheless, the further detailed optimization of ablation procedure, in particular, wavelengths of laser radiation, power density on a target surface, focusing conditions number of laser shots is necessary.

The results obtained have confirmed the suitability of the proposed approach and have proved its potential for the rapid, direct and sensitive microanalysis of any solid-state materials with minimum sample consumption and without solid-state certificated reference materials. All instrumentation and methodical advantages of the LA-ICP-OES standard equipment in combination with calibration procedure by standard aqueous solutions are provided.

In the practical case of impossibility to combine both techniques (LA and OES-ICP) in on-line apparatus it will be necessary to study and optimize the time delay between both procedures to discriminate influence of a possible nanoparticle agglomeration on the reproducibility of quantitative data or to take this phenomenon into account.

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