

Anomalous behaviour of the non-selective ionisation signal pulse under laser ablation into a flame

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10.1070/MC2001v011n04ABEH001417

When applying to the probing electrode the potentials with the different polarity one can notice that the non-selective and selective signals behave quite differently. In case of the positive potential compared with the negative one the non-selective signal shows anomalous behavior: it changes the shape and polarity and its amplitude increases dramatically while the selective one only changes the polarity that can be explained by the electrical properties of the flame reaction zone, which effectively eliminates the charges from laser plasma by the recombination.

Laser-enhanced ionisation spectrometry (LEIS) is based on the selective laser excitation followed by ionisation of atoms in flames. It is a powerful analytical method for trace element determination.¹ The combination of LEIS with laser ablation (LA) of solid samples into a flame allows us to perform local microanalysis of the sample surface.² Here, we report the observations of pulsed LEIS signals under LA of a lithium-containing aluminium alloy into a flame. We found that there were two ion current pulses: the first one was associated with strong ablating laser radiation, and the second one was associated with selective exciting laser radiation. The first signal was called non-selective because it was formed by thermal ions in the laser plasma.

The experimental set-up was described in detail elsewhere.³ The geometry of the sample, electrodes, laser beams and flame is presented in Figure 1. The iridium wire electrode (1) was used as a probe. The positive or negative potential (500–1000 V) was applied to the electrode with respect to the grounded burner head (2). The radiation (3) of the Nd³⁺:YAG laser with a pulse energy of about 70 mJ was used for LA of a sample (4). The atoms from laser-produced plasma reached the detection zone of a flame where the lithium atoms were resonantly excited by the radiation of two dye lasers with wavelengths of 670.8 (5) and 610.4 nm (6).

First, the temporal shape of ionisation signals (both non-selective and selective ones) has been recorded (Figure 2, curve 1) at the negative potential (–800 V) applied to the electrode. Then the electrode potential was switched to the positive (+800 V) value. The temporal shape of the ionisation signal in the latter case is presented in Figure 2, curve 2. It is evident from Figure 2 that ionisation signals behave differently. When the electrode potential is negative (*i.e.*, the probe is a cathode), we observed both signals being negative. It is related to the positive ions arrival to the cathode. Making the electrode potential positive (*i.e.*, the probe is an anode), we can see that the selective signal changes

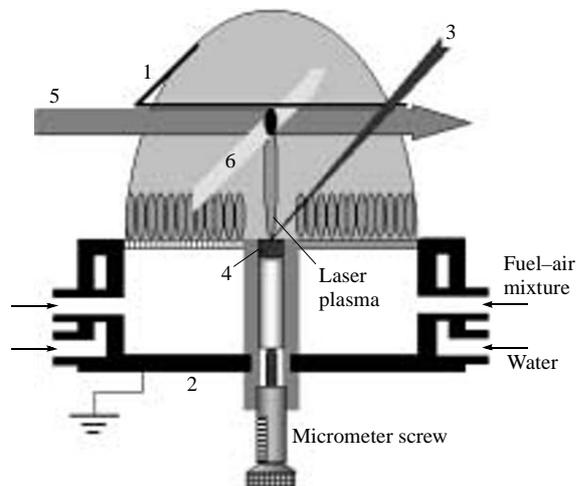


Figure 1 The arrangement of a burner head, a sample, a probing electrode and laser beams.

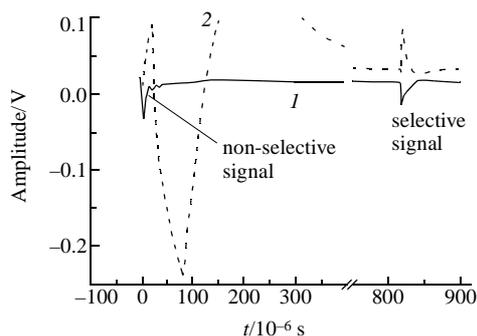


Figure 2 The amplitude-temporal characteristics of the non-selective and selective signals (marked by the arrows) at different electrode potentials: (1) –800 V; (2) +800 V.

its polarity but its magnitude remains almost the same. The non-selective signal exhibits an anomalous behaviour splitting into two components (peaks). The first peak has a positive polarity and near the same amplitude as for the probing cathode but the second one has a negative polarity and its amplitude (or peak area) greatly exceeds the amplitude (area) of the first peak.

We believe that the cause of such a behaviour is the following. Both laser ablation and selective ionisation produce positive ions and electrons. In the case of selective laser ionisation these particles are produced in the outer cone of a flame where the number density of intrinsic charges of the flame is low. Therefore, the recombination in this region is negligible. Thus, the selective signal intensity is independent of the polarity of the electrode. In the case of the non-selective signal, the formation of charged particles proceeds in the flame reaction zone. In this area of the flame, the number density of intrinsic charges is very high. Therefore, the recombination of the ions and the electrons from a laser plasma with the flame charges is very effective. However, the mobility of the ions is significantly lower than that of the electrons. When the positive potential is applied to the electrode, the more mobile electrons leave the reaction zone faster than the ions do. Thus, the recombination of these electrons is not complete. This results in a great increase of the non-selective signal.

This work was supported in part by the Russian Foundation for Basic Research (grant no. 00-03-32355).

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Received: 9th January 2001; Com. 01/1743