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# LASER-ENHANCED IONIZATION SPECTROMETRY OF ATOMS BY THE LASER EVAPORTIONS OF SAMPLE

***Abstract**: This work is dedicated to investigation of laser evaporation of samples in flame. Double volume nitrogen laser ($\lambda$=337,1nm, $\tau$=8ns, E=20mJ) was used in the experiment. Objects of analysis were high purity GaAs, rocks and aqueous solutions of Al, Na. Two excitation schemes for the atoms Al, Na were realized in the flame of acetylene-$N_20$ and propane-butane-air respectively. Laser evaporations of samples was suggested from graphite rod groove. Optimum disposition of laser beam and discharge of burning gas and oxidant is found for atoms Al and Na in proportion 1:6 and 1:28 respectively. The detection limits of Al and Na in aqueous solutions were $8\cdot10^{-7}$ % and $1\cdot10^{-7}$ % respectively.*

***Key words**: laser evaporation, flame, double volume, nitrogen laser, burning gas, acetylene propane-butane-air.*
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## Introduction

Creation of laser with the tunable frequency of radiation led to discovery of new fields of science. Laser resonance ionization spectrometry (RIS) of atoms in vacuum, laser optogalvanic spectrometry in electric gas-discharge (LOGS) or laser-enhanced ionization (LEI) spectrometry is such a field. Last time investigation by the LEI was carried out in following atomizers: the flame atomizer in atmospheric pressure, rod-flame system, lasers ablation in flame, the electro-thermal atomizer in the inert medium [1-4]. The high selectivity of the method opens wide possibilities of its application to analyze the objects of the complicated composition in the field of geology, medicine, etc. Owing to the high selectivity of the method its use is perspective in electronics, in controlling the material purity.

Idea of the method.Under the action of the laser radiation free atoms of analyte are selectively excited into the high-lying electronic states followed by the collision ionization in a flame or by the collision photoionization, (Fig. 1). This ionization is monitored by applying an electric field. The formed charged particles create the current pulse carrying the information of element content in the analyzed specimen.

The many physical methods are used in the atom-spectroscopy and laser analytical spectroscopy for

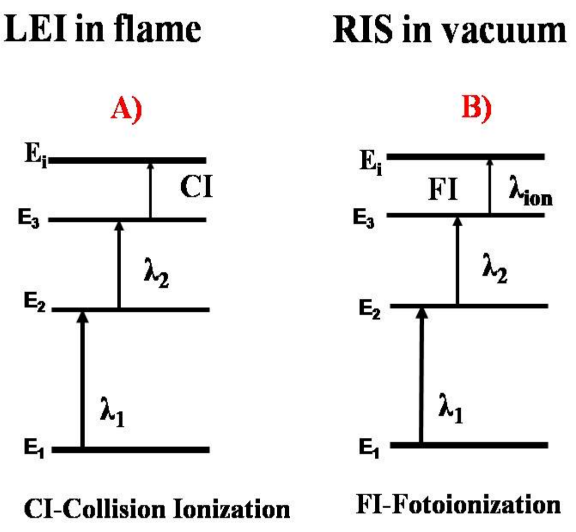


**Fig. 1. Idea of the method**

determination of spectral parameters, quantitative and qualitative analysis of the studied atoms. The spectral parameters may be served for optimization of the spectrometer with the aim of increase of analytical signals. At laboratory of laser spectroscopy of Samarkand State University for this aim we created laser photo ionization and atom-ionization spectrometers. This spectrometers work synchronic in regime of the atomic beam in vacuum and in regime of the flame in atmosphere pressure. It present we have investigated high excitation Rydberg and auto-ionization states Au, Pt, Hg, Zn, Cd, In, Al, Ga, Ta elements. In the results of study of this elements we exactly determined ionization limit, quantum defects, main quantum numbers, effective schemes of excitation, evaporation velocity, and disposition of effective Rydberg and **auto**ionization states [1-13]. Investigation of Rydberg and autoionizing states of NaI and AlI are not only of significance in the atomic spectroscopy but also of great practical value in laser-analytical spectroscopy.

Moreover scientific investigation are carried out method of laser-enhanced ionization [LEI] spectroscopy or atom-ionization [AI] spectroscopy. Last time, investigation by the LEI was carried out in following atomizers: the flame atomizer in atmospheric pressure, rod-flame system, laser ablation of samples in flame, the electro thermal atomizer in the inert medium [8-13]. The high selectivity of the method gives possibilities of its application to analyze the objects of the complicated composition in the field of geology, medium. Also use of this method is perspective in microelectronics, in controlling purity materials. Contents Au, Pt, Cr, Co, Ni, Mn, Na, Cs, Ca of elements were determined in high-purity substances, chemical reagents, technological solvents and natural objects [3-5].

The present work was dedicated to laser evaporation of samples in flame. We suggested laser evaporation of solid and liquid samples from graphite rod groove by the method LEI. It has been applied for determination of contents Al and Na in the samples GaAs and trapp.

Preparing standard aqueous. Standard solvents of Al by solving lg of metallic Al in 30 ml of diluted 1:1 HC1, and dipping Pt rod cover in order to speed up the process. Than it was diluted with de-ionized water (up to 11, for obtaining Al solution of 1 mg/ml).

Standard solution of Na were prepared by solving NaCl powder being measured on analytical scales in bi-distillated water. In order to get 1% of the solution it was diluted with 100 ml of deionized water.

**Experimental.** The scheme of an atomic ionization spectrometer is shown in Fig.4 and has been described earlier [3,13]. It is composed of pumping lasers – an excimer laser or a double beam nitrogen laser ($\lambda$=337 nm), two tunable dye lasers, an atomization-ionization system, and a registration system. The dye lasers were tuned in the range 270 nm -900 nm; pulse energy was 2 mJ in visible and 100 $\mu$J in UV region; line width: 0.3-0.9 cm$^{-1}$ , spectral contrast- $10^5$. The free atoms of the element to be determined were obtained by air pressure nebulization of the sample into a slot burner flame. Acetylene-air flames were used in these studies. The sample was consumed at a rate of 1.5 ml\min with a nebulization efficiency of 13%. The signal was detected with a water-cooled collector placed in the flame with a negative potential (1.5kv) relative to the burner head.

Optical-scheme experimental device is presented on the Fig.2. A double beam nitrogen laser with energy of pulse 20 mJ. We used for evaporation of sample from graphite rod groove. Atomic transitions were excited by radiation of laser on dye, which being pumped by radiation of double volume Nitrogen laser. Output energy of dye laser is 150 $\mu$J; and width of generation line is -0,8cm$^{-1}$. Laser rays were directed on flame. Due to a double beam nitrogen laser focusing on the center of the groove substance is evaporated. The formed vapours interacts with resonance radiation of dye laser. Ions formed under effect of laser rays collected between parallel electrodes. One of those electrodes was earthed and the other had potential of - 1,3kV. Current pulse of charge particles was measured after passing low frequency filters and amplified signal came to stroboscope integrator. Averaged signal registered by digital voltmeter

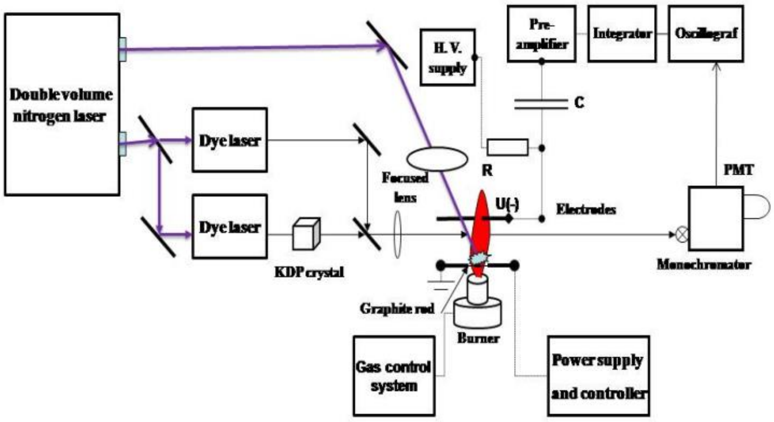


**Fig.2. Block diagram of the LEI spectrometer with the laser evaporation sample**

Discussion.

Working out of the method of determinations in standard water solvents was carried out in flame of ***propane***-butane-air. Ionization signal from sodium in the flame reached maximum value of proportion of ***propane***-butane of 0.211/min and air of 1,81/min (Fig.3).

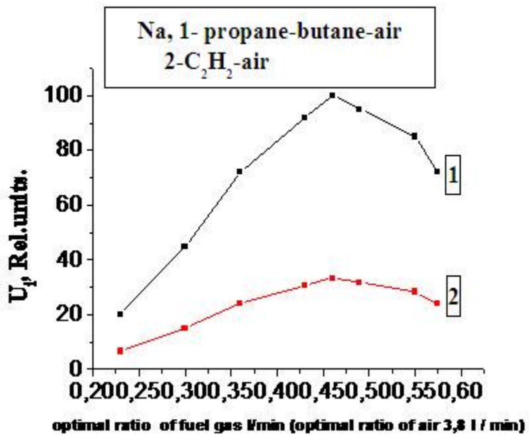


**Fig.3. Depends of ionization signal of sodium in the flame reached maximum value**

Two step scheme of excitation from ground state was used (Fig.4). Well known resonance line of Na was used in all spectral methods [6]:

$3s\ ^2S_{1/2}\ \lambda_1=589{,}0\ nm \rightarrow 3p\ ^2P_{1/2}\ \lambda_2=568{,}8\ nm\ 4d\ ^2D_{5/2}$

Output energy of dye laser of first step was $E_1$=100µJ, second step - 120µJ. Dye Rodamin-6J was used for the purpose. Two step schemes of Aluminum excitation were realized (Fig.6). Excitation scheme of Aluminum has the following stages:

$3p\ ^2P_{3/2}\ \lambda_1=396{,}l\ nm \rightarrow 3s\ ^2S_{1/2}\ \lambda_2=555{,}7\ nm\ 4p\ ^2P_{1/2}$

The two step scheme has not been described so far in references. At second step determination accuracy turned out to be 100 time bigger than it was obtained according to the known schemes described in [12]. In order to get maximum effectiveness of atomization dependence value of aluminum signal on type of flame (acetylene-air, acetylene-nitrogen oxide) and proportions of burning gas and oxidant. Results of the investigation are presented fig.5. Ionized signal of Al in flame of acetylene-air depended on proportions of burning gas and oxidant and reached maximum value at 1:6. When nitrogen oxide was used instead of air component, signal increased 8 times. Dependence of ionized signal on composition of flame and temperature obviously connected with low atomization of Al compounds in flame.

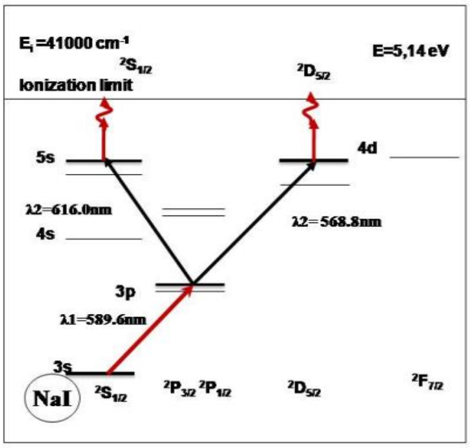


**Fig.4. Two step scheme of excitation of sodium**

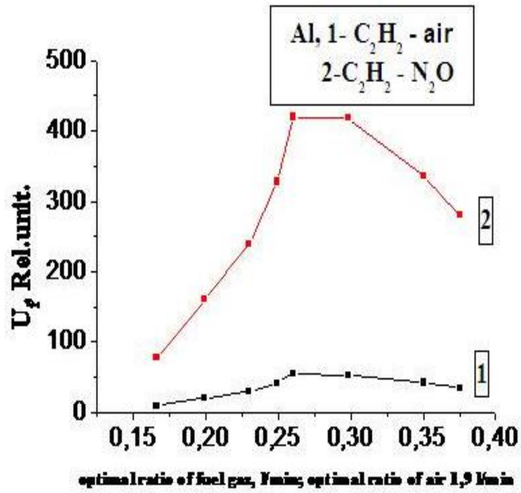


**Fig.5. Depends of ionization signal of aluminum in the flame reached maximum value**

A double beam nitrogen laser was used for evaporation of sample from graphite groove into flame, and by means of the delay shaper $N_2$-laser was started for dye-laser pumping. Pulse-recurrence frequency of $N_2$ laser is (5-10) Hz. Distance between pair of pulses was changed on the internal 1-10ms. Radiation of a double beam nitrogen laser being for sample evaporation, was focused with lens of F=10cm (focus distance) on to the center of the groove.

It was supposed, that first pulse of a pair evaporates sample from the groove, and formed vapours of the substance moves with speed of passing through flame. On 3 cm height from the groove it interacts with radiation of dye-laser, which was started by second pair of pulses.

Registration system was switched on synchronically with second pair of pulses. After focusing of a double beam nitrogen laser laser rays on flame, big background signal was observed. The signal saturates the registration system. Due to pulse delay we were able to change distance between pulses in a pair from 1 till 10ms. Energy of evaporating laser pulse is E=10mJ.

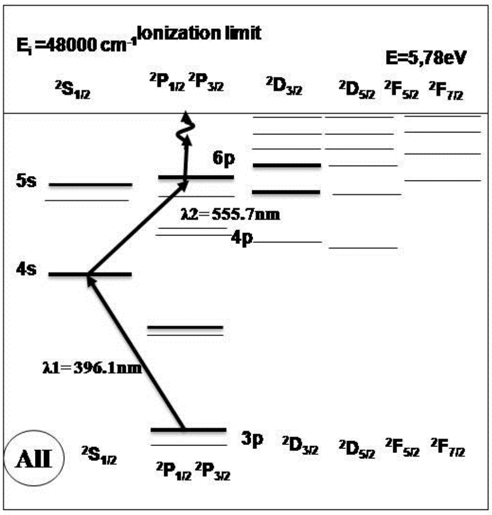


**Fig.6. Two step scheme of excitation of aluminum**

At first we tried to analyze small pieces of Al, but under effect of focused rays the dose went up. That is why bigger piece of Al was analyzed and ionization signal was registered.

Experiments were carried out in GaAs crystals and solvents of GaAs. So liquid solvents of GaAs with concentration of 10 g per liter were analyzed. Excitation of Al and Na atoms was provided according to double stage scheme of excitation. Contents of Na and Al in GaAs in system of graphite rod flame were determined. The amount of Na and Al are $2.7 \cdot 10^{-2}$ % and $1.7 \cdot 10^{-2}$ % respectively.

Stable signal of 10 mV during some laser pulses from Na was obtained in 10 µl of GaAs solvent of concentration 10 g/1, signal decreased until noise level. Resonance signal was not observed to tune out from wavelength of dye-laser. Due to absence of standard samples for GaAs,, 30 g/1 of trapp solvent with concentration of Na - 2,49% was used. Analytical signal in case, with 30 g/1 trapp solvent on the rod was 3000 mV. Results of the analysis are presented on table.

Generally, the atomic ionization spectrometry is yet of little use in practice but continues to be developed and has its potentials. As with other laser-based techniques, a hindering factor relates to a slow progress in the development of tuneable lasers that cannot yet support in practice the multielement analysis. High susceptibility of the ionization degree to the matrix composition presents another serious drawback of this technique. A fundamental possibility of the absolute analysis is one of the potentially important merits of the atomic ionization technique. An absolute number of the collected electrons (charge) is equal to the absolute number of the analyte atoms, the 100% ionization of which can be easily achieved in the analytical volume limited by the intersection area of the laser beams, while a correction for the non-selective background is obtained by tuning the laser over the full profile of the analytical absorption line. It is necessary to know either the atomized mass or the degree of sample vaporization, as well as the dinamics of vapour transport. These parameters can be estimated using mathematical models.

**Table. Real sample analysis by the laser evaporations in flame**

| Analyze | Sample | Solution, 1 g/l<br>Content $10^{-2}$% | Solid Sample Content $10^{-2}$% | Detection limit in water solution $10^{-7}$% |
| --- | --- | --- | --- | --- |
| Al<br>Na | **GaAs** | 1,9±0,1<br>2,9±0,3 | 1,5±0,2<br>2,5±0,4 | 8<br>1 |
| Na | **Rocks**<br>**(trapp)** | Solution, 30 g/l<br>2,49% | | |

*Conclusion.*

The method of laser evaporation of samples from graphite rod groove in flame is one of the new and perspective direction of investigation of chemical elements. The method requires improvement of optimization of analysis conditions.

Basis for using the method and its preferences among the other methods are the following:

The methods allow to work with micro samples, does not require much time and can provide reproductive results. Relative standard deviation of the obtained results of ionization signals does not exceed 0.05 in wide range of elements concentration values.

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