

# Analytical Laser Ionization Spectrometry in Flame: Choice of the Analytical Form for the Determination of Rare Earth Elements

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**Abstract**—Based on the ionization potentials and dissociation energies of rare earth monoxides, these molecules are classified into two groups. For the molecules of the first type, the ionization potential is lower than the dissociation energy. Laser excitation of these molecules leads to their predominant ionization. For the molecules of the second type, the ionization potential is higher than the dissociation energy. Depending on the absolute values of the latter, atomic lines can be observed in the ionization spectrum. The elements that form molecules of the first type in flame should be determined as monoxide molecules. For the elements forming molecules of the second type, determination in the atomic form gives better results.

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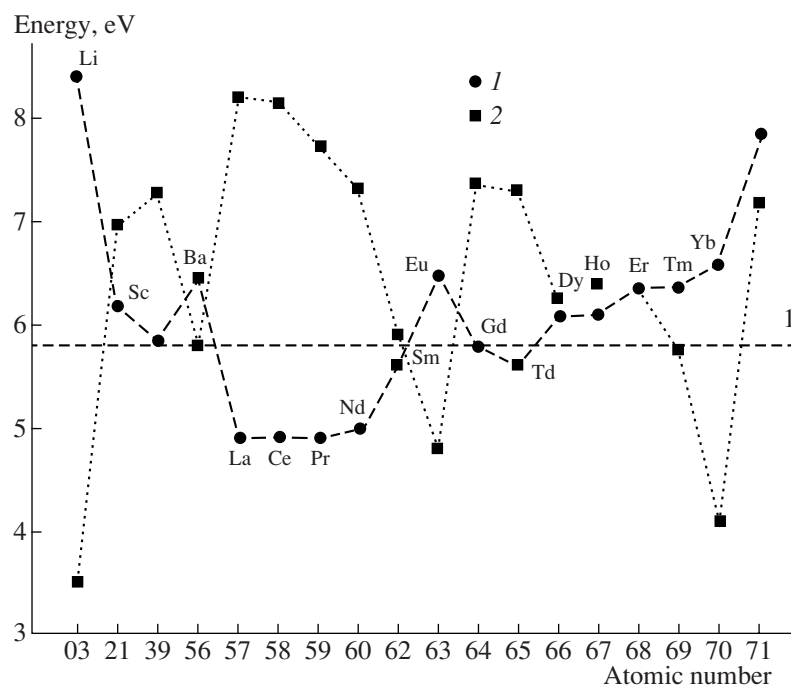
Laser atomic ionization (AI) spectrometry, which is based on laser excitation and ionization of atoms in flames, is successfully used for the ultrasensitive determination of chemical elements [1]. The degree of atomization of an element depends on its nature, the temperature and composition of the flame, and other factors. The degree of atomization of some elements in low-temperature flames is extremely low. Laser AI spectrometry fails to determine these elements with acceptable detection limits. The use of higher temperature flames, for example, acetylene–nitrogen(I) oxide, makes it possible to increase the degree of atomization. However, the detection limits of these elements remain higher than a few micrograms per milliliter. We developed a method of determination of elements as molecules in flames, namely, laser molecular ionization (MI) spectrometry, which uses molecules containing the elements to be studied rather than atoms. This method affords lower detection limits as compared to ionization of atoms even in high-temperature flames [2].

It is worth noting that this approach is not applicable to all elements under consideration. This work deals with estimates of the applicability limits of the AI and MI methods when a sample is introduced into a low-temperature flame.

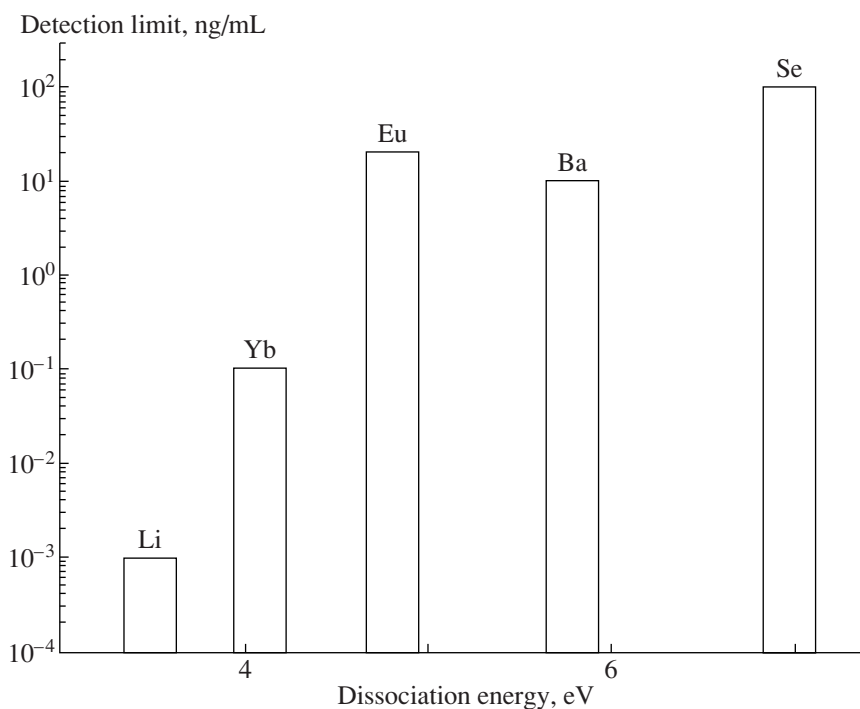
## DISCUSSION

For some elements, for example, Li and Eu, the ionization spectrum of monoxide molecules in flame cannot be recorded [3]. For barium, the detection limit obtained with the use of the ionization of the atom is

two orders of magnitude lower than for the BaO molecule. Analysis of these findings shows that the ionization potentials (IPs) of monoxides of all these elements are higher than their dissociation energy (DE). Figure 1 shows the IPs and DEs of monoxides of all elements under consideration and some other rare earth elements [4–6]. As is seen, for some of them, the DEs are higher than the IPs. Hereinafter, such molecules are referred to as monoxides of the first type. The other elements form monoxides of the second type, for which the IPs exceed the DEs. It is worth noting that some elements (Sm, Dy, Ho, Er) are characterized by close IP and DE values. Straight line 1 in Fig. 1 is the lower limit of the DE range in which no noticeable dissociation of monoxide molecules is observed. We may assume [7] that, upon laser excitation of monoxides of the first type, ionization will dominate over dissociation; conversely, for monoxides of the second type, dissociation will be predominant. In this case, laser excitation of the molecule will lead to its dissociation and its MI spectrum will not be observed. To confirm this hypothesis, let us consider the AI detection limit for elements as a function of the DE of the corresponding monoxide molecules (Fig. 2). In general, the detection limit tends to increase with an increase in the DE. For comparison, we used the results obtained by means of one-step excitation [8, 9]. The use of two-step excitation schemes can considerably decrease the detection limit in the AI method; however, it was not used for all of the elements under consideration [8]. All elements in Fig. 2, except Sc, form monoxides of the second type.



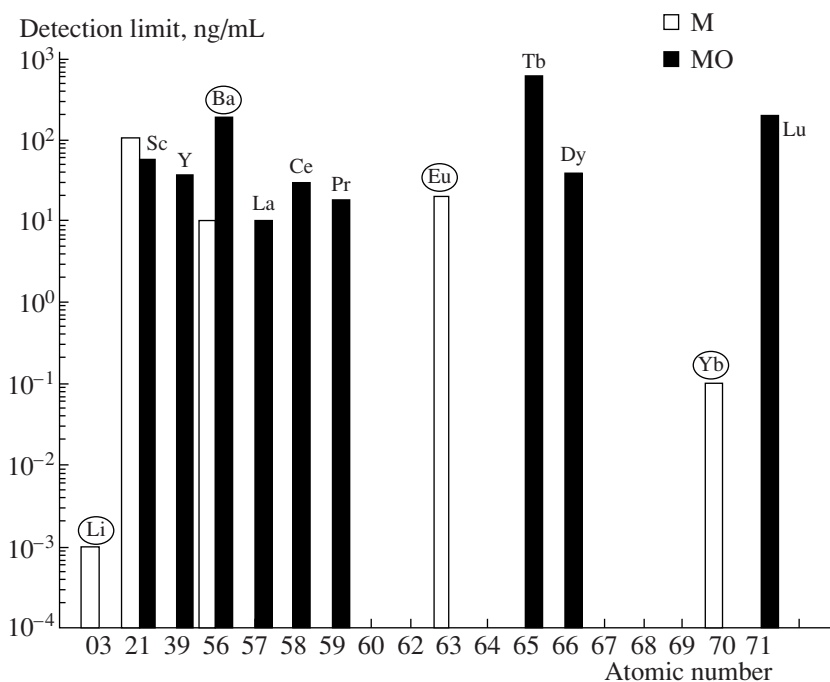
**Fig. 1.** (1) Ionization potentials and (2) dissociation energies of rare earth monoxides and barium and lithium monoxides (see text for details).



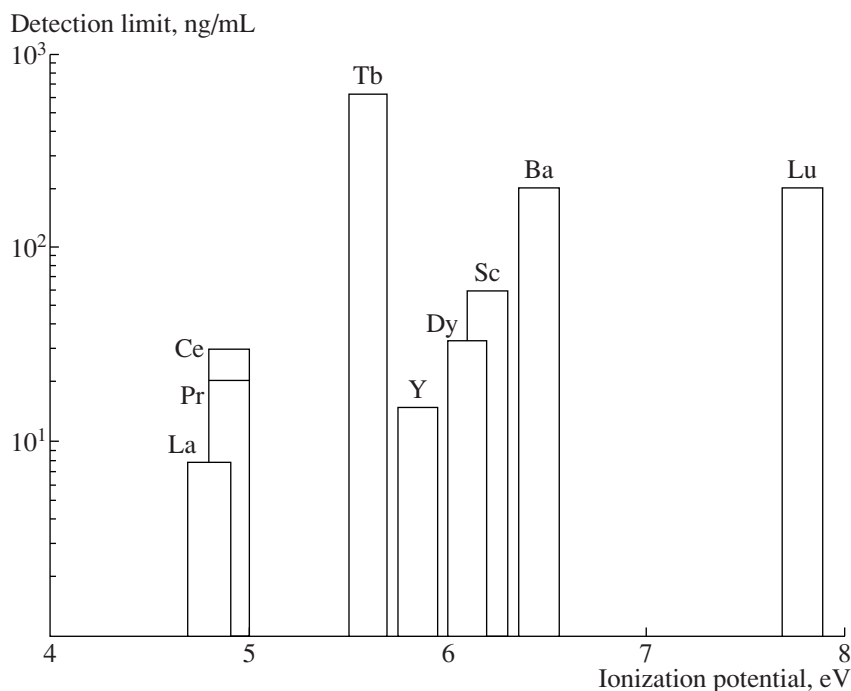
**Fig. 2.** Detection limits of elements in AI determination vs. the dissociation energy of their monoxides.

Figure 3 shows the detection limits of the elements provided by the AI and MI methods. For scandium and barium monoxides, the difference between the IP and DE is not as large as for the other elements in Fig. 2. For barium (first type), the AI method is preferable, and for

scandium (second type), the MI method gives better results. Unfortunately, currently, not all the elements have been studied to the same extent. As is known, no atomic lines are observed in a low-temperature flame upon laser excitation of Y, La, Ce, Pr, Dy, and Tb. All



**Fig. 3.** Detection limits of elements as atoms (M) and monoxides (MO). Elements that form monoxides of the second type are circled.



**Fig. 4.** Detection limits of elements in MI determination vs. the ionization potential of their monoxides.

these elements form monoxides of the first type [3, 10]. Atomization of Li and Ba solutions in flame does not give rise to MI spectra, since these elements form monoxides of the second type.

Ytterbium was determined as atoms [11]; as far as we know, no attempts have been made to record its MI spectrum. Some elements have not been determined by any of the laser ionization methods in flame. These are

Nd and Gd (form monoxides of the first type); Tm (forms the monoxide of the second type); and Sm, Ho, and Er, which form monoxides of the intermediate type. Therefore, Nd and Gd should be determined as monoxide molecules, whereas Tm should be determined as atoms. As for Sm, Ho, and Er, their rather high DEs will evidently prevent their determination as atoms (presumably, except Sm since the DE of its monoxide is close to that of BaO).

The sensitivity of the MI determination of elements depends on the degree of ionization of their monoxide molecules. As shown above, the sensitivity of the MI method is higher for the elements that form monoxides of the first type. Within this class, molecules have different detection limits as determined by the MI method. As is known, upon laser excitation, species with lower IPs are more efficiently ionized [9]. The higher the IP of the atom/molecule, the higher the excitation energy. Figure 4 shows the MI detection limit of elements as monoxides as a function of the IP of the molecules. This dependence is complex, although some trends can be discerned. We may conclude that the sensitivity of MI determination decreases with an increase in IP. In this context, the high detection limit of Tb seems strange; however, there is no rational explanation for this fact. From this dependence, we may try to estimate the detection limits for Nd and Gd. In its IP and DE values, the NdO molecule closely resembles the PrO molecule, and the GdO molecule resembles the YO molecule (Fig. 1). Our estimate shows that the detection limits for Nd and Gd as monoxides as determined by the laser MI method should be about 20 and 40 ng/mL, respectively.

Thus, the use of the AI method for determination of elements in low-temperature flame gives better results if the DE of the corresponding monoxide does not exceed 5.6 eV. For more stable monoxides, MI determination in molecular form is preferable. The lower the IP of the corresponding monoxide, the higher the sensitiv-

ity of the MI method. To decrease the detection limits of molecules with high IPs, excitation to higher energy states should be used.

## ACKNOWLEDGMENTS

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