

APPLICATION OF DUAL LASER IONIZATION TO TRACE ANALYSIS OF SODIUM IN A FLAME

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Dual laser ionization (DLI) is a technique which can be used to detect trace elements in a flame by ionizing the analyte via a dual-laser stepwise excitation. As a powerful method for flame diagnostics, DLI can detect trace amount of Na at a concentration of ppb (ng/mL), more sensitive by two orders of magnitude than laser-enhanced ionization (LEI), in which only single laser is used. To demonstrate its potential in trace analysis, we compare the detection limit of DLI for Na with other methods utilizing LEI, atomic emission and laser atomic absorption.

INTRODUCTION

Lasers have opened up many new avenues in atomic and molecular spectroscopy. Dye lasers are making it possible to obtain spectral information that was difficult or even impossible to access with conventional light sources, and to investigate many new modes of radiation-matter interaction. In analytical chemistry the dye laser has also led to impressive improvements in detection for atomic fluorescence flame spectroscopy and molecular fluorescence spectroscopy. In addition, it has led to the development of new trace analysis techniques like laser-enhanced ionization (LEI) and resonance ionization spectroscopy (RIS). The latter has even achieved the enviable goal of detecting single atom events.¹ Obviously, the tunable dye laser is showing promising prospects in analytical chemistry.

Laser-enhanced ionization, a tunable dye laser-based ionization technique, which was first developed in 1976, has demonstrated its potential in detecting trace elements in a flame.^{2,3} For some elements, a lower limit of detection as low as 0.001 ppb has been achieved.⁴ As a potential diagnostic for flames LEI has also been used to determine the flame temperature, and the ion yields and structures of the radicals

produced in a flame.⁵⁻⁸ To achieve optimal sensitivity and selectivity in trace detection, the characterization of the ion signal, electrode design, the ion collection configuration as well as the influence of the space charge and the biased voltage applied have been investigated.⁹⁻¹⁵ The basic setup of LEI is to use a dye laser to promote the population of the trace element from the electronic ground state to its excited state, and then monitor the ion yields.⁴ In this work we adopt a setup analogous to LEI, but employ two lasers in counter propagation to enhance the ionization rate. The ionization processes involving a single laser are called laser-enhanced ionization (LEI), and those involving two lasers dual laser ionization (DLI).^{5,16-18}

Based on the Boltzmann theory, the ionization rate of a species increases exponentially with a decrease of the energy defect between the populated discrete electronic state and the ionization continuum. As a result, excitation of the analyte with a dye laser tuned to a selected absorption line may lead to substantial enhancement of the ion yield. Since only the ion product is detected, the DLI (or LEI) method avoids problems arising from stray light, optical interference, flame optical background, self-absorption, the quantum efficiency limitation of

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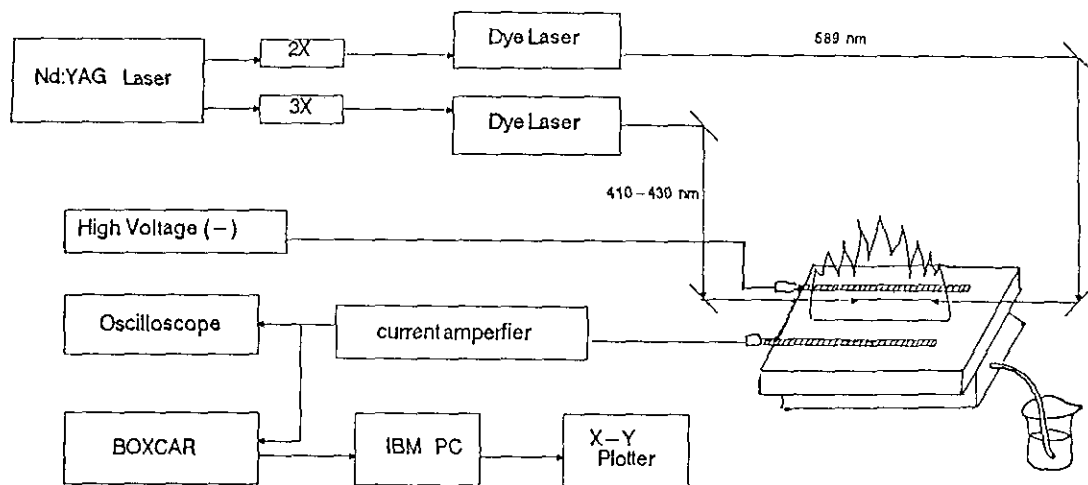


Fig. 1 Schematics of the DLI experimental apparatus.

the optical detectors, and detecting angle restrictions. These and other severe problems are inherent in conventional optical methods. (e.g. fluorescence, absorption, emission, etc.)^{4,19}

In this paper, we show the potential of DLI as an analytical tool in trace elements analysis. First, DLI is used to monitor free sodium in a flame to demonstrate its detection sensitivity and selectivity. Second, the limitations of detection efficiency of the sodium analyte are compared for DLI, LEI and other optical methods.

EXPERIMENTAL SET-UP

The basic set-up of DLI contains three parts: sampling system, radiation source and detecting system. We adopt an analytical flame to release the atomic species of interest, dye lasers as radiation sources and the voltage-biased metal electrodes as the ion collectors. The schematics illustrated in Fig. 1 and described in brief as follows.

The C_2H_2 /air flame system employed in this work contains a burner, a nebulizer and flow meters. The metallic salt solution is sprayed through a pen-

matic nebulizer, and the metal element may be released from a slot burner head. The ratio of the fuel C_2H_2 and air is regulated by a set of flow meters and valves and premixed prior to the burner head.

A frequency-doubled and -tripled 10 Hz Nd:YAG laser (Quanta Ray, Model DCR-2A) is used to simultaneously pump two dye lasers. Kiton red 620 and stilbene 420 dyes are used in the two dye lasers throughout the work. The pulse duration is about 10 ns and the power outputs are in the range of $500\mu J - 5 mJ$ from the dye lasers. Upon irradiation of a dye laser at 589 nm, the free Na atoms can be resonantly excited and consequently ionized either by absorption of other photons from the second dye laser tuned from 410 to 440 nm, or by collisions with components in the flame. The resulting ions are thus collected by a pair of biased electrodes, which are set about 1 cm apart and suspended 1 cm above the burner head. The ion current obtained is amplified via a current to voltage converter (Keithley, Model 427) and then fed into a boxcar averager (PAR, Model 4402, 4420 and 4422) for signal processing. The result is displayed on an oscilloscope (Tektronix, Model 2445) and output by a strip chart recorder or stored in an IBM PC computer for further data

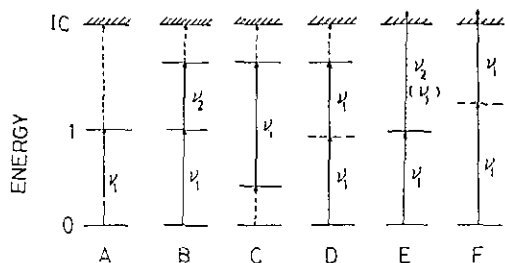


Fig. 2 Ionization pathways that can be followed by DLI (b, e) and LEI (a, c, d and f) processes. a. single photon excitation and collisional ionization; b. stepwise two-photon excitation and collisional ionization; c. thermally-assisted single photon excitation and collisional ionization; d. two-photon excitation and collisional ionization; e. two-step photoionization; f. two-photon ionization (off resonance).

treatment.

In the atomic emission apparatus, the radiation from the thermally excited sodium in the flame is focused onto the entrance slit of a monochromator (Spex, Model 1680B). As the monochromator is scanned across the D lines, the $\text{Na}(3^2P_J - 3^2S_{1/2})$ emission is detected by a photomultiplier tube (RCA, Model 1P28), attached closely to the exit slit. In the laser atomic absorption, the dye laser is used as radiation source operating on the $3^2S_{1/2} - 3^2P_J$ transition. The absorbed fraction of the light is then monitored by the photomultiplier tube positioned along the axis of the incident beam. Reagent grade of NaCl purchased from the Merck Co. was used in the work without further purification.

RESULTS AND DISCUSSION

Fig. 2 shows the possible ionization pathways that the DLI or LEI mechanisms may follow. To optimize the sensitivity of detection, various factors such as the ionization potential of the analyte and the oscillator strength for the selected transition have to be taken into account. In the process of LEI, the

excited state is populated either by single or multi-photon absorption, as shown in Fig. 2a, c, d and f. However, in DLI the atomic analyte is first excited to a lower state, and then excited further to a higher Rydberg state, or directly to the ionization continuum by a second laser. The depiction is illustrated in Fig. 2b and 2e, respectively. Consequently, the energy defect is greatly reduced and the resulting ion yield is thus substantially enhanced in the DLI mechanism.

In this work we have monitored trace Na with a concentration of ppb using the DLI method. Fig. 3 demonstrates the detection sensitivity of Na by DLI and LEI with a Na concentration of 1 ppm in the salt solution. In the former case, the Na ion is obtained upon irradiation of one laser tuned across the $3^2S_{1/2} - 3^2P_J$ transition while the other dye laser is fixed at 428 nm for the $3^2P_{3/2} - 10^2D_J$ transition. In contrast, the Na signal in LEI is obtained by scanning the wavelength of one dye laser across the $3^2S_{1/2} - 3^2P_J$ transition while the other dye laser is blocked. Notice that the sensitivity scale of LEI is enlarged by a factor of 50. The signal of DLI is better than that of LEI by a factor of two orders of magnitude. Along with a better sensitivity in detection, DLI is capable of selecting a higher, unique state in the stepwise transition to avoid any possible spectral interference from the flame background.^{4,9} In this sense, DLI provides better selectivity in trace detection than LEI, which involves a single dye laser.

As shown in Fig. 4, the DLI ionization pathway is via a variety of second-step transitions excited by a dye laser operating from 416 to 440 nm, and the first-step excitation by the other dye laser fixed at 589 nm. Accordingly, DLI may be employed to probe those Rydberg states which are difficult to monitor using the fluorescence method. Since the transition probability for a selected transition varies in proportion to $1/n^3$, where n is the principal quantum number, the fluorescence technique is poor in identifying the high-lying states.²⁰ In Table I we list the Na ion enhancement between DLI and LEI.

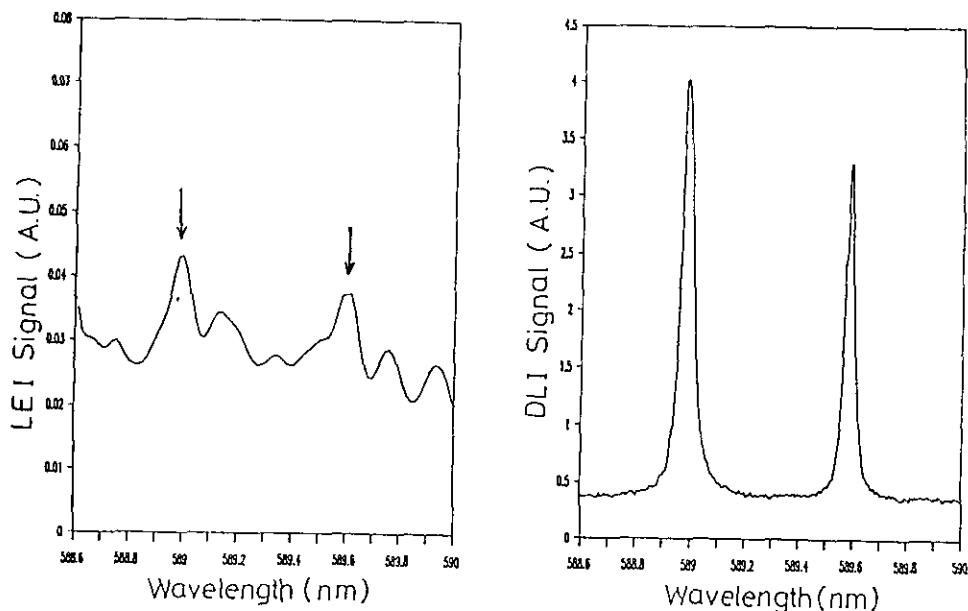


Fig. 3 Ionization signal of 1 ppm sodium in a salt solution using the DLI and LEI methods. The DLI signal is obtained upon irradiation with one dye laser fixed at 428 nm for the $3^2P_{3/2} - 10^2D_J$ transition, and the other dye laser operating across the transition of the D lines. LEI is obtained by scanning the single laser across the transition of the D lines. To obtain the LEI signal, the sensitivity scale is enlarged by a factor of 50. The signals indicated by the arrows are only a little larger than the noise.

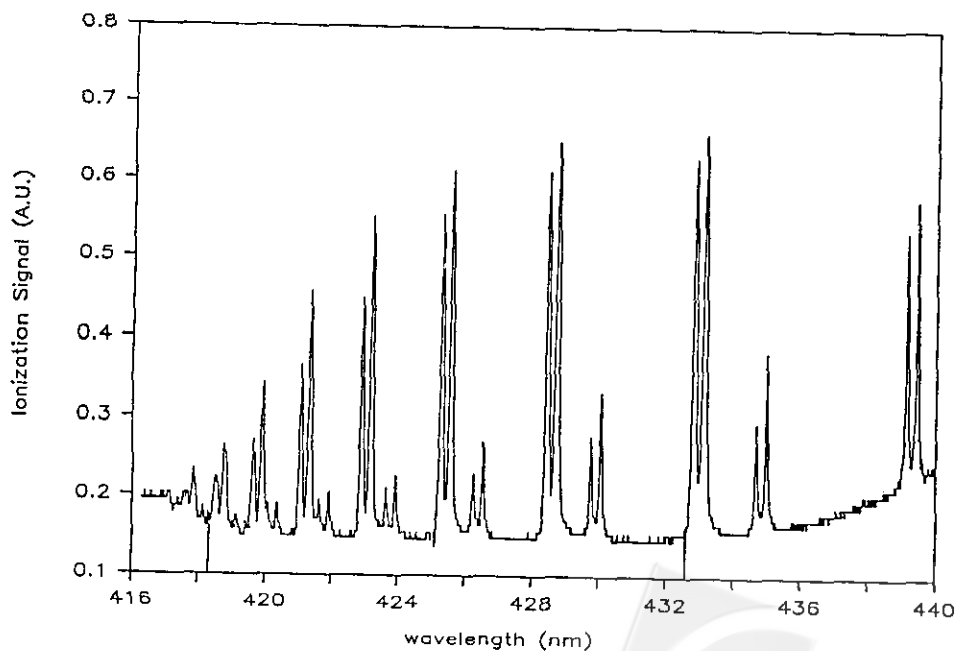


Fig. 4 The Na Rydberg states which can be detected in the salt solution containing 1 ppm Na in an acetylene/air flame. Na atoms are first pumped to the 3^2P_J state at 589 nm and then synchronously excited to the Rydberg states by an additional dye laser tuned from 416 to 440 nm.

Table 1

transition of the second step excitation	energy of states ^a (cm ⁻¹)	second step wavelength (nm)	A _{ki} ^a (X10 ⁸)	ion enhancement
3 ² P _{1/2} → 10 ² S _{1/2}	39983	434.47	.0032	110
3 ² P _{3/2} → 10 ² S _{1/2}	39983	434.15	.0016	50
3 ² P _{1/2} → 11 ² S _{1/2}	40271	429.10	.0024	90
3 ² P _{3/2} → 11 ² S _{1/2}	40271	428.78	.0012	40
3 ² P _{1/2} → 12 ² S _{1/2}	40482	425.25	.0017	60
3 ² P _{3/2} → 12 ² S _{1/2}	40482	424.94	.0009	30
3 ² P _{1/2} → 13 ² S _{1/2}	40641	422.32	.0014	50
3 ² P _{3/2} → 13 ² S _{1/2}	40641	422.02	.0007	30
3 ² P _{1/2} → 14 ² S _{1/2}	40763	420.10	.0012	30
3 ² P _{3/2} → 14 ² S _{1/2}	40763	419.80	.0006	20
3 ² P _{1/2} → 8 ² D _J	39728	439.33	.0097	310
3 ² P _{3/2} → 8 ² D _J	39728	439.00	.0081	270
3 ² P _{1/2} → 9 ² D _J	40090	432.46	.0066	200
3 ² P _{3/2} → 9 ² D _J	40090	432.14	.0055	140
3 ² P _{1/2} → 10 ² D _J	40349	427.68	.0047	180
3 ² P _{3/2} → 10 ² D _J	40349	427.36	.0036	150
3 ² P _{1/2} → 11 ² D _J	40540	424.21	.0035	160
3 ² P _{3/2} → 11 ² D _J	40540	423.90	.0029	130
3 ² P _{1/2} → 12 ² D _J	40685	421.59	.0026	180
3 ² P _{3/2} → 12 ² D _J	40685	421.29	.0022	130
3 ² P _{1/2} → 13 ² D _J	40798	419.59	.0020	180
3 ² P _{3/2} → 13 ² D _J	40798	419.29	.0017	110

^a A_{ki} (spontaneous emission coefficient from the k to i state) and energy (in wavenumber) taken from ref. 22.

Obviously ionization enhancement is strongly influenced by the oscillator strength of the second-step excitation. The enhancement decreases with an increase of the principal quantum number. Therefore, the appropriate selection of the stepwise excitation of an analyte may optimize the ionization enhancement and consequently accomplish detection for an extremely low concentration of the trace.

Fig. 5 shows a comparison of the detection limits of DLI and LEI, atomic emission and laser atomic absorption under the same sampling condi-

tions with various concentrations of NaCl solution. In the plot of DLI signal against Na concentration, the DLI is obtained by operating one dye laser across the 3²S_{1/2} – 3²P_J transition simultaneously with the other fixed at 428 nm for the 3²P_{3/2} – 10²D_J transition. The conditions for LEI are the same as those for DLI but with one dye laser alone. As to the methods of atomic emission and laser atomic absorption, they have been described in the previous section. The ion and photon signals all associated with the sodium D lines, as obtained with

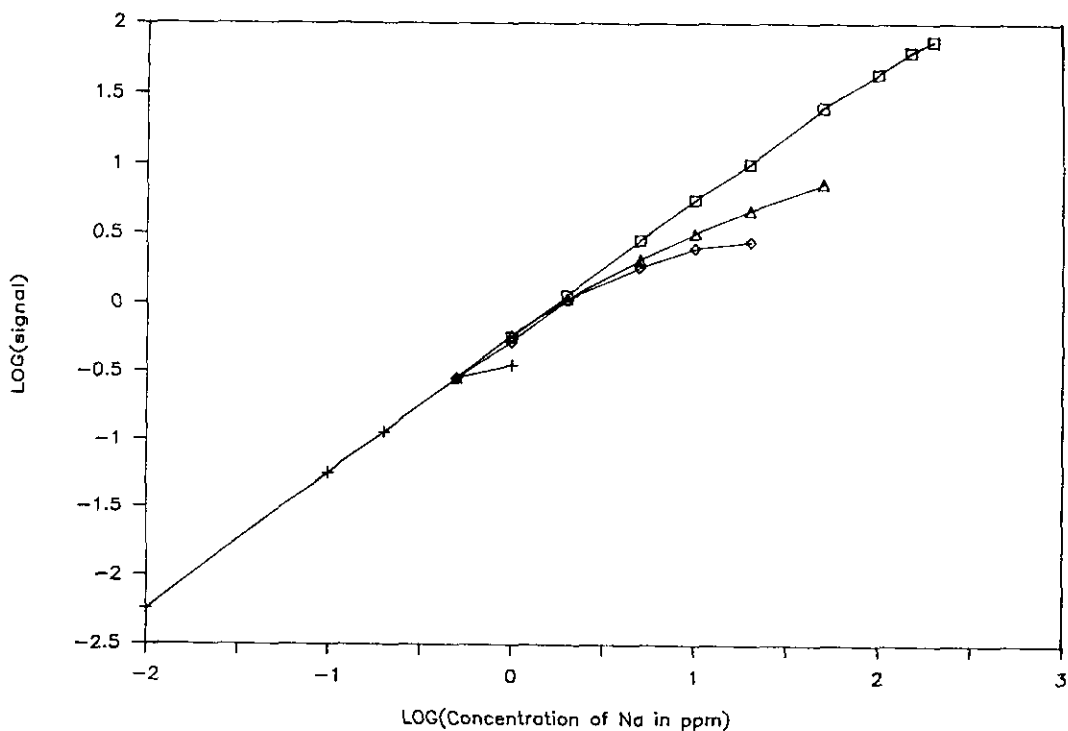


Fig. 5 Comparison of the detection limits for Na in flame under the same sampling conditions. + indicates DLI method; □, LEI; △, atomic emission; ◇, laser atomic absorption. see text for details.

the solution containing Na of 0.5 ppm, are normalized to the same scale. Among the techniques employed, obviously DLI is the most sensitive tool to monitor the concentration of Na extended to the ppb range, better by a factor of two orders of magnitude than the others. Laser atomic absorption, in which the concentration of the NaCl is related to the intensity ratio of absorbed and incident radiation at 589 nm, shows no advantage in using laser radiation rather than a conventional hollow cathode lamp. Taking advantage of a low excited energy in the Na case, atomic emission appears comparable with atomic absorption and LEI. It is worthwhile to notice that in the concentration dependence, the dynamic linear range of LEI is more extensive, over two orders of magnitude. The factors causing the leveling off of the linear range are complicated; however, prevention of the self-absorption may give LEI a larger dynamic range. As for DLI, the space

charge effect due to the production of a much greater number of ions and electrons may reduce the collection efficiency of the biased electrodes,^{10,16} which causes the DLI signal to deviate from linearity.

In addition to the trace element analysis, the free radicals produced in the post combustion flame can also be detected using the DLI technique. The monitoring of radicals in flames is mostly conducted by laser-induced fluorescence or CARS methods.²¹ Here DLI may provide an alternative way to identify the radical species and determine its excited structure. The DLI spectra of radicals such as CH and C₂ are under investigation.

CONCLUSION

In this paper, we have demonstrated the DLI to be a powerful tool in trace analysis. By compari-

son with other techniques such as LEI, atomic emission and laser atomic absorption, DLI method appears more sensitive in detecting trace Na by two orders of magnitude. The ion enhancement of DLI/LEI for Na varies depending on the higher states selected and is roughly determined by the transition probability of the second-step excitation of the analyte.

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