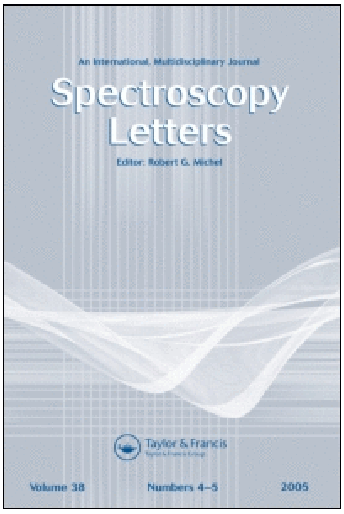

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Lasers in Analytical Atomic Spectrometry-An Overview[1]

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LASERS IN ANALYTICAL ATOMIC SPECTROMETRY-AN OVERVIEW[1]

Key Words: Laser atomic fluorescence, laser-enhanced ionization, laser-induced plasma, and laser sampling

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ABSTRACT

This paper discusses the use of lasers in analytical atomic spectrometry. Following a brief discussion on the properties of lasers that attract analytical atomic spectroscopists, the major uses of lasers, i.e., in laser excited atomic fluorescence, laser-enhanced ionization, laser-induced breakdown emission and laser sampling are described, particularly its application to real samples. A very brief description of theory or basic principles, laser used in experimental set up and selected and representative applications are presented. Finally, the potential future of the laser in analytical atomic spectrometry will be discussed.

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1. INTRODUCTION

The laser (light amplification by stimulated emission of radiation) has been involved in many aspects of analytical chemistry since its invention nearly forty years ago[1,2]. Areas in which the laser is proving indispensable include Raman Spectrometry, and molecular and fluorescence spectrometry. The laser has not been widely adopted in analytical atomic spectrometry due, in part, to the success of conventional analytical atomic spectrometry. However, the laser has attracted the analytical atomic spectroscopistist to some degree and, given the promise of newer and better lasers, more dependable, and less expensive, and the desire to push detection to lower and lower levels, it is safe to assume that the laser could play an increasing role in analytical atomic spectrometry, particularly where it can provide improved performance over conventional analytical atomic spectrometry. The purpose of this paper is to briefly discuss the laser as it pertains to analytical atomic spectrometry, and briefly describe its current application and postulate the future of lasers in analytical atomic spectrometry. The reader is referred to a recent book which deals in more depth on this subject[3].

2. LASER AND ITS PROPERTIES

In analytical atomic spectroscopy, an ideal laser would consist of the following properties: stable and reliable over a significant period of time, tuneable in both the ultra-violet and visible spectrum, noise free, high output power in excess of terrawatts to allow a measurable amount of light to pass through optically dense samples, and physical pluses including lightweight, easy to operate, easy to maintain, inexpensive to obtain and minimal running costs. Unfortunately all these parameters cannot be simultaneously obtained with current commercial laser systems, and the laser analytical atomic spectroscopist must choose the laser characteristics which best fit their need.

The theory and basic principles of the laser is beyond the scope of this paper and the reader is referred to publications in this area [3, 4]. The types of lasers used in analytical atomic spectrometry and their properties are shown in Table 1.

It should be pointed out that the lasers and properties shown in Table 1 are general and new lasers with new and improved properties are becoming available which will prove to be very useful in analytical atomic spectroscopy, e.g., Ti: Sapphire, tuneable in the UV solid state lasers, etc.

Table 1

Types of Laser and Their General Properties which are Useful to the Analytical Atomic Spectroscopist

Laser	Properties
Liquid	
Dye (around 200)	340 nm-1 μm, pulse widths of 6-10 ns, pulse of few hundred Hz, and tens of mJ of energy
Gas	
He-Ne	632.8 nm, energies in milliwatts
Noble Gas Ion (Ar and Kr)	Many wavelengths in visible spectrum, high power energies
Carbon Dioxide	10.6 μm, pulse widths of 1-200μs, pulse energies of 0.5-500 J
Nitrogen	337 nm, pulse widths of 300 ps, pulse energies of <10 J, repetition rates of 1-100 Hz
Excimer	ArF(193 nm) KrF(248 nm) XeCl(308 nm), repetition rates up to 250 Hz, pulse widths of 7-20 ns, pulse energies up to 250 mJ
Semiconductor diode	630-1600 nm, pulse widths of 0.1-100 ns, pulse energies of 30-40 mW(continuous) or 10 W(pulsed)
Solid State	
Ruby	693.4 nm, pulse widths of 25 μs, pulse energies of 10 J
Neodymium (Nd: YAG, Nd: glass, etc.)	YAG 1064 nm, glass at 1053 nm, pulse energies of 1-2 J

2.1. Tunability

A laser should be tuneable over the wavelength region of 180-900 nm, ideally by merely turning a dial or similar device. However such a system is not available, and, in practice the analytical atomic spectroscopist selects a laser system for the wavelength region of interest. Dye lasers are the most commonly used tuneable lasers. There are over 200 fluorescent organic dyes which can be used. The wavelength regions are in the visible spectrum, and cover a limited range, typically around 50 nm. If another wavelength region is required then a new dye must replace the old dye (Nb. this is not recommended as it causes all sorts of problems in terms of performance). Diode lasers are tuneable but most work in the near infra red region of the spectrum and have limited use.

2.2. Power Density

Power is the rate at which the laser beam is delivered. Power is measured in Watts or J/s. A large power density of even moderate power from a laser of a few milliwatts is much brighter than conventional light sources. A pulsed laser will produce 10^{15}-10^{30} photons/s whereas a conventional hollow cathode lamp may produce 10^{6}-10^{8} photons/s at a single wavelength. A high power density allows a measurable amount of light to pass an optically dense solution so that small absorbances can be detected. Power densities range from less than a mW to tens of KW for commercial lasers. Irradiance is power per unit area. This is an important factor in using the laser as a sample introduction system (see section 4.4).

2.3. Monochromaticity

A laser beam consists of an extremely narrow range of wavelengths. This occurs because almost all the photons are emitted from transitions between two energy levels that have the same frequency.

2.4. Directionality

Laser light travels in a single direction within a narrow cone of divergence. All laser beams will eventually spread (diverge). However, over a limited length it essentially produces a parallel beam which allows it to be straightforward to collect emitted radiation and focus it onto a small area using simple optics.

2.5. Pulsing

Pulse repetition rates can vary from a few tens of pulses (Ruby and Nd: glass) to thousands of pulses per second (excimers). Pulse repetition rates can be adjusted using several techniques including Q-switching, mode-lockers, cavity dumpers, etc. (see sections 3.1 to 3.3)

2.6. Coherence

This describes the in-phase or in-step property of light waves. It is the most fundamental property of a laser and, a laser can be defined as a source of coherent light.

3. LASER INSTRUMENTATION

Based on the above discussion it would appear that current commercial laser instrumentation would have limited applications given the fact that they do not often meet the needs of analytical atomic spectrometry. However there is available a number of instrumental modifications and techniques which make the laser more attractive to the analytical atomic spectroscopist including frequency conversion, Q-switching and cavity dumping, and ultrashort pulse techniques[3].

3.1. Frequency conversion

As indicated in the text, few lasers work in the UV region of the spectrum. This region can be reached using second harmonic generation (SHG), commonly called frequency doubling. This is best illustrated by an example. A Nd: YAG laser has a wavelength output at 1064 nm. This can be frequency doubled to 532 nm or frequency quadrupled to 256 nm. It should be noted that there is reduction in incident efficiency, usually from 10 to 40 % with frequency doubling. Methods of frequency doubling are described elsewhere[3].

3.2. Q-switching and Cavity Dumping

These techniques are used to obtain high pulse energies. The basic principle is where the Q-switch acts as a shutter within the laser cavity. When the shutter is closed, light leaving the active medium is blocked or reflected out of the cavity. The Q-switch introduces sufficient loss in the laser cavity to prevent lasing, which, in turn allows the amplifier gain of the laser to increase far above the normal lasing threshold. When the Q-switch is opened, lasing is initiated, and the energy stored in the active medium is subsequently released in one intense pulse.

In cavity dumping, the energy within the cavity is allowed to build up with fully reflective mirrors until a sufficiently high population inversion is achieved. The laser beam is then directed out of the cavity by other mirrors with all of the energy dumped in a single pulse.

3.3. Ultra-Short Pulse Techniques

Ultrashort laser pulses, in the femtosecond to picosecond range and very high peak power, can be achieved using mode-locking. Methods of achieving these ultra-shot techniques are discussed elsewhere[3].

4. APPLICATIONS OF LASERS IN ANALYTICAL ATOMIC SPECTROMETRY

The major use of lasers in analytical atomic spectrometry is in four areas, namely laser excited atomic fluorescence spectrometry, laser-enhanced ionization spectrometry, laser-induced breakdown (emission) spectrometry, and laser sampling. It has found use in diagnostic studies, been shown by Niemax and workers[5] as a potential light source in atomic absorption spectrometry, and in the related technique of resonance ionization spectrometry (and resonance ionization mass spectrometry). This papers focuses on its major use.

4.1. Laser Excited Atomic Fluorescence Spectrometry

Laser-excited atomic fluorescence spectrometry (LEAFS) involves the excitation of analyte atoms by a laser for subsequent detection by fluorescence and is powerful technique capable of detecting femtogram leveels. This is due to the fact that when using a laser, it is possible to populate the excited levels much more compared to a conventional light source such as a hollow cathode lamp.

The ideal laser for LEAFS would be wavelength tuneable and capable of generating high peak energy and high average power. This has resulted in the dye laser being the most widely used, due to its tunability. However, the frequency doubled ruby laser, flashlamp-pumped dye laser, Nd:YAG laser, nitrogen laser, argon ion laser, copper vapor laser and excimer lasers have all been successfully used in LEAFS. A detailed discussion on basic theory on AFS with laser excitation is available elsewhere[3].

Selected and representative applications of LEAFS are presented in Table 2. In general the accuracy was assessed by comparison to standard reference materials (SRMs) and found to be very good with absolute detection limits in femtogram to nanogram. A limitation of LEAFS is that it is a single element technique when there is significant interest in multielement determinations.

4.2. Laser-Enhanced Ionization Spectrometry

Laser-enhanced ionization (LEI) spectrometry is a technique which involves the light from a laser impinging on, and exciting atoms (or molecules) created in a conventional atomizer such as a flame or graphite furnace, to a sufficiently high level to induce an enhancement in the rate of collisional ionization compared to background rates of ionization. The incorporation of an electric field in the atomizer allows measurement of the ionized species as a current.

Selected and representative application of LEI to real samples is shown in Table 3.

Table 2

Selected and Representative Applications of LEAFS

Element	Sample	Laser	Comments	Ref.
Sn	Ni-based alloys	Tuneable dye laser pumped by excimer	Detection limit of 1.5 ng/g and good accuracy	6
P	Polymers (poly(ethylene-terphthalate))	Tuneable dye laser pumped by excimer	ETA-LEAFS for direct sampling. Detection limit of 8 ng	7
Pb	Great Lakes waters	Tuneable dye laser pumped by copper vapor lamp	Detection limit of 0.4 ng/L	8
Tl	SRM standards, pine needles, bovine liver, tomato leaves	Tuneable dye laser pumped by excimer	Good accuracy	9

The ideal laser for LEI spectrometry would have wide wavelength coverage over the UV-Visible spectrum, high intensity, high repetition rate, and narrow laser linewidth. The most widely used laser is the dye laser and excimer pumped laser which is often frequently doubled or tripled.

The technique has been around for over twenty years and is discussed in great detail in a recent monograph[14]. Its lack of commercial availability, frequency of interferences from easily ionized elements often need sample pretreatment, and the fact that it is a single-element technique has limited its widespread use and acceptance. However it does have great potential for detecting low levels in combination with graphite furnace atomization.

4.3.Laser-Induced Breakdown (Emission) Spectrometry

When the light from a laser is focused onto a small spot of a surface of a sample, an optically induced plasma, frequently called a laser-induced

Table 3

Selected and Representative Applications of LEI Spectrometry

Elements(s)	Sample	Laser	Comments	Ref.
Organotin	SRM oysters	Dye laser pumped by Nd: YAG laser	Detection limit of 0.9 ng/mL Combined flame LEI with high performance liquid chromatography	10
U	Hollow cathode lamp	GaAlAs diode at 773-797 nm and 4 mW power	Showed potential in actinide monitoring	11
Ca, Ga, In, Li, Na, Sr	Aqueous solutions	Dye laser pumped by continuous wave argon ion laser	Poor performance in visible region	12
Cu, In, Na	Cu in Ge, In in CdHgTe, and Cu and Na in H_3PO_4	Excimer (XeCl)	ETV for solid or solution introduction	13

plasma, laser-spark, or laser-ablated plasma is formed. This occurs when the laser power density exceeds the threshold breakdown value of the surface of the sample. The plasma formed can be used as a source for atomic emission spectrometry (AES) and the technique is frequently and commonly referred to as laser-induced breakdown (emission) spectrometry (LIBS).

LIBS appears to have significant potential in remote sensing, use in a hostile environment, and direct use with minimal sample preparation in different phases (gases, liquids, and solids). It is an inherent multielement technique. Its disadvantage could be in the more complex (and increased cost) instrumentation to accurately take advantage of the transient plasma, lack of suitable standards must make the technique semi-quantitative, and detection limits are somewhat poorer than conventional analytical atomic spectroscopic techniques.

Table 4

Selected and Representative Applications of LIBS

Element	Sample	Laser	Comments	Ref.
Cu, Cr, Mn, Si	Brass, Al, and steel	Q-switched Nd: YAG	Analysis under water	15
K	Glasses	Excimer (ArF)	Detection limit of 0.13 ng/g	16
Ba, Cr	Soil	Q-switched Nd: YAG	Remote sensing using fiber optic cable	17
Cr	Metal alloys and NIST Standards	Excimer (ArF)	Good accuracy	18

4.4. Laser Sampling

The use of the laser as a sampling device was recognized almost as soon as the laser was invented. Like LIBS, it involves focusing a laser light on a sample and when the power density is sufficiently high, an ablated mass, typically ng to mg of small solid particles, solidified liquid drops, free atoms, and other entities "erupt" from the surface and can be transported to conventional flame, furnace, or plasma for AAS, AES, or AFS. This method is a direct solid sampling method with minimal sample preparation, and has found widespread interest and use when combined with inductively coupled plasma (ICP)-AES. and more recently with ICP-mass spectroscopy (MS).

The most frequently used lasers in this area have been solid state lasers such as ruby, frequency double and tripled , Nd: YAG, as well as CO_2 and N_2 gas lasers. The use of lasers which emit in the ultra-violet region of the electromagnetic spectrum such as excimers lasers will find increasing use in the future.

Table 5 shows selected and representative applications of laser sampling to real samples.

Laser sampling combined with conventional analytical atomic spectroscopy is a useful addition to the analyst who is interested in direct solid sampling, particularly difficult to digest or dissolve such as polymers,

Table 5

Selected and Representative Applications of Laser Sampling Combined with Various Analytical Atomic Spectroscopic Techniques

Element(s)	Sample	Laser	Technique	Comments	Ref.
Pb	Polyethylene pellets, soil, standards	Nd:YAG	ICP-MS	Optimization study of solids and dried aerosols	19
Cu	Standard	Nd: YAG frequency doubled	ICP-MS	Simultaneous m/z using twin quadropoles	20
Al, Ba, Ca, Co, Cr, Fe, K, Mg, Mn, S, Si, Ti	Glasses	Excimer(XeCl) and Nd: YAG frequency tripled and quadrupled	ICP-AES	Influence of color and wavelength, mass ablated and crater sizes and shaped studied	21
Cu, Mg	Solids	Nd: YAG	Optical Emission Spectrom. (OES)	Detection limit of 4 ppm (Mg) and 40 ppm (Cu)	22

without the tedious, time-consuming and contamination prone sample preparation techniques currently used for solid samples. Recently, it has been used in conjunction with ICP-AES and ICP-MS.

5. CONCLUSION AND FUTURE USE OF LASER

As noted earlier, the laser has not been widely used in analytical atomic spectrometry at present. However, where it has been applied, it has shown improved performance over conventional atomic spectroscopy. as more reliable and less complex laser systems become available, and, given the desire and drive for lower levels of detection, the laser could play an increasing role in analytical atomic spectroscopy. Reduced cost, both in intial cost and running costs, would also drive the use of the laser.

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