Laser-Excited Atomic Fluorescence Spectroscopy for Heavy Metals Detection

There are some types of research projects which could be formulated in a simple manner and require knowledge of only basic math. The project below proposes to find the simple conversion process from available laser wavelengths mentioned in Table II to get the excitation wavelength mentioned in Table I. The conversion rules are simple and include only arithmetic operations. Despite this simple formulation, the outcome could be important for laser sensing applications, and it also includes the possible *patent application* of the simplest solution. All information required to understand the project goal is located below. However, advanced students can skip this narrative and go directly to the Rules of the game.

Laser-Excited Atomic Fluorescence Spectroscopy (LEAFS) is a very sensitive method for the analysis and detection of atoms and molecules in the gas phase. The figure illustrates the concept of LEAFS. Laser radiation is employed to excite atoms or ions from their ground state into an excited state. As the Atoms or Ions relax back into the ground state, they emit fluorescence signals. This fluorescence could be detected and analyzed. The LEAFS sensitivity could be as high as a single atom in a sample because each atom or ion has a very specific and very narrow absorption and emission spectral lines. So, a measured photo signal for a unique combination of excitation wavelength (λ_{ex}) and detection wavelength (λ_{det}) will provide information on the specific atom concentration. The table below shows several examples for excitation and detection wavelengths of Cd, Mn, and As atoms. As one can see all these excitation and emission lines are in the UV region of the spectra.

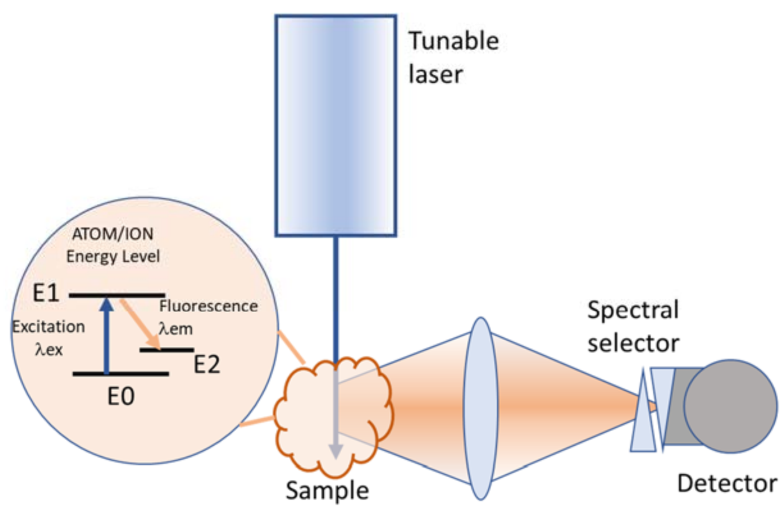

Figure 1. Schematic representation of Laser-Excited Atomic Fluorescence Spectroscopy .

TABLE I

ELEMENT	Excitation Wavelength, (Frequency)	Detection Wavelength
Cd	228.8 nm (43706 cm^{-1})	326.1 nm
As	197.3 nm (50682 cm^{-1}) 193.7 nm (51626 cm^{-1})	249.3 nm 246.7 nm, 243.7 nm
Mn	279.48 nm (35781 cm^{-1})	403.3 nm

In most LEAFS systems, an excitation wavelength is varied using a tunable laser which allows one to select a specific atom or ion. A tunable laser system could be designed to get any specific excitation wavelength for any specific ion. But their cost is usually measured in hundreds of thousand dollars and its operation requires at least two Ph.D. students. However, there is a class of very robust low cost solid-state lasers which do not require any Ph.D. student and have only one button for operation. They are solid-state lasers based on Rare Earth (RE) ions. Unfortunately, they are not tunable (the oscillation wavelength can't be changed) and oscillation wavelengths are in the mid-IR spectral region. For example, a green laser pointer is usually based on Nd laser. Table II shows the oscillation wavelength of some mostly used solid-state lasers.

TABLE II

Solid-Sate Laser	Oscillation Wavelength, λ, nm	Oscillation Frequency ν, (cm^{-1})
$Yb{:}YVO_4$	1020	9804
$Yb{:}Y_3Al_5O_{12}$	1030	9709
$Nd{:}LiYF_4$	1047	9551
$Nd{:}Y_3Al_5O_{12}$	1052	9506
$Nd{:}\ LiYF_4$	1053	9497
$Nd{:}Y_3Al_5O_{12}$	1064	9399
$Nd{:}\ YVO_4$	1067	9372
$Nd{:}YAlO_3$	1080	9259
$Nd{:}\ LiYF_4$	1313	7616
$Nd{:}Y_3Al_5O_{12}$	1319	7582
$Nd{:}Y_3Al_5O_{12}$	1341	7457
$Nd{:}YVO_4$	1343	7446
$Nd{:}YAlO_3$	1351	7402
$Er{:}YVO_4$	1604	6234
$Er{:}Y_3Al_5O_{12}$	1617	6184
$Er{:}Y_3Al_5O_{12}$	1645	6079
$Er{:}YAlO_3$	1662	6017
$Ho{:}LiYF_4$	2064	4845
$Ho{:}Y_3Al_5O_{12}$	2091	4782

Therefore, the idea to develop a laser system based on simple non-tunable robust, cost-effective solid-state lasers looks very attractive. In this project, we are looking for Cd atoms detection platform with an excitation wavelength of 326 nm. *Why Cadmium?* Historic and ongoing air, water, and soil pollution in North Birmingham with heavy metals and other toxic compounds from open quarries, steel mills, coal-fired power plants, and coke furnaces remains a problem. Inhalation of heavy metals carried on dust causes Chronic Obstructive Pulmonary Disease (COPD) which is ranked as the third leading cause of death in the USA. The preliminary data suggest that soil in some of these polluted areas contains a very high level of Cd, As, and Mn. The researchers of the Laser Lab at Physics Department actively participate in multidisciplinary projects in UAB Superfund Research Center which addresses the legacy of environmental airborne pollution with heavy metals and its impact on respiratory health and environmental degradation in the Birmingham Area. Therefore, the development of a robust heavy metal laser detection platform (and specifically for Cd) is important for many environmental projects.

How RE solid-state lasers could help with selective excitation of the specific atom if their wavelength locates in near-IR spectral range while for the selective excitation, the UV range is required?

There are two simple processes that allow changing of a wavelength of laser radiation. However, the conversion rules are easy to formulate for radiation frequency. A radiation wavelength (λ) and frequency (*f*) are connected by a simple fundamental equation

$$f = \frac{C}{\lambda}$$

, where c is speed of light. Also, in the spectroscopy, frequency is usually measured in special units (wavenumbers, ν) which is

$$\nu[cm^{-1}] = \frac{f}{c} = \frac{1}{\lambda[cm]}$$

So, to calculate wavenumbers (frequency) in cm^{-1}, one needs to calculate $1/\lambda$, where the wavelength is measured in cm units. For example, green radiation with wavelength λ=550 nm=5.5×10^{-5} cm correspondents to wavenumber $\nu=1/(5.5\times10^{-5}$ cm)=18,181 cm^{-1}. For convenience, Tables I&II show the wavenumbers in addition to the radiation wavelength. The most used processes of radiation frequency conversion are Harmonic Generation and Raman Frequency Conversion. Both processes occur during the propagation of radiation in specially oriented crystals. These processes are shown in the next figure.

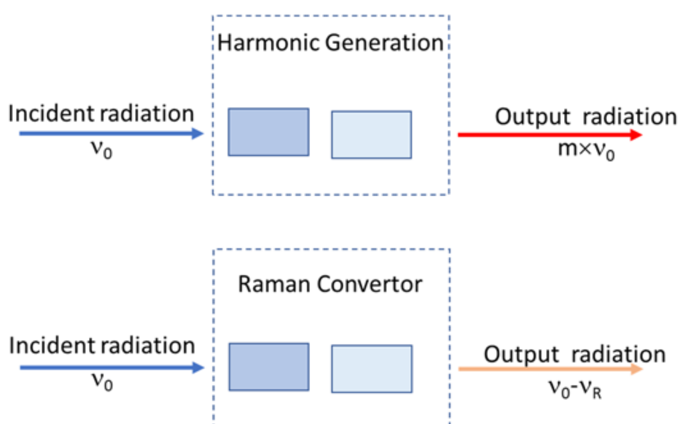

Figure 2. Frequency conversion in Harmonic Generation and Raman Convertor

In the first process, the radiation frequency of the incident light could be converted to its harmonics

$$\nu_{out} = m\nu_0 \ ,$$

, where m is integer number (2,3,4…). So, harmonic generation results in increased radiation frequency. In the second process, a radiation frequency is decreased by special value ν_R (called Raman frequency).

$$\nu_{out} = \nu_0 - \nu_R \ ,$$

Raman frequency (ν_R) depends only on crystal structure, and it is specific for each crystal. Table III summarizes the Raman frequencies of most used crystals for Raman converters. So, the Raman process results in a decrease in radiation frequency.

TABLE III

CRYSTAL	RAMAN FREQUENCY (ν_R, cm-1)
Diamand	1332
$Ba(NO_3)_2$	1048
ZnM_OO_4	971
$BaWO_4$	925
$SrWO_4$	921
$CaWO_4$	911
$PbWO_4$	905
$KGd(WO_4)_2$	901
$BaMoO_4$	892
YVO_4	890
$CaMOO_4$	879
$KGd(WO_4)_2$	767

Rules of the game:

The goal of the project is to propose a nonlinear frequency conversion scheme (Harmonic Generation, and Raman Conversion) based on a solid-state laser from Table II and Raman crystals from Table III for generation of specific excitation wavelength which could be used for laser detection of heavy metal concentration (see Table I) with initial focus on Cd detection

Possible outcome: The simplest combination of the frequency conversion scheme for the sensing application could be a subject for submission of Patent Application.

Appendix.

The Table II includes the most common RE solid state lasers, other oscillation wavelengths of RE solid state lasers are summarized in "Springer Handbook of Lasers and Optics", (2007) Träger, Frank (Ed.); (Part C: Coherent and Incoherent Light Sources, Chap. 11 Lasers and Coherent Light Sources, 11.2 Solid-State Lasers, pp 619-674)