FINAL TECHNICAL REPORT

TITLE: Development of Laser Excited Atomic Fluorescence and Ionization Methods

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The research supported by DE-FG05-88ER13881 during the past (nearly) 3 years can be divided into the following four categories: (1) Theoretical Considerations of the Ultimate Detection Powers of Laser Fluorescence and Laser Ionization Methods; (2) Experimental Evaluation of Laser Excited Atomic Fluorescence; (3) Fundamental Studies of Atomic and Molecular Parameters in Flames and Plasmas; (4) Other Studies. References are given at the end of the Progress Report.

- (1) Theoretical Considerations of the Ultimate Detection Powers of Laser Fluorescence and Ionization Methods^{1,2}.

We have developed theoretical expressions (see Table 1) for the efficiency of detection, ϵ_d , which is defined as the number of photoelectrons (events) produced in laser excited fluorescence (see Fig. 1) or laser excited ionization (see Fig. 2) per single laser probing a detection efficiency of unity means that every atom within the probed region is detected. If $\epsilon_d \rightarrow 1$, then it is possible for the laser based technique to achieve the best possible detection limit, called the intrinsic detection limit, which is based upon the discrete nature of matter (atoms within the probed region and/or detected photons within the probed region). In Table 2, ϵ_d values are given for several typical laser systems¹. In Table 3, we have evaluated typical laser systems with regard to the approach of intrinsic detection limits and in Table 4, we have compared typical laser systems as to their capability of achieving the single atom detection (SAD) concept. The conclusions drawn from this theoretical study are shown below.

- (i) the fluorescence technique presents serious limitations in terms of collection and detector efficiencies. This is of course not new, but the presently used set-ups require radically new designs in

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Figure 1. Simplified energy level schemes for a resonance fluorescence (A) and a direct line Stokes fluorescence (B) processes. l - lower level; m - metastable level; u - upper level; N_l , N_m , N_u - number of atoms in levels l , m and u , respectively; g_l , g_u - statistical weight of levels l and u , respectively; N_T - total number of atoms.

Figure 2. Simplified energy level schemes for several ionization processes. The symbols are the same as in Figure 1, with the addition of level i (ionization continuum) and v (virtual). See captions of Table 1 for the name of the different processes.

TABLE 1. Theoretical Expressions for the Total Number of Fluorescence Photons and Total Number of Ions Detected by Pulsed LIF and LEI-RIS Techniques During One Probing Time Per Atom^{(a)(b)(c)}

TECHNIQUE	PERTINENT SCHEME (Figs. 1 and 2)	THEORETICAL EXPRESSIONS
LIF-RF	1A	$A_{ul} g \Delta t_i \left(\frac{\Omega_F}{4\pi} \right) \eta_t \eta_{PMT}$
LIF-DLF	1B	$[1 - \exp(-g A_{um} \Delta t_i)] \left(\frac{\Omega_F}{4\pi} \right) \eta_t \eta_{PMT}$
SC-LEI	2A	$[1 - \exp(-g k_{ui} \Delta t_i)] \eta_d$
SC-LEI-MT	2B	$\left(\frac{k_{ui}}{k_{ui} + z_{um}} \right) \{1 - \exp[-g(k_{ui} + z_{um}) \Delta t_i]\} \eta_d$
TC-LEI	2C	$[1 - \exp(-g' k_{u,i} \Delta t_i)] \eta_d$
TC-RIS	2D	$\{1 - \exp[-g B_{ui} \rho_{ui}(\lambda_{ui}) \Delta t_i]\} \eta_d$
TC-RIS-MT	2E	$\left[\frac{B_{ui} \rho_{ui}(\lambda_{ui})}{B_{ui} \rho_{ui}(\lambda_{ui}) + z_{um}} \right] \{1 - \exp[-g(B_{ui} \rho_{ui}(\lambda_{ui}) + z_{um}) \Delta t_i]\} \eta_d$
TP-LEI	2F	$\{1 - \exp[-\sigma^{2ph} I_L^2(\lambda_{uv}) \Delta t_i]\} \eta_d$

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(a) GLOSSARY:

For the derivatives of the expressions, see Refs. [9,10].

A_u = Einstein coefficient of spontaneous emission between upper level, u , and lower level, l ; (s^{-1})

g = $(\frac{g_u}{g_l + g_u})$, where g_i is the statistical weight of level, i ;
dimensionless

Δt_i = interaction time. This time is defined as the probing time of the process (fluorescence and ionization) and is given by the laser pulse duration, since a pulsed laser is assumed here whose duration does not exceed $1 \mu s$; (s).

$\frac{\Omega_F}{4\pi}$ = fraction of the fluorescence solid angle collected by the detection optics; (dimensionless)

η_t = transmission efficiency of the dispersion device; (dimensionless)

η_{PMT} = quantum efficiency of the photomultiplier tube (PMT); (dimensionless)

A_{um} = Einstein coefficient of spontaneous emission between upper level, u , and metastable level m , which is acting as a trap for the atoms within the interaction time, Δt_i ; (s^{-1}).

k_{ui} = "effective" collisional ionization rate coefficients from levels u into the ionization continuum; (s^{-1}).

$k_{u',i}$ = "Effective" here means that, in collision-dominated systems, this coefficient cannot be referred to a single level u since collisions might be effective in redistributing the excited atoms between neighboring levels; u' represents the level reached by the 2nd excitation step (s^{-1})

Z_{um} = ($\equiv A_{um} + k_{um}$): total deactivation rate coefficient for atoms from level u to metastable level m taking into account radiative (A_{um}) and quenching (k_{um}) transitions; (s^{-1}).

η_d = detection ($\equiv$ collection) efficiency for the ions created in the process; (dimensionless)

g' $\equiv$ $(\frac{g_{u'}}{g_l + g_u + g_{u'}})$

$B_{ui}\rho_{ui}(\lambda_{ui})$ = radiative ionization rate (s^{-1}) for the transition between level u and the ionization continuum, induced by the laser radiation tuned at λ_{ui} , of spectral energy density ρ_{ui} ($J\ cm^{-3}\ Hz^{-1}$). B_{ui} is the Einstein coefficient for stimulated absorption ($J^{-1}cm^3\ Hz\ s^{-1}$).

B_{ui} = $\int \sigma(\lambda)d\lambda \left(\frac{c}{h\lambda_{ui}}\right)$, where $\sigma(\lambda)$ is the wavelength dependent cross section (cm^2), c is the velocity of light ($cm\ s^{-1}$), λ_{ui} is the wavelength of the transition (cm), and h is the Planck constant ($J\ s$).

σ^{2ph} = absorption cross section for the 2-photon process; $cm^4\ s$

$I_L(\lambda_v)$ = laser photon irradiance at λ_v (v = virtual level); $s^{-1}cm^{-2}$

(b) ASSUMPTIONS FOR THE EXPRESSIONS

The laser is assumed to be broad-band, i.e., its spectral profile is larger than the absorption profile of the atoms in all the atomizers considered. In addition, the rate equations approach is used to derive the expressions, and the laser is assumed to be characterized by a rectangular temporal profile. For the ion yield expressions, recombination between ions and electrons is neglected. In all expressions, the transitions are considered to be optically saturated during the entire interaction time.

(c) ACRONYMS

LIF-RF = Laser Induced Fluorescence - Resonance Fluorescence
 LIF-DLF = Laser Induced Fluorescence - Direct Line Resonance
 SC-LEI = Single-Color-Laser Enhanced Ionization
 SC-LEI-MT = Single-Color-Laser Enhanced Ionization-Metastable Trap
 TC-LEI = Two-Color-Laser Enhanced Ionization
 TC-RIS = Two-Color-Resonance Ionization Spectroscopy
 TC-RIS-MT = Two-Color-Resonance Ionization Spectroscopy-Metastable Trap
 TP-LEI = Two-Photon Excitation-Laser Enhanced Ionization

TABLE 2. Total number of fluorescence photons ($N_{f,d}$) and total number of ions ($N_{i,d}$) detected per probing time per atom with typical experimental laser systems^(a)

TECHNIQUE	$N_{f,d}$		$N_{i,d}$	
	$\Delta t_1 = 10^{-8} \text{ s}$	$\Delta t_1 = 10^{-6} \text{ s}$	$\Delta t_1 = 10^{-8} \text{ s}$	$\Delta t_1 = 10^{-6} \text{ s}$
LIF-RF	$10^{-5}(0.5)^{(b)}$	$10^{-3}(50)^{(b)}$	---	---
LIF-DLF	$7.9 \times 10^{-6}(0.4)$	$2 \times 10^{-5}(1)$	---	----
SC-LEI	---	---	5×10^{-3}	0.39
SC-LEI-MT	---	---	9.9×10^{-4}	10^{-3}
TC-LEI	---	---	0.96	1
TC-RIS	---	---	0.39	1
TC-RIS-MT	---	---	0.09	0.09
TP-LEI	---	---	0.63	1

^(a)The two values for the interaction times refer to two typical pulsed laser systems, i.e., N_2 -or Nd-YAG or Excimer-or Cu-vapor-pumped dye lasers (10^{-8} s) and flash-lamp pumped dye lasers (10^{-6} s).

^(b)The values in parenthesis refer to the photons emitted per probing time per atom, emphasizing the extremely low photon collection efficiency.

Table 2 (continued)

Numerical values used for the calculations:

$$A_{ul} = A_{um} = 10^8 \text{ s}^{-1}$$

$$g = 0.5$$

$$\left(\frac{\Omega_F}{4\pi}\right) = 10^{-3} \text{ (f/2 lens system)}$$

$$\eta_t \eta_{PMT} = 2 \times 10^{-2}$$

$$k_{ui} = 10^6 \text{ s}^{-1}$$

$$\eta_d = 1$$

$$Z_{um} = 10^9 \text{ s}^{-1}$$

$$g' = 0.33$$

$$k_{u,i} = 10^9 \text{ s}^{-1}$$

$$B_{ui} \rho_{ui}(\lambda_{ui}) = 10^8 \text{ s}^{-1}$$

(corresponds to $B_{ui} = 1.6 \times 10^{26} \text{ s}^{-1} \text{ J}^{-1} \text{ Hz cm}^{-3}$; $E_v = 2 \times 10^{-8} \text{ W/cm}^2 \text{ Hz}$ and $E_\lambda = 5 \times 10^5 \text{ W/cm}^2 \text{ nm}$)

$$\sigma^{2ph} I_l^2 = 10^8 \text{ s}^{-1}$$

(corresponds to $\sigma^{2ph} = 10^{-50} \text{ cm}^4 \text{ s}$ and $\Delta E = 10^{11} \text{ W/cm}^2$ at $\lambda = 300 \text{ nm}$)

TABLE 3. Evaluation of Typical Laser Systems with Regard to the Approach of Intrinsic Detection Limits (IDL)

TECHNIQUE	CAN IDL BE REACHED?	COMMENTS
LIF-RF in Flames, Furnaces, ICP	NO	Background Emission and Laser Scattering are limiting noises
LIF-DLF in Flames, Furnaces, ICP	NO	Background Emission is limiting, assuming scattering is eliminated by filtering
LIF-DLF in Pulsed Glow Discharges	YES	Laser can be switched on when the discharge is off, so back- ground radiation is absent.
TC-LIF in Furnaces	YES	Fluorescence emission in the low uv; therefore background emission negligible and scattering avoided
LEI or RIS in Atmospheric Pressure, Flames and Furnaces	NO	Limiting noise is due to background current fluctuations and multi- photon ionization of native species
LEI and RIS in Glow Discharge	DIFFICULT	Limiting noise may still be due to to background current fluctuations in the discharge, which can how- ever be low.
RIS in Vacuum Atomizers	YES	Background noise can essentially be eliminated

TABLE 4. Evaluation of Typical Laser Systems as to their Capability of Conforming to the SAD concept.

TECHNIQUE	CAN IT BE CONSIDERED SAD?	COMMENTS
LIF-RF in Flames, Furnaces, ICP (Inductively Coupled Plasma)	NO	Limiting noise is extrinsic and chance of photon detection is much less than unity
LI-DLF in Flames, Furnaces, ICP	NO	
LIF-DLF in Pulsed Glow Discharges	VERY UNLIKELY	With μ s-pulses producing saturation, avoiding scattering and having an overall instrumental efficiency of ~ 0.01 , (which would be hard to reach in practical systems), SAD might be reached.
TC-LIF-AS in Furnaces	VERY UNLIKELY	
LEI or RIS in atmospheric pressure, flames furnaces	NO	Flame background fluctuations are the cause of extrinsic noise. In addition, multiphoton ionization causes additional background and noise.
LEI and RIS glow discharges	VERY UNLIKELY	Discharge background current fluctuations in are probably still limiting.
RIS in vacuum atomizers nature.	YES	Both conditions for SAD satisfied, ie., chance of collecting one ion per atom is unity and limiting noise is of intrinsic

- order to improve the situation. Only cw lasers, or pulsed lasers with extremely high ($> 1\text{MHz}$) repetition frequency can offset the rather poor collection efficiency and result in the technique approaching the SAM limit;
- (ii) the fluorescence technique can indeed approach the intrinsic detection limit in a few selected cases;
 - (iii) the ionization techniques involving atmospheric atomizers can achieve unity detection efficiency but probably can never reach the intrinsic detection limit. Again, a radical change in the atomizer is needed here;
 - (iv) pulsed glow discharges can be efficient atom reservoirs for LEI since single atom detection will be approached, due to the unity detection and collection efficiency and the intrinsic detection limit may be available;
 - (v) only the ionization technique with a vacuum atomizer can be considered a truly SAD technique; and finally
 - (vi) for atom counting, the technique must meet the requirement of unity overall efficiency, i.e., unity atomization efficiency, unity probing efficiency and unity detection efficiency. In this case, it is important in our opinion to stress the temporal aspect of the probing efficiency, in addition to its spatial aspects, since most pulsed laser systems have a very low duty cycle and are therefore far from the ideal condition expressed by the relationship $f\tau_{\text{res}} \geq 1$, where f is the repetition rate of the laser and τ_{res} is the residence time of the atoms in the probing volume, assuming $1/f > \tau_l$, where τ_l is the laser pulse width
 - (vi) for a given laser system, excitation sequence, and a given atomizer, fluorescence detection always has a greater spectral selectivity than ionization detection.
 - (vii) although SAD is likely to be achievable in no cases of fluorescence and in only one ionization case, SAM which is

more significant analytically is likely to be achieved in several LEF cases, by either increasing the repetition rate of the pulsed dye laser or using a cw dye laser or by "trapping" the atoms (or atomic ions) for an appreciable time, such as tens of milliseconds or longer.

We² have thoroughly reviewed the statistical considerations of counting atoms and molecules. In the review, we stress the importance of proper definitions of the LOD (Limit of Detection) and LOG (Limit of Guarantee of Purity) and give a table denoting the signal levels needed to achieve a single species detection with various background levels. This tutorial approach contains the necessary theory to apply Laser Induced Fluorescence (LIF) and Laser Ionization/Resonance, Photo-, Field, Auto, to single species detection. Many tables, figures, and examples of the presented approach are given².

In a series of three tutorial and research papers, Stevenson and Winefordner³⁻⁵ have evaluated the statistics of counting atoms and molecules.

In the first paper in the above series³, the limit of detection (LOD) of a trace analytical method is often used as a gauge of the sensitivity of the method. Improvements and comparisons of similar methods usually involve comparisons of the LOD's. However, the calculated LOD value is sensitive to a number of factors such as the method of calculation used, the choice of calibration standards and the number of background (blank) measurements. In this paper³, the calculated LOD of a particular analytical method is viewed as an estimate of the true, unknown LOD. Factors which affect the variability of the estimate are investigated. Knowledge of the variability of the estimated LOD can help when comparing analytical methods on the basis of LOD values. In addition, by knowing which experimental factors contribute to the uncertainty in the calculated LOD, it is possible to determine the analytical protocol which estimates the true LOD most efficiently with no loss in precision. Expressions are given to allow a quick estimate of the LOD during optimization and to allow an evaluation of the quality of the estimate.

In the second paper⁴, we have introduced some general principles which may apply in many ultratrace laser-based experiments possessing sensitivity high

enough to measure the signal associated with single atoms in the laser beam. The detection of atoms in the presence of background noise, the use of the detection efficiency (ϵ_d) as a means of defining, evaluating and comparing (near-)SAD methods, the presence of "extra" variance due to variation in ϕ_s (flux of counts due to analyte species) or t_i , (interaction time of analyte with laser beam), and the extra sensitivity required to count atoms by LIF have all been discussed and demonstrated with the computer simulations presented in this paper.

However, the SAD (Single Atom/Molecule Detection) theory presented, and the computed simulations used, are only as good as the model upon which they are based. A brief look at some of the assumptions inherent in the general SAD model presented here is warranted. The assumptions of Poisson processes for both the background noise and the detection process are not serious obstacles. It is quite likely that in many situations the first assumption is not valid; however, some assumption of the form of I_b (background counts) had to be made and a distribution other than a Poisson merely signifies that a different value of X_d (signal detection limit) must be chosen. The assumption of a Poisson detection process is usually a valid assumption in the time frame of most experiments. However, the characteristics of Poisson processes must be kept firmly in mind. The presence of metastable traps, detector "dead" time, or space-charge effects can all alter the distribution of the detection process.

One of the largest idealizations in the general SAD model involves the use of a well-defined probe volume. In many analytical experiments, it is simply not possible to have a well-defined probe volume due to either the collection/detection efficiency of laser-induced events in the atoms, or the spatial characteristics of the laser-beam itself. For example, a common method of describing the radius of a laser beam involves the use of the $1/e$ distance-- i.e., the distance at which the intensity decays to $1/e$ of its peak value. However, the laser beam obviously still has some intensity at values beyond this distance, and may cause atoms to be detected with a non-zero probability. Likewise, in LIF experiments, the collection efficiency of most optical systems is a function of the distance of the emitter from the central axis of the system. Stating where the probe volume "stops" may not have much meaning in LIF

experiments, although the use of spatial filtering can help in this.

The concept of the detection efficiency itself is obviously only as well defined as the probe volume, despite the fact that the requirement for a method to be considered SAD has been given in terms of this FOM (Figure of Merit). Thus, it may well be that the concept of an SAD experiment may be an idealization if there is an attempt to apply SAD theory to a particular experiment⁴.

Despite some of the sobering realities mentioned in the paper⁴, many of the concepts of the theory of SAD as presented are of value to the general laser spectroscopist. Even the analytical chemist interested only in ultratrace analysis by laser-based techniques should probably be aware of many of the concepts presented for SAD, even if there is no desire to count individual atoms, since at the detection limit there may be few atoms or molecules of analyte being actively probed by the laser. Obviously, the analytical or physical chemists, who are actually concerned with measuring the signals or properties dealing with single atoms, struggle with concerns which do not arise in more conventional experiments; the formulation of the general SAD model and the related concepts have demonstrated this fact most clearly⁴.

The third paper⁵ in the series concerns special methods of counting species. Laser spectroscopic methods which are sensitive enough to detect single atoms or molecules are termed single atom detection (SAD) techniques. The detection theory of SAD methods, presented in the second paper in this series and summarized above, allows for the evaluation and comparison of these techniques. In the third paper⁵, SAD theory is applied to one task in particular: monitoring analyte atoms or molecules as they flow through a continuous wave laser beam using fluorescence detection (CW-LIF). Several possible single processing methods are described and evaluated through the use of SAD theory and Monte Carlo simulations. The relative merits of these methods for SAD by CW-LIF are illustrated.

It must be emphasized that SAD techniques, as defined here⁵, can detect single atoms (or molecules) which enter the probe volume, V_p , during the measurement; this ability must be differentiated from the conventional concept of detection of bulk analyte concentration/amount. It is interesting to imagine

the performance of an SAD method in a more conventional sense -- i.e., in terms of bulk detection limits, rather than N_p (the number of species detected). Comparison of the detection limit of resonance ionization spectroscopy (RIS) and laser-induced atomic fluorescence in an electrothermal atomizer (ETA-LIF) demonstrated that, even though RIS has traditionally been an SAD method, the actual detection power of the two techniques are very similar. The reason of this apparent disparity is that the detection power of a technique depends on the overall efficiency of detection, ϵ_o , rather than ϵ_d , as explained originally by Alkdemede. The value of ϵ_o depends on such factors as duty cycle and atomization efficiency, in addition to ϵ_d .

Thus, the performance of a method with respect to ϵ_d and ϵ_o must be kept firmly in mind when applying an SAD method of conventional analysis. To further illustrate this point, imagine that a given CW-LIF technique can achieve SAD over a certain measurement time using simple integration of the signal during the measurement, limited by background shot noise. Further increasing the measurement time will result in $\epsilon_d < 1-\beta$; thus, SAD can no longer be achieved (β = probability of a type II error, false positive). However, the bulk concentration detection limit will improve with $(t_m)^{1/2}$, even though SAD is no longer possible over the measurement time, t_m .

(2) Experimental Evaluation of Laser Excited Atomic Fluorescence⁶⁻¹⁰

The performance of graphite tube electrothermal atomizers were evaluated for Laser Excited Atomic Fluorescence Spectrometry (LEAFS) for several elements³. Three pulsed lasers systems were used to pump tunable dye lasers which subsequently are used to excite Pb, Ga, In, Fe, Ir, and Tl atoms in the hot graphite tube. The dye laser systems used were pumped by nitrogen, copper vapor, and Nd:YAG lasers. Detection limits in the femtogram and subfemtogram range (see Table 5) are typically obtained for all elements. A commercial graphite tube furnace is important for the successful utilization of the laser based method when the determination of trace elements is intended, especially when complicated matrices may be present.

Based on these experiments, it is felt that some of the most important parameters are: the use of a fast heating atomizer, a probing volume as large as possible, careful baffling of blackbody furnace emission, and optimization of the laser irradiation. The use of commercially available graphite tube atomizers is strongly advised not only because the rate of heating can be easily controlled but also because new conditions such as stop-flow and ramp heating steps are possible which can be very important when real samples are determined.

The use of a non-dispersive system was also studied during this work. It can be concluded that such a spectrometric system could be very useful when the wavelength of fluorescence emission lies in the region between 185-310 nm.

Work is now under way to assess the ultimate analytical capabilities of this technique when applied to other elements using single step and two-step excitation.

Figure 3. Schematic Diagram Showing Arrangement of Excitation and Detection Optics Used for Laser Excited Atomic Fluorescence in a Graphite Tube Furnace.

Figure 4. Schematic Diagram of Experimental System Used for Laser Excited Atomic Fluorescence in a Graphite Tube Furnace.

TABLE 6
EXPERIMENTAL PARAMETERS

Laser/optical system	Repetition Rate (Hz)	Beam Diameter (nm)	Energy (mJ/p)	Probing ^a Efficiency
Nitrogen pumped dye 0.35 m spectrometer	20	2	0.025	40%
Nitrogen pumped dye ellipsoidal mirror spectrometer	20	2	0.025	40%
Nd:YAG pumped dye 0.22 m double spectr.	30	2	1	55%
Cu vapor pumped dye 0.25 m spectrometer	6000	1	0.0004	25%

^aDefined as volume of atomizer probed divided by the total volume of atomizer times 100.

TABLE 7
LASER EXCITED FLUORESCENCE OF LEAD IN A GRAPHITE TUBE ATOMIZER:
ABSOLUTE DETECTION LIMITS AS OBTAINED BY SINGLE-STEP EXCITATION
AT 283.306 nm AND FLUORESCENCE DETECTION AT 405.789 nm^(a)

Experimental Systems	Detection Limits (fg)	
	(b)	(c)
Cu vapor pumped dye laser, 0.25 m spectrometer ^(d)	0.08	0.5
Nd:YAG pumped dye laser, 0.22 m double spectrometer	0.2	3
Nitrogen pumped dye laser,, 0.35 m spectrometer	0.2	3
Nitrogen pumped dye laser off-axis ellipsoidal mirror spectrometer	0.3	18

- (a) S/N = 3, off line, sample volume: 10 μ L
- (b) obtainable under ideal conditions (detector noise limit)
- (c) obtained under our experimental conditions (laser irradiance attenuated 10X), laser scatter limited.
- (d) no attenuation of laser irradiance

Laser-excited atomic fluorescence spectrometry using double-resonance excitation and graphite tube electrothermal atomization was evaluated⁸ for the determination of trace elements. Two dye lasers pumped by a Nd:YAG laser were used to excite atoms inside a graphite tube furnace simultaneously. Collisional coupling between the highest level reached by the laser excitation and nearby levels resulted in several fluorescence transitions in the ultraviolet region for each specific element. The fluorescence was collected at 90° by combining a pierced plane mirror, a plano-convex MgF₂ lens and a double monochromator equipped with a solar blind photomultiplier tube. The detection limits are given in Table 8.

Table 8. Limits of detection for In, Ga and Yb by laser-excited atomic fluorescence in a graphite tube atomizer⁶

Excitation Wavelength/ Scheme nm		Element	This work*	ETAAS ^a
λ_1	410.1	In	2	2000
λ_2	571.0			
λ_{fl}	271.4, 271.0			
λ_1	403.3	Ga	1	1000
λ_2	641.4			
λ_{fl}	250.0			
λ_1	398.8	Yb	220	1000
λ_2	666.7			
λ_{fl}	246.4			

*20- μ l injections.

^a100- μ l injections.

Further work is now in progress including the use of the copper vapor laser with an enclosed type graphite atomizer with hopes of improving the detection power for lead (and other elements), especially since we have recently improved the frequency doubling efficiency by a factor of 5 by improved optical alignment. With the Nd:YAG laser system, double resonance excitation with fluorescence emission in the low ultraviolet region has been achieved. In addition, β -Barium Borate (BBO) crystals for SHG should allow us to reach the excitation wavelengths of elements such as Zn, As, and Se with excellent output efficiency.

Table 5. Absolute detection limits (fg) using LEAFS.

Element	Laser System	$\lambda_{exc} -- \lambda_{fl}$ (nm)	This work	Previous Work
Fe	Cu-vapor ^a	296.7 -- 373.5	500	100
Ga	Cu-vapor ^a	287.4 -- 294.4	2,000	10.000
	Nd:YAG ^b	403.3 -- 417.2	25	
In	Nd:YAG ^b	410.1 -- 451.1	10	20
Ir	Nitrogen ^b	295.1 -- 322.1	10,000	6,000
Pb	Cu-vapor ^a	283.3 -- 405.8	0.5	1.5
	Nd:YAG ^b		3	
	Nitrogen ^b		3	
Tl	Nitrogen ^b	276.8 -- 352.9	7	0.7

Three laser pumped dye laser systems (see Table) were used in combination with graphite tube electrothermal atomization to detect ultratrace quantities of lead atoms in pure aqueous solutions⁷. The frequency doubled radiation of a dye laser pumped by either a frequency doubled Nd:YAG laser, a nitrogen laser or a Cu vapor laser, was used as the light source in the atomic fluorescence study (see Figures 3 + 4). The fluorescence was collected at 90° with a combination of a plane mirror, having a 0.2 cm diameter hole in its center to the laser beam, a spherical lens, and a monochromator or an interference filter. The direct line fluorescence measured at 405.78 nm gave detection limits in the femtogram range (see Table 7). The best case occurred when the high repetition rate Cu vapor laser was used where a 0.5 fg detection limit was obtained.

A commercial hollow cathode lamp (see Figure 5) is used as an atom reservoir for the atomic fluorescence of lead excited by a copper laser pumped dye laser⁹. The glow discharge source is nearly an ideal atom cell for such measurements, having very low background emission and excellent atomization characteristics. A detection limit of 1.8 ag (1.8×10^{-18} g) of lead within the laser beam was easily obtained. Based on the limiting extrinsic noises, the limiting detectable number of atoms within the probed region were less than 10^4 (see Table 9) and in the case of PMT noise only was $\sim 10^3$ atoms.

Figure 5. Laser Excited Fluorescence - Glow Discharge Spectrometer System.

Table 9. Limits of Detection (LOD) Based on Limiting Noise in LEAFS-Glow Discharge System.

	RMS Noise	LOD (Atoms)
Emission + Scatter + RFI + PMT	10.6 μ V	6000
Emission + RFI + PMT	8.3 μ V	4700
Scatter + RFI + PMT	4.3 μ V	2430
RFI + PMT	4.4 μ V	2430
PMT	1.9 μ V	1100

A pulsed glow discharge as an atomizer for atomic fluorescence spectroscopy with a copper vapor laser pumped dye laser excitation source was further investigated¹⁰ with respect to physical and analytical characteristics. The discharge system was synchronously pulsed with the laser to provide a low noise background and the low pressure, inert gas atmosphere insured an almost ideal environment for fluorescence measurement. The high repetition rate of the copper vapor laser (6000 Hz) improved the detection efficiency over lower repetition rate laser systems. Disposable graphite cup electrodes were used as demountable hollow cathode cups and dried using a programmable electrothermal device for reproducibility. The discharge chamber was a commercially available vacuum chamber adapted for both flowing and static gas environments (see Figures 6 and 7 for schematic of setup). Operational parameters, such as chamber pressure, discharge voltage, sample volume, and cathode cup diameter were evaluated for maximum fluorescence signal. The maximum signals were observed at discharge voltages of 480 V for solid samples and above 1000 V for aqueous samples. The chamber pressure (2-14 Torr) was not critical. Sample sizes of 40 μ L gave the largest response with no increase at higher sample volumes. Maximum fluorescence signals were obtained 10 to 15 s (60,000 to 90,000 shots) following the initiation of laser-discharge pulsing. Linear calibration curves were obtained for lead and iridium with limits of detection of 15 fg and 2 pg, respectively. Although the signal was higher in a static gas environment, the signal to noise ratio was lower than in a flowing gas system.

Laser excited atomic and ionic fluorescence¹¹ of metal vapors in the inductively coupled argon plasma using both one color and two color excitation with an excimer pumped dye laser system has been evaluated. Detection limits obtained by the one and two color excitation processes are given in Tables 10 and 11. Although poorer detection limits are obtained using the two color excitation process, the spectral selectivity is enormous. It is likely that much better detection limits can be obtained when more efficient excitation schemes are found; the latter is difficult because the energy level diagrams for most ions and atoms are poorly known for the 2nd excitation step.

ICP-LIF measurements of five rare earth elements have been performed¹² using

a single dye (pumped by an excimer laser) which limits the range of excitation wavelengths to the range from 360 to 370 nm. All five of the elements have been determined (see Table 12) with a high degree of sensitivity which is comparable to that which is achieved using ICP-ES. By using a single laser dye, the complexity of ICP-LIF method is greatly reduced and is not much more difficult of perform than ICP-ES. The spectral selectivity of ICP-LIF is inherently better than that of ICP-ES. However, it has been shown that because of the complex nature of the energy levels of the rare earth elements, spectral interferences are still possible in ICP-LIF especially when high intensity laser excitations used. As an example, the spectral interference of Gd with Dy fluorescence has been studied; it has been shown that the spectral interference in ICP-LIF can be relatively large. It has also been shown that the interference is greatly reduced by lowering the laser intensity which minimizes the amount of saturation broadening. We have recently developed a model of a spectral interferences based on the theory of saturation broadening and are studying spectral interferences in LIF for rare earth and transition metal elements. Further investigations will focus on the importance of these spectral interferences for selective trace level determinations of the rare earth elements by ICP-LIF.

Table 12. Detection limits for 5 rare earth elements by ICP-LIF and ICP-ES

	λ_{exc} (nm)	λ_{fl} (nm)	ICP-LIF ^a (ng/ml)	ICP-ES ^b (ng/ml)	ICP-ES ^c (ng/ml)	ICP-MS ^d (ng/ml)
Ce(II)	365.585	413.765	30	40	-	0.1
Dy(II)	364.541	353.852	15	4	23	0.1
Er(II)	363.536	369.264	15	3	-	0.06
Gd(II)	364.619	354.580	8	4	30	0.1
Sm(II)	363.429	373.598	17	8	66	0.2

- a. Results-this work.
- b. Thermo Jarrell Ash commercial literature, 1987 [19].
- c. R.K. Winge et al., Appl. Spectrosc. 33, 206, 1979 [20].
- d. K.E. Jarvis, Journal of Anal. Atomic Spectrometry 4, 563, 1989 [21].

Figure 6. Schematic Diagram of Machined Brass Cathode Holder With Expanded View of Disposable Graphite Electrode.

Figure 7. Schematic Diagram of Copper Vapor-Dye Laser Excited Glow Discharge System.

Table 10. Comparison of Detection Limits (ng/mL) by ICP-LEAF and Other AFS Studies.

<u>Element</u>	<u>Excitation Wavelength (nm)</u>	<u>Fluorescence Wavelength (nm)</u>	<u>ICP-LEAF^a</u>	<u>Best AFS Value</u>
Cr(II)	283.563	284.325	97	
Cr(II)	283.563	283.563	51	
Cr				0.4 ^b
In(I)	275.388	293.263	23	
In				2 ^b
Ru(I)	273.572	273.572	109	
Ru(I)	273.572	281.055	163	
Ru(I)				500 ^c
W(II)	276.427	364.141	364	
W				200 ^d

^a This work. The detection limit = 3 σ of the blank.

^b Hollow cathode lamp excitation ICP-AFS system with desolvation; no wavelengths were given.

^c Pulsed dye laser excitation AFS in nitrous oxide-acetylene flame; the excitation wavelength and the fluorescence wavelength are 372.803 nm and 349.894 nm, respectively.

^d Hollow cathode lamp excitation ICP-AFS system with ultrasonic nebulization; no wavelengths were given.

Table 11. Detection Limits (ng/mL)^a by Double-resonance ICP-LEAFS.

<u>Element (species)</u>	<u>First Excitation Line (nm)</u>	<u>Second Excitation Line (nm)</u>	<u>Fluorescence Line (nm)</u>	<u>Detection Limits (ng/mL)</u>	<u>Det.^b Ratio</u>
Co(I)	304.400	545.456	534.271	530	35.3
Cu(I)	324.754	521.820	515.324	5	1.7
Ni(I)	300.249	561.479	463.4	174	34.8
Pb(I)	283.306	600.193	239.379	8	11.4
Sc(II)	361.384	261.122	303.993	13	5.0

^a This work. The detection limit = 3 σ of the blank.

^b The detection ratio is equal to the detection limit of double resonance detection to that of the single resonance detection.

(3) Fundamental Studies of Atomic and Molecular Parameters In Flames and Plasmas¹³

Theoretical considerations¹³ are given on the potential and practical capabilities of a detector of fluorescence radiation whose operating principle is based on a multi-step excitation-ionization scheme involving the fluorescence photons as the first excitation step. This detection technique, which was first proposed by Matveev et al. (Zh. Anal. Khim., 34, 846, 1979), combines two independent atomizers, one analytical cell for the excitation of the sample fluorescence and one cell, filled with pure analyte atomic vapor, acting as the ionization detector. One laser beam excites the analyte fluorescence in the analytical cell and one (or two) laser beams are used to ionize the excited atoms in the detector (see Figure 8 and 9). Several difference causes of signal and noise are evaluated, together with a discussion on possible analytical atom reservoirs (flames, furnaces) and laser sources which could be used with this approach. For properly devised conditions, i.e., optical saturation of the fluorescence and unity ionization efficiency, detection limits well below pg/ml in solution and well below femtograms as absolute amounts in furnaces can be predicted for atomic fluorescence in furnaces. However, scattering problems, which are absent in a conventional laser-enhanced ionization set-up, may be important in this approach.

A Raman detector based on the use of a novel resonance ionization detector¹⁴ has also been described by us. The detector is based upon the production of Raman scatter with a tunable pulsed or cw dye laser, collecting a large fraction of the Raman scatter, and transferring it efficiently into an ionization detector containing a metal (M) vapor, such as Li. The resonance ionization detector (RID) is simultaneously illuminated by a 2nd dye laser (see Figure 10). When the 2nd laser is tuned to an excited state transition of the metal vapor M and when the 1st laser is at such a wavelength that the Raman scatter ($\Delta\nu_v = \lambda_{\ell 1}^{-1} - \lambda_R^{-1}$) appears at the ground state absorption transition of the metal, then a current will be produced in the RID which is proportional to the Raman scatter intensity (see Figure 11 for excitation/ionization processes in a hypothetical atom). Both the production and collection of this current can

Figure 8. Schematic principle of operation of the ionization detector. SA: Sample Atomizer; ID: Ionization Detector. Wavy arrows indicate laser and fluorescence excitation (at frequency $\nu_f = \nu_{12}$), while straight arrows indicate collisional ionization, with rate coefficients k_{21} and k_{31} . Since k_{21} is considered to be small, the process is indicated by a broken arrow. Direct photoionization in the continuum (λ_{21}) is also shown.

Figure 9. Schematic illustration of the use of fluorescence with a filter to prevent the resonance scattered signal from reaching the ID. The meaning of the arrow is the same as that of Figure 8.

be made very efficient (approaching 100%) and should result in improved sensitivity compared to conventional dispersive or FT Raman techniques. The new approach should be much less sensitive to scatter, should have a spectral resolution better than 0.1 cm^{-1} and should allow Raman scatter measurements to be made at wavenumbers below 100 cm^{-1} and under certain conditions to 0.01 cm^{-1} . The approach should be especially useful in highly scattering environments like Ag-sols in surface enhanced Raman Spectrometry (SERS) and should be useful for detection of ultratrace levels of drugs and metabolites in biological fluids. The Raman-RID approach should also be useful for resonance Raman since laser scatter and molecular fluorescence should have minimal effects. In Table 13, Raman signal estimates and limits of detection are given for several Raman cases and for cw and pulsed laser cases. As can be seen, the estimated detection power is in the sub part per billion range as long as either resonance enhancement or surface enhancement is present.

By the use of a rate equation approach and a disregard for recombination between ions and electrons, we¹⁵ calculated the variation of fluorescence and ionization signals as a function of laser intensity. Plots of ion and photon yields vs. laser intensity for various values of important parameters are given and are discussed with respect to the significance of collisional ionization and photoionization upon inspection of the plots, the following conclusions can be made (k_{21} is the collisional ionization rate constant from level 2, I_l is the laser irradiance, I_s^a is the saturation irradiance, and σ_{21} is the absorption cross-section for photoionization from level 2).

- (1) The presence of a plateau for both fluorescence and ionization indicates that collisional ionization rather than photoionization is the dominant process of ion production.
- (2) The fluorescence plateau depends upon the value of k_{21} and decreases when k_{21} increases. This is expected, since, for the short interaction times considered, the ionization continuum acts as a trap (no recombination effects) much in the same way as would be the case if a metastable level were present between levels 1 and 2; the saturation curve is indeed affected.

Figure 10. The sample in the Sample Cell, SC, is excited by λ_1 to produce line emission, fluorescence or line scatter (Raman), and the resulting fluorescence, fl, or scatter, sc, produced in the SC is collected and impinges on the Resonance Detector, RD, where λ_{fl} or λ_{sc} excites an atom M in RD to an excited level. The laser at λ_2 present only in RD excites the same M atom into a level near the ionization limit where collisional ionization occurs. λ_2 can also directly ionize M. The optogalvanic signal is an ionization current. The RD could also be based on fluorescence where the 2 excitation processes occur but then fluorescence in the UV ($\lambda_{fl} < \lambda_1$ and $\lambda_{fl} < \lambda_2$) is measured.

Figure 11. Energy level diagram of Metal M in Resonance Ionization Detector. Dye laser at λ_2 is fixed and Dye Laser #1 scans until $1/\lambda_{p1} - 1/\lambda_1 = \Delta\tilde{\nu}$, resulting in Raman scatter at λ_1 .

Table 13. Estimation of Signals, S, Signal-to-Noise Ratios, SNR, and Detection Limits, LOD (S/N = 3) for Several Cases (See Table 1) Assuming Thermal Background Current Shot Noise*

	SR	RR	SER	SERR
S^{*S}				
cw (linear)	10	10^5	10^7	10^{11}
cw (saturated)	10^4	10^8	10^{10}	10^{14}
pulsed	10^3	10^7	10^9	10^{13}
SNR^{*S}				
cw (linear)	10^{-5}	10^{-1}	10	10^5
cw (saturated)	10^{-2}	10^2	10^4	10^8
pulsed	1	10^4	10^6	10^{10}
LOD^{*S}				
cw (linear)	$3 \times 10^{21} (3 \times 10^8)$	$3 \times 10^{17} (3 \times 10^4)$	$3 \times 10^{15} (3 \times 10^2)$	$3 \times 10^{11} (3 \times 10^{-2})$
cs (sat'd)	$3 \times 10^{18} (3 \times 10^5)$	$3 \times 10^{14} (3 \times 10)$	$3 \times 10^{12} (0.3)$	$3 \times 10^8 (3 \times 10^{-5})$
pulsed	$3 \times 10^{16} (3 \times 10^3)$	$3 \times 10^{12} (3 \times 10^{-1})$	$3 \times 10^{10} (3 \times 10^{-3})$	$3 \times 10^6 (3 \times 10^{-7})$

Acronyms

SR - Spontaneous Raman, RR - Resonance Raman, SER - Surface Enhanced Raman

SER - Surface Enhanced Resonance Raman; SER and SERR only apply to solid or liquids

S - Signal level or N_s (counts), SNR - Signal to Noise Ratio

*A H_2 -Air Flame is used as the RID (see Table 1)

†All values in terms of species/cm³ are for gases and liquids. LOD values in (ng/mL) are only for liquids.

*S and SNR refer to 1 μ g/mL (see Table 1)

§For cw case, there are two subcases, namely the laser at λ_2 interacts with M atoms linearly (Eqn 2b) or results in optical saturation (Eqn 2a).

- (3) Despite the decrease in the fluorescence plateau, no dip can be experimentally observed when photoionization is negligible, unless the composition of the flame (and therefore k_{21}) is significantly altered.
- (4) The difference in the fluorescence plateau values at increasing values of k_{21} decreases when T_i decreases, which is understandable in view of the decreased interaction time.
- (5) When photoionization dominates the interaction at high I_i values, the fluorescence signal decreases (fluorescence dip); the onset of the decrease occurs at lower I_i values for increasing values of σ_{21} and/or T_i . The same applies to the onset of the inflection point in the ion yield shapes.
- (6) As intuitively expected, photoionization is more important if k_{21} is low (the other parameters being kept constant).
- (7) When I_i is high (i.e., when it is difficult to optically saturate the transition $1 \rightarrow 2$) and interaction times are short, no plateau can be seen, and ion production keeps increasing for increasing values of I_i .

Despite the many simplifying assumptions made in the derivation, it is felt that this treatment give some useful indication of the basic shape of the curves which can be experimentally obtained when the laser intensity is increased. An example which might well fit into the cases given above is that of strontium atoms in the air/acetylene flame. It is worth noting, however, that at the maximum value of laser intensity considered ($10^{26} \text{ s}^{-1} \text{ cm}^{-2}$, which would correspond to a laser pulse of 500 kW peak power at 400 nm, focused to a spot size of 0.02 cm^2), coherence effects, such as power broadening, would need to be taken into account, even for a broad-band excitation field and a collision-dominated system such as a flame. Therefore, the above description has to be considered on a qualitative basis only.

A resonance ionization detector (RID) based on the two-step laser-enhanced ionization of Mg in a miniature acetylene/air flame is described by Petrucci, Badini, and Winefordner.¹⁶ The resonance absorption of Mg at 285.2 nm serves as the signal transition, i.e., photons to be measured. Magnesium atoms excited by absorption of photons at 571.2 nm or 435.2 nm, from which collisional ionization

could occur, or by absorption of photons at 300.9 nm, which directly ionized the excited Mg atoms via an autonionizing level above the ionization continuum (IC); refer to Figure 12 and Table 14. The miniature flame used (~ 2 mm diameter) had very low noise characteristics and the minimum detectable number of photons (MDP) was limited, in some cases, by the noise of transimpedance amplifier used (see setup in Figure 13). The lowest MDP, obtained for the excitation scheme $3s^2\ ^1S$ (285.2 nm) $\rightarrow$ $3p\ ^1P^0$ (435.2 nm) $\rightarrow$ $6d\ ^1D$, was experimentally determined to be 1×10^3 (7×10^{-16} J). The quantum efficiency (η) of this excitation scheme, defined as the number of electrons created per photon absorbed at the signal transition, was determined to be mostly Lorentzian in nature, due to pressure broadening in the atmospheric pressure flame, with a stray light rejection (SLR) ratio of approximately 10^{-5} at 100 cm^{-1} displacement from the absorption maximum of the RID at 285.213 nm. An application of the RID is given in the detection of weak Raman scatter of CCl_4 , CHCl_3 and dimethylsulfoxide (DMSO).

Table 14. Transitions and energy levels considered*.

Scheme	Wavelength of second step (nm)	Transition	Energy level of final state (cm^{-1})	Energy defect (cm^{-1})
A	571.1	$1^3P\ ^1P^0 \rightarrow 5s$	52556	-9113
B	300.9	$3p\ ^1P^0 \rightarrow \text{continuum}$	68285	+6616
C	435.2	$3p\ ^1P^0 \rightarrow 6d\ ^1D$	58023	-3646

A - (+) sign indicates a final energy level below (above) the ionization limit of the atom. * In all cases, the first step was provided by signal photons at 285.213 nm ($3s^2\ ^1S \rightarrow 3p\ ^1P^0$).

Figure 12. Three ionization cases (see Table 15).

Figure 13. Instrumental system for Resonance Ionization Detector.

Table 15. Results of MDP, η_{exp} and η determinations for schemes 1-3.

Scheme	Wavelength of second step (nm)	η_{exp} (e ⁻ /ph)	η (e ⁻ /ph)	MDP	MDE* (fJ)	LDR
A	571.1	0.054	0.069	2.4×10^4	17	10^4
B	300.9	0.0039	0.0049	2.7×10^5	190	ND**
C	435.2	0.59	0.75	1000	0.7	10^5

* Minimum detectable energy at 285.213 nm

** ND - Not determined

η_{exp} $\equiv$ Quantum efficiency of RID determined experimentally

η $\equiv$ True quantum efficiency of the RID (see Section 5.1)

Several examples of the relationship between resonant and non-resonant collisional ionization and photoionization, laser intensity and the ability to saturate both resonant and non-resonant transitions are illustrated by Petrucci and Winefordner¹⁹. The effect of energy deficit and effective energy overshoot in determining the dominant ionization pathway are also discussed. An approximation of the lifetime of the virtual level is made and its relationship to the probability of two-photon non-resonant absorption is discussed. The theoretical model (see Table 16 and Figure 14) described above is fitted to the optogalvanic data for two single-step resonance transitions of Ne to determine the applicability of the model developed for flame LEI to the hollow cathode discharge environment (under our experimental conditions) and to obtain estimates of the collisional ionization rate constant, k_{21} , and photoionization cross-section, σ_{21} (see Table 17).

The experimental results presented¹⁷ illustrate that a variety of excitation/ionization mechanisms can occur in a hollow cathode discharge which provides a convenient reservoir of both ground and excited state atoms. Applicability of the theory developed for flames and plasmas to the low pressure discharge was also shown¹⁷. Qualitative agreement was observed between the proposed excitation/ionization mechanisms (see Figure 12) and the values of the collisional ionization rate constants and photoionization cross-section estimated by the model. It was determined that photoionization, where applicable, provides additional ionization beyond that which is possible with optically saturated, one- or two photon excitation followed by collisional ionization.

Figure 14. Four Ionization cases in Optogalvanic Effect studies.¹⁷

It was shown that ionization¹⁷ can proceed by two competing mechanisms: photoionization or collisional ionization (see Table 17). The total ionization rate is a combination of the two and is sensitive to the energetics of the system. For example, when the effective energy overshoot is small, favoring the probability of photoionization, an ionization rate enhancement is observed due to photoionization, even at moderate laser powers. However, when the effective energy deficit is small, favoring collisional ionization, very little contribution to the total ionization rate is made by photoionization (refer to table 18).

Finally¹⁷, using the Heisenberg uncertainty relation, the lifetimes of two virtual levels for Ne and U were found to be 350 fs and 2.5 ps, respectively. The longer lifetime of the U levels translates into a larger probability for two-photon absorption. One result of this longer lifetime is the ability to optically saturate this two-photon transition at moderate laser powers and to then observe photoionization of U by absorption of a third photon of the same energy.

Table 16. Transitions, wavelengths, ionization limits, effective energy deficits and overshoots for Ne (Cases 1,2,3) and for U (Case 4).

Transition	λ (nm)	Energy levels (cm^{-1})	Ionization limit (cm^{-1})	ΔE_{def} (cm^{-1})	$\Delta E_{\text{os}}^{\text{eff}}$ (cm^{-1})
Case 1 $3p_2 \rightarrow 1p_1$	597.55	134,044- 150,774	173,932	23,158	---
Case 2 $(2p_{3/2}^0)3s \rightarrow (2p_{3/2}^0)4d$	598.80	150,317- 167,013	173,932	6,919	9,777
Case 3 $(2p_{3/2}^0)3p \rightarrow (2p_{1/2}^0)4d'$	599.56	134,461- 167,810	137,932	6,122	27,227
Case 4	599.24	0-33,366	49,035	15,669	1,014

Table 17. Estimates of saturation irradiance, I_a^s , collisional ionization constants, k_{21} , and photoionization cross-sections, σ_{21} , using model and plots in Figures 4 and 5.

	Transition (nm)	$I_a^{s(*)}$ ($s^{-1} cm^{-2}$)	$I_a^{s(**)}$ ($s^{-1} cm^{-2}$)	k_{21} (s^{-1})	σ_{21} (cm^2)
Case 1	597.55	3.4×10^{23}	3.2×10^{23}	1×10^7	0
Case 2	598.80	5.4×10^{22}	5.5×10^{22}	1×10^8	7×10^{-17}

(*) Estimated by fitting the experimental data with Eq. 1.

(**) Estimated from the experimental ion yield curves as the point of intersection between the linear portion of the curve at low laser intensities and the asymptote at optical saturation.

We developed¹⁸ a special water-cooled, coiled electrode for use in laser enhanced-ionization (LEI) and found matrix effects of thermally ionized elements to be minimized. The behavior of four different coils was studied. The coils, of the same length and inner diameter, differed only in the spacings between turns. Spacings of 1-, 2-, 4-, and 6-mm were used. The laser was directed either below or through the coil; effects of both orientations were studied. The performance of each coil was compared to that of a reference electrode fitting the description of the water-cooled, rod-like cathode designed at the National Institute of Standards and Technology. An overall reduction in susceptibility to the matrix effect was observed. The coil with the 4-mm separations and the laser directed through the center displayed the greatest tolerance to matrix effects: No susceptibility to sodium concentrations up to at least 2000 $\mu g/ml$ was observed (applied voltage = -1000 V). Both the linear dynamic range and limit of detection for this coil were generally comparable to those of the conventional water-cooled reference electrode.

Fluorescence dip spectroscopy has been used by Simeonson, Ng, and Winefordner¹⁹ to study transitions of silver, copper, iridium, and lead atoms in an inductively coupled plasma environment. Quantum efficiencies of fluorescence and steady state saturation dip parameters have been measured and are reported for each of the transitions studied (see Table 18). A steady state model that has been used to interpret the results is shown to be a useful tool for

predicting the behavior of the fluorescence dip, even for atomic systems possessing a high density of states which are prone to rapid collisional deactivation.

Table 18. Compilation of results in Fluorescence Dip Study¹⁹. (λ_{23} = probed wavelength; Δ' max = maximum relative dip; Y_{32} = fluorescence quantum efficiency at λ_{23} ; Δ' int = fluorescence dip obtained from intercept of plot of Δ' vs $Pv(v_{23})$; $Pv(v_{23})$ = spectral energy density of laser at λ_{23} ; $Pv(v_{23})$ = saturation spectral energy density at λ_{23}).

	λ_{23} (nm)	Δ' max (mod)	Δ' max (obs)	Y_{32}	Δ' int	$\rho^s_v(v_{23})$ J/m ³ Hz
Ag	546.549	0.57	0.53	0.0020	0.50	1.9×10^{-11}
Cu	521.820	0.56	0.50	0.071	0.35	4.0×10^{-11}
Ir	545.450	0.69	0.72	0.0026	0.74	1.5×10^{-11}
Pb	600.193	0.90	0.41	2.3×10^{-5}	0.40	1.1×10^{-10}

In an OH study²⁰, two optical double resonance pump-probe approaches were used to determine the ground state rotational population distributions of OH in an C₂H₂/air flame when a saturating laser beam was tuned to the Q₁4 transition of the (0,0) Σ - Π band. The saturated absorption technique was based upon the detection of absorption by a probe laser under conditions of saturation with a pump laser and no saturation. In the fluorescence approach, a probe laser was scanned through the (1,0) band while a saturating pump laser, tuned to the (0,0) band, was on or off. We found that about 15% of the total population of the ground state was transferred to the excited state. Perturbation of the rotational population distribution was greater for rotational levels close to the directly excited laser coupled level. The rotational energy transfer rate in the ground state was somewhat greater than in the excited state. The assumption of the balanced cross-rate model was verified as a means of determining the absolute OH number density with adequate accuracy.

We²¹ have measured the decrease in the laser induced resonance fluorescence of magnesium atoms at 285.213 nm, caused by photoionization of the $3p-1p_1^0$ state with a second laser tuned to the autoionization transition at 300.9 nm to

determine the autoionization cross-section¹⁵. The autoionizing resonance was found to have a cross-section of $3(\pm 0.5) \times 10^{-16} \text{ cm}^2$ and a full-width half maximum of 2.5 nm. These values agree well with previous literature data obtained by measuring the total number of charges produced. The method works best for low-to-moderate values of the product of autoionization cross-section and laser fluence, i.e., when $\sigma_{ai} \leq (I_l \Delta t_l)^{-1}$ where σ_{ai} is the autoionization cross-section (cm^2), I_l is the laser irradiance ($\text{s}^{-1}\text{cm}^{-2}$) and Δt_l is the laser interaction time (s).

(4) Other Studies

We²² have given a theoretical treatment describing the presence of negative fluorescence dips (an increase in the monitored fluorescence signal) when performing 2-step excitation experiments in atmospheric pressure atomizers. Briefly, the technique consists in monitoring the fluorescence emission from a given excited state, populated with one tunable laser, when a second laser is allowed to perturb this population. In the most common case, the second laser depletes the population of the excited state reached with the first laser; as a consequence, the fluorescence signal decreases. The magnitude of the effect can then be used to evaluate fundamental atomic parameters, characteristic of the second excitation step, e.g., absorption and ionization cross sections. Such an inverted dip is due to an increased population of the fluorescent level, caused by cascade deexcitation step. No coherence effects are involved. These considerations are supported by the experimental observation of the inverted dip in the stepwise, non-resonance fluorescence of silver atoms present in an inductively coupled plasma.

We²³ are involved in the development of Resonance Line Lasers (RLL) for atomic spectroscopy. Like most dye lasers, RLLs require a pump laser for operation and are usually pumped by an ArF excimer laser. The light from the ArF laser is focused into the end of the RLL cell which is a simple sealed quartz cell with windows on both ends for light transmission. The cell is evacuated and is empty except for a small amount of a metal in the form of a halide salt and a few torr of an inert buffer gas. The RLL cell is placed in a furnace and is

heated during operation to produce a vapor of the salt inside the tube. A typical system used by us²³ is shown in Figure 15. The principle of operation is shown in Figure 16.

RLLs are simple in their design and operation and produce moderate powers and irradiances of resonance line radiation by stimulated emission. Like hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs), RLLs are line sources and the emitted wavelengths are fixed, being inherently tuned to atomic transitions. They offer the same narrow linewidth and high spectral selectivity as incoherent line sources. Like dye lasers, RLLs are coherent light sources, having peak powers as high as several kW. The major differences between a dye laser and an RLL are the simplicity of the RLL design which does not require a grating or tuning element and the multiwavelength emission of the RLL. The effective combination of the high selectivity and narrow linewidth of a line source and the high irradiance and coherence of a laser makes the RLL unique as a true coherent line source.

We reported²³ the measurement of Tl and In by laser excited fluorescence with resonance line laser excitation for the first time. The thallium and indium resonance line lasers were described in terms of operation and output characteristics. The results of resonance line laser excited atomic fluorescence analysis are presented along with results of other atomic spectrometric methods for comparison purposes. This initial study has shown RLLs to be simple to use and produce results comparable to other laser sources in LEAFS. Considerable study is in progress on the production and optimization of the RLLs as well as the preparation of multielement tubes.

We²⁴ have also given a comprehensive table of atomic fluorescence detection limit and experimental conditions.

Figure 15. Schematic Diagram of the Experimental Set-Up.

Figure 16. Schematic of Potential Energy Curves for a Typical Metal Halide Molecule and the Physical Processes Involved in the Operation of a Resonance Line Laser.

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