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WINTER COLLEGE ON

ATOMIC AND MOLECULAR PHYSICS

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(ANALYTICAL LASER SPECTROSCOPY 1)

Analytical Applications of Laser Induced Fluorescence

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Laser excited analytical atomic and ionic fluorescence in flames, furnaces and inductively coupled plasmas—II. Fluorescence characteristics and detection limits for fourteen elements

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Abstract—An account is given of the analytical characteristics of the elements Al, B, Ba, Ga, Mo, Pb, Si, Sn, Ti, Tl, V, Y, Zr and ■ in atomic and ionic fluorescence spectrometry using an excimer (XeCl) pumped pulsed dye laser as excitation source. The inductively coupled argon plasma was mainly used as atom/ion reservoir. The detection limits were found to be in the range 0.4–20 ng ml^{-1}, improving "standard" tabulated ICP emission values by factors between 1 and 66. The separated air–acetylene flame and the carbon rod were also used as atom reservoir for a few volatile elements, the practical detection limit for lead with the latter being 6×10^{-15} g. The advantages and disadvantages of such an analytical system are discussed, one of the main advantages being certainly the high spectral selectivity of the technique.

1. INTRODUCTION

AFTER the general discussion of some important experimental parameters in analytical laser excited fluorescence spectrometry given in our previous paper [1], as well as the preliminary communication of the detection limits for several elements reported in Ref. [2], we want to present here some detailed experimental data on our excimer pumped dye laser system as well as the fluorescence characteristics exhibited by 14 elements.

The title may be somewhat misleading with respect to the investigation of flames and graphite furnaces as atom reservoirs. In fact, apart from an analytical application of the determination of lead in blood with a separated air–acetylene flame [3], only a limited number of elements (2 for the graphite furnace and 4 for the flame) were measured with these reservoirs, the purpose being to get only an indication of their potentials and limitations.

The main part of this paper is thus concerned with the analytical atomic and ionic fluorescence characteristics of the inductively coupled plasma (ICP) as atom/ion reservoir and a high power pulsed laser as excitation source. As already pointed out [1], the main reasons for the choice of the ICP are the improved accuracy that it affords due to freedom from chemical and ionic interferences, and its ability of atomizing refractory elements. The advantages of this combination is fully considered in the discussion section.

The choice of elements investigated is biased towards the refractory elements like Zr, Ti, Mo, etc., and a few elements that do not give good detection limits in ICP emission (Ga, Pb, Tl and Sn). For all the elements only non-resonance fluorescence was measured, i.e. the fluorescent wavelength was different from the absorption wavelength. We consider non-resonance fluorescence as the only practical option for *routine analytical* measurements, due to the elimination of the scattering problem and the fact that this affords virtually complete freedom from spectral line interference (see the DISCUSSION).

2. EXPERIMENTAL

2.1. *Excimer laser*

The dye pumping source in our set-up is a rare gas halide excimer laser, operated on XeCl at 308 nm

*On leave from CSIR, National Institute for Materials Research, Pretoria, South Africa.

[1] N. OMENETTO and H. G. C. HUMAN, *Spectrochim. Acta* **39B**, 1333 (1984).
[2] N. OMENETTO, H. G. C. HUMAN, P. CAVALLI and G. ROSSI, *Spectrochim. Acta* **39B**, 115 (1984).
[3] N. OMENETTO, H. G. C. HUMAN, P. CAVALLI and G. ROSSI, *Analyst* (in press).

(Model EMG-102, Lambda Physik, Göttingen, Germany). At a repetition rate of 1 pulse per s, with fresh gas filling, clean windows and properly adjusted thyratron voltage settings, the beam energy was measured as 157 mJ per pulse, with a relative standard deviation of 3.5 %. The measurements were taken with a pyroelectric joulemeter whose aperture (4.8 × 4.8 cm) was sufficient to accomodate the entire rectangular laser beam (Model ED-500 Joulemeter, Lambda Physik, Göttingen, Germany). The resulting output voltage pulse was read with an oscilloscope (Model 5403, Tektronix, Inc, Beaverton, Oregon, USA) over a 1 MΩ load resistance, since in this case, according to the manufacturers, the responsivity of the instrument is insensitive to the temporal duration of the energy of the incident radiation pulse. The duration of the laser pulse was measured with a fast photodiode, of calibrated spectral response (Type F-4000, S-5 response, Electrooptical Products Division, ITT, Fort Wayne, Ind., U.S.A.) and found to be approximately 12 ns FWHM. This width can be reduced to 8 ns by simply removing the cavity mirror while losing less than a factor of 2 in the peak power.

The repetition rate of the laser can be varied up to 100 Hz. In our fluorescence experiments, a maximum rate of 50 Hz was used.

2.2. *Dye laser*

The tunable dye laser is manufactured by Jobin–Yvon (Instruments S. A., Division Jobin–Yvon, Longjumeau, France) and consists of the eight cell oscillator–amplifier system described by Bos [4]. This system was chosen because of its capability of covering quickly the wide spectral range necessary for analytical work by simply commuting from one dye cell to another. The oscillator configuration includes a beam expander (× 22.5), a holographic grating (1500 or 3000 groove mm^{-1}) and eight independently adjustable, flowing dye cells of quartz. The oscillator and amplifier turrets accomodating the dye cells are motor driven for coupled rotation. Six frequency doubling crystals (3 KDP and KPB) are available to cover the wavelength range from 217 to 360 nm. To separate the u.v. beam from the fundamental, a bandpass wavelength filter is provided.

A suitable filter (Type AP 400 2405, Millipore Corp., Bedford, Mass., U.S.A.) is installed in the circulation line of the dye so as to remove possible photolysis products from the lasing region and from the walls of the dye cells. A small amount of a surfactant (Triton X-100) added to the dye solution also prevents to some extent such an effect [4].

Table 1 collects the dyes used in this work, their measured power as well as the elements investigated with the selected dye. The average power for each dye in the fundamental frequency was measured by means of a volume absorbing disc calorimeter (Model 38-0101, Scientech., Inc., Boulder, Colorado, U.S.A.) having an output calibration of 92.5 mV W^{-1} and sustaining a maximum pulse energy density of 3.3 J cm^{-2}. The frequency doubled output was usually directed to the fast calibrated photodiode, with a neutral density filter and a quartz diffuser plate in front of it. It is worth mentioning that the laser power was measured at the output of the u.v. visible wavelength separator and therefore the figures given in Table 1 should not be directly taken as an evaluation of the lasing efficiency of the dye.

The duration of the dye laser pulse was measured with the ITT photodiode operated at + 2500 V and a fast oscilloscope (Model 7904, Tektronix Inc., Beaverton, Colorado, U.S.A.) and found to vary between 5 to 8 ns for the fundamental beam and from 3 to 5 ns for the frequency doubled wavelength. When the cavity mirror was removed from the excimer laser, reducing correspondingly the duration of the excitation pulse, even less than 2 ns could be observed for the FWHM of the frequency doubled radiation.

It is important to mention here that the laser pulse shape modifies especially with regards to its rise time, for small adjustments of the cavity parameters; one should be aware of this effect since it will have important consequences for the evaluation of the saturation curves for diagnostic purposes [5, 6].

The laser spectral bandwidth was measured for the Rh 590 dye by slowly scanning the laser across the resonance absorption profile (285.213 nm) of 1 μg ml^{-1} of magnesium aspirated in a separated air–acetylene flame while simultaneously monitoring the wavelength integrated fluorescence signal. The power of the frequency doubled output was decreased with neutral density filters in order to avoid saturation broadening [7]. The FWHM for the 3000 groove mm^{-1} grating was found to be 0.012 nm. Such bandwidth could be further decreased by inserting a Fabry–Perot etalon between the beam expander and the grating.

[4] F. Bos, *Appl. Opt.* **20**, 3553 (1981).
[5] N. Omenetto, C. A. van Dijk and J. D. Winefordner, *Spectrochim. Acta* **37B**, 703 (1982).
[6] H. G. C. Human and N. Omenetto, to be submitted for publication.
[7] N. Omenetto, J. Bower, J. Bradshaw, C. A. van Dijk and J. D. Winefordner, *J. Quant. Spectrosc. Rad. Transfer* **24**, 147 (1980).

Table 1. Characteristics of the dyes used to cover the spectral range 220–640 nm, with their measured averaged power and the elements excited with each dye

Dye and solvent*	Wavelength† range (nm)	Measured‡ average power (mW)	Elements investigated
BBQ (Ethanol–Toluene)	366–400	20	Mo, Tl
PBBO + BBQ (Ethanol–Toluene)	378–413	20	Al
DPS (Dioxane)	397–417	30	Ga, Y
Coumarin 450 (Methanol)	430–482	50	Ba
Coumarin 503 (Methanol)	480–564	40	B, Si, Y
Coumarin 540 (Methanol)	517–612	40	Tl, V, Zr
Rh 590 (Methanol)	563–615	50	Ga, Mo, Pb, Si, Sn, V
Rh 640 (Methanol)	608–668	40	Al, Mo, Ti, V, Y, Zr

*The dyes were supplied by Exciton (Dayton, Ohio, U.S.A.) and the solvents, whose purity was specified as suitable for fluorescence spectroscopy, by Merck (Darmstadt, Germany).
†As given by Bos [4].
‡Measured at 10 Hz with the volume absorbing calorimeter described in the text. The figures given refer to the fundamental frequency, i.e. without frequency doubling crystals. For the frequency doubled outputs, approximately 10 and 1% conversion efficiences should be considered in the ranges 260–330 nm and 220–260, respectively.

2.3. *Atom reservoirs*

An air–acetylene flame burning on a home-made Meker type burner of 16 mm dia. was used as flame atomizer. An argon shield surrounding the burner assembly enabled to produce a separated flame with a viewing region approximately 20 mm above the burner top essentially free from secondary reaction zone emission. The burner was fitted on a conventional premixing chamber with pneumatic nebulization.

For use as a graphite furnace atomizer, a modified commercial mini-Massman type furnace was used (Model CRA-90, Varian Techtron, Victoria, Australia). The originally transversely clamped tube was longitudinally clamped between the supporting rods, while these rods were drilled to enable them to conduct a small flow of argon gas that swept the vapour through the sample injection hole into the analytical (irradiated) volume directly above the heated rod [8].

The inductively coupled plasma used as atom reservoir was a standard commercial model (Plasma Therm, Kresson, NJ, U.S.A., Model 2500) operating at 27 MHz with a cross-flow nebulizer (Labtest, Ratingen, Germany, Model GMB) fed by a peristaltic pump. Typical operating parameters were: power 0.7–1 kW; plasma coolant gas flow 12 l min^{-1}; auxiliary gas 0.2–0.8 l min^{-1}; sample carrier gas 0.8–1.2 l min^{-1}; height of observation 20 mm above the load coil. A quartz tube (chimney) was available which could be fitted over the plasma torch to provide a 40-mm extended plasma. Although the plasma background emission was lower at the end of the extension tube, no significant improvement in detection limits were found by its use, probably due to a decrease in atom population with height. Moreover, we felt that this region of the plasma, with its significantly lower temperature [9], constitutes a source quite different from the ordinary ICP, and its use was abandoned after a while in favor of the conventional source with its better known characteristics.

Before traversing the atomizer, the laser beam, after some spatial filtering, was expanded with a

[8] N. Omenetto, H. G. C. Human, P. Cavalli and G. Rossi, *Abstracts 23 Coll. Spectrosc. Int.*, Amsterdam 1983; *Spectrochim. Acta* **38B**, *Supplement*, p. 250 (1983).
[9] M. A. Kosinski, H. Uchida and J. D. Winefordner, *Talanta* **30**, 339 (1983).

variable beam expander (Oriel-Corporation, Stamford, Conn., U.S.A.). Due to somewhat poor beam quality with some u.v. dyes, a significant loss of power (up to × 2) was observed.

2.4. *Spectrometer and measuring system*

Two monochromators were evaluated for dispersing the fluorescent light from the ICP, viz. a 1.29-m, f/9 monochromator with a 1200-lines mm^{-1} grating blazed at 250 mm, reciprocal dispersion 0.5 nm mm^{-1} and a 0.30-m ("Minimate"), f/5 monochromator with a 1200 lines mm^{-1} grating blazed at 300 nm (dispersion 2.4 nm mm^{-1}). Both monochromators are manufactured by SPEX, Metuchen, NJ, U.S.A. No significant difference in detection limits were found with these two monochromators as shown in the data for barium and yttrium in the next section. The larger 1.29-mm monochromator is preferred because of the better resolution that it offers. For the flame and graphite furnace measurements a 10-cm focal length, grating monochromator was used (Model H-10, Jobin-Yvon, Longjumeau, France).

The ICP could be imaged 1:1 on the slits of either the 1.29- or 0.3-m monochromators. With the larger monochromator, the same optics used for conventional emission work were retained also for the fluorescence detection [2]. The flame or carbon rod atomizer was focused 50 mm before the entrance slit of the 0.1-m monochromator by an ellipsoid mirror. This detection arrangement was dictated by simple geometrical considerations aimed at filling the collimator of the monochromator with fluorescence radiation from the laser irradiated volume.

As described in the previous paper [1], the photomultiplier–amplifier system used for measurement of the fast transient (5 ns halfwidth) analytical signal should be carefully selected. The gain of the photomultiplier should not be too high ($\sim 10^6$) and external amplification must be used in order to avoid saturation of the PMT and to increase the linear dynamic range. Furthermore, the load resistor at the input of the amplifier should be optimized to maximize the signal (large R required), and at the same time give a fast response (small R) so as to avoid measurement of the tails of preceding (emission) noise pulses during the time at which the analytical signal occurs. The use of a Hamamatsu R 928 S PMT (Hamamatsu Corporation, Japan) with a built-in preamplifier (Jobin-Yvon, Longjumeau, France) with 470 Ω input resistance proved to be a good solution. The PMT has a wide spectral response (185–800 nm), fast response (2 ns risetime) and a gain of 10^6 at −1000 V supply (EMI Ltd, London, U.K., Model PM 28B Power Supply). The amplifier is situated right at the base of the PMT in the same housing so that rf interference is minimal, and produces a Gaussian appearing output pulse of 70 ns half-width. The pre-amplifier produces a 14-mV output with a 1 μA input current.

The output from the pre-amplifier was fed to a gated integrator and boxcar averager (EG & G, P.A.R., Princeton, NJ, U.S.A., Models 165 and 162) with a minimum gate width of 2 ns and variable time constant, which determined the effective time constant and the number of pulses averaged [1].

The boxcar was triggered either with the synchronous pulse available from the excimer laser power supply or with a pin-hole photodiode. In this case, it was necessary to delay the photomultiplier signal in order to bring it within the aperture range of the gated integrator. As discussed in Ref. [1], the processing of a relatively long photomultiplier pulse has the practical advantage that gate jittering and drift can be tolerated. In addition, one can increase the number of pulses averaged by the boxcar by using a gate width smaller than the fluorescence pulse, which is equivalent to increasing the time constant of the gate.

For the investigation of the fluorescence characteristics of the elements reported here, the gate width was set at 50 ns and the time constant of the gate at 10 μs, with a laser repetition rate of 10 Hz. For the evaluation of the detection limits [2], the gate width and the laser frequency were optimized with respect to each other, while maintaining 10 μs as the gate time constant.

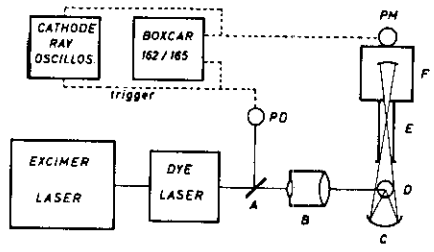
Figures 1 and 2 give a schematic layout of the different experimental arrangements used for flame/graphite furnace atomization and for ICP atomization. As shown in Fig. 2, laser excitation downwards the ICP z-axis was also possible by tilting the mirror(s) M.

3. Results

3.1. *General*

As stated above, non-resonance fluorescence [10] was always employed. Usually direct line fluorescence (DLF) from an excited state was measured (Stokes or anti-Stokes), but in cases where such transitions were not available or too low in gA value, collision induced fluorescence was resorted to (from levels either lower or higher than the excited level). Since more than one combination of excitation and fluorescence wavelengths were usually

[10] N. Omenetto and J. D. Winefordner, *Appl. Spectrosc.* **26**, 555 (1972).



A = QUARTZ PLATE; B = BEAM EXPANDER; E = LIGHT BAFFLE; C = ELLIPSOIDAL MIRROR; D = ATOM RESERVOIR; F = MONOCHROMATOR.

Fig. 1. Schematic layout of the experimental set-up used with flame and carbon rod atomization. PD = photodiode, PM = photomultiplier.

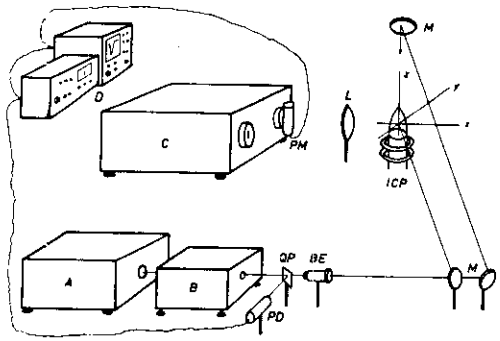


Fig. 2. Schematic layout of experimental set-up for ICP atomization. A = Excimer laser; B = dye laser; QP = quartz plate; PD = photodiode; BE = beam expander; M = mirrors (three mirrors were always used to direct the laser beam into the ICP); L = lens; PM = photomultiplier; C = 1.29-m grating monochromator; D = boxcar and oscilloscope.

investigated, the relative detection limits obtained should serve only as a rough guide, since the excitation beam power was very seldom at maximum due to degradation of the dyes. This argument also holds for the final value of the detection limits reported in our previous paper [2]. In addition, it was found that a significant loss of beam power ($\sim 50\%$) occurred due to the approximately 3 m beam path to the ICP and the use of 3 folding mirrors. It was estimated that the beam peak power at the ICP was not more than 100 kW for the fundamental wavelength range (340 nm), less than 25 kW for the frequency doubled range 260–340 nm, and approximately 1 kW for the range 220–260 nm.

As seen from the data collected in Table 2, in the case of the air–acetylene flame, the limiting noise of the entire measuring system (PMT-amplifier-gated integrator) was not due to radiofrequency interference noise but to the background emission shot noise of the atomizer. Similar results were also obtained for the ICP measurements. Because of this, the measured detection limits improve when longer observation times are used.

The detection limits already published [2] were obtained at 10 Hz repetition rate and for an observed time constant 9 s, i.e., 45 s observation time is necessary to achieve a steady state signal. As already reported, in the much more practical case of 1.8 s observed time constant

Table 2. R.m.s. noise data evaluated at the direct line fluorescence of lead (405.782 nm) for the excimer pumped-dye laser and the separated air–acetylene flame*

Type of measurement†	R.m.s. noise (mV)	Observations
Laser OFF Flame OFF	0.095	Boxcar and PMT noise
Laser ON Flame OFF	0.175	rf noise added
Laser ON Flame ON	0.80	Flame noise added

* PMT conditions: −900 V; boxcar: 10 μs gate time constant, 100 ns gate width; monochromator: 2 mm slit width, 10 mm slit height.

† The data refer only to the excimer laser, since with the dye laser in operation, some environmental scatter of the laser light into the monochromator was also observed [3].

(9 s observation time) achieved by increasing the laser repetition rate to 50 Hz the detection limits deteriorate by a factor 1.5, as was experimentally measured [2].

3.2 *Individual elements with the ICP as atom/ion reservoir*

In the following subsections, results for the individual elements are described.

3.2.1. *Aluminium.* As seen in Fig. 3, direct line fluorescence (DLF) and anti-Stokes direct line fluorescence (AS-DLF) are possible combinations for the excitation and fluorescence processes of the aluminium atom. The last results were obtained by exciting at 394.403 nm and observing the DLF at 396.153 nm. With a plasma power of 700 W and a slit width of 1 mm (Spex 1.29 m monochromator) a detection limit of 0.4 ng ml^{-1} was obtained at an observation height in the ICP of 20 mm [2].

Poorer results were obtained with the 308.216 and 309.271 nm combination, mainly because of the interference due to the excitation of OH fluorescence. Indeed, with the laser tuned at 309.271 nm, the OH band heads at 309.278 and at 309.239 nm [11] are also excited and the resulting fluorescence interferes with the aluminium fluorescence (AS-DLF) at 308.216 nm. When the laser excitation is set at 308.216 nm and the atom fluorescence (DLF)

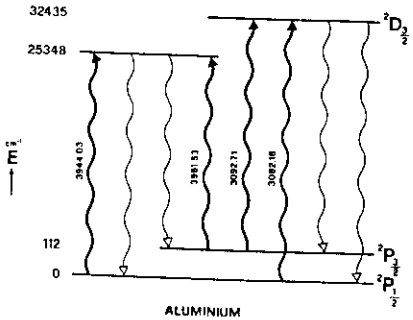


Fig. 3. Schematic partial energy level diagram for the aluminium atom. Wavelengths are indicated in Angstrom.

[11] G. H. DIEKE and H. M. CROSSWHITE, *J. Quant. Spectrosc. Radiat. Transfer* **2**, 97 (1961).

is measured a. 309.271 nm, the high emission noise signal of the OH band heads produces a poor signal-to-noise ratio.

3.2.2. *Boron.* The only resonance lines accessible to the laser are the two atomic lines at 249.678 and 249.773 nm (see Fig. 4). As in the case of aluminium, DLF and AS-DLF represent possible excitation/fluorescence combinations. In this case, however, the use of the better resolution 1.29-m monochromator is essential to separate the two lines in order to avoid the measurement of resonance fluorescence. Figure 5b and 5c shows the monochromator scans, with a spectral bandwidth of 0.03 nm, over the two lines with the laser tuned at each line. Since the stronger component is always at the longer wavelength, it is clear that the best results will be achieved for the DLF process, i.e. by exciting at 249.678 nm and measuring the fluorescence at 249.773 nm. Figure 5a shows the tracing obtained when the monochromator spectral bandwidth is large enough to accept both lines and the frequency doubled output of the dye laser is slowly scanned, i.e. it represents the excitation spectrum of the boron

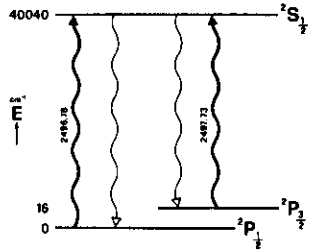


Fig. 4. Schematic partial energy level diagram for the boron atom. Wavelengths are indicated in Angstrom.

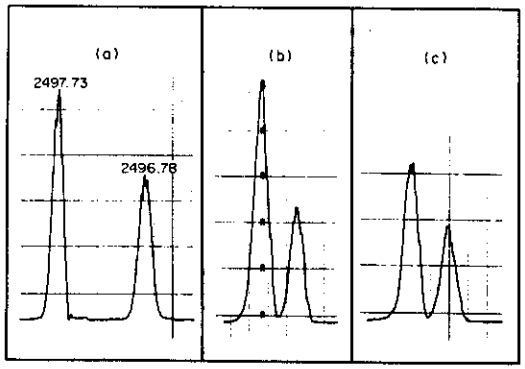


Fig. 5. Recorder tracings of the atomic fluorescence of the boron atom. (a) excitation spectrum; monochromator spectral bandwidth: 0.6 nm; laser grating slowly scanned while manually tilting the frequency doubling crystal to keep the output power constant. (b) emission spectrum; laser excitation: 249.773 nm; fluorescence monochromator spectral bandwidth: 0.03 nm (50-μm slits). (c) emission spectrum; laser excitation: 249.678 nm; fluorescence monochromator: same as in (b). Wavelengths are indicated in Angstrom.

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atom in this narrow wavelength region. The small bandwidth of the exciting radiation (measured in this case as 0.014 nm) and the resulting good resolution are clearly evident.

Figure 5 also clearly illustrates the extremely high selectivity afforded by the laser induced non resonance fluorescence technique. Indeed, for spectral line interference to occur, the interfering element must have an absorption line within approximately ± 0.02 nm from the excitation wavelength, *and* the fluorescence wavelength must be within the spectral bandpass of the monochromator, which is set at the fluorescence wavelength of the analyte. This circumstance appears to be extremely unlikely.

With a plasma power of 800 W and at an observation height of 20 mm, the DLF process (excitation set at 249.678 nm and fluorescence observed at 249.773 nm with a 70-μm slit width) resulted in a detection limit of 4 ng ml^{-1} [2].

It is worth stressing here that the peak power of the frequency doubled laser beam at the ICP was only approximately 1 kW, due to the poor doubling efficiency of the crystal and to the use of the beam expander and the 3 folding mirrors. Therefore, no saturation could be approached. It is then easy to anticipate a much better detection limit for greater laser excitation power.

3.2.3. *Barium.* For this element, only ionic fluorescence was investigated. As seen in Fig. 6, when the laser excitation is set at 455.403 nm, both DLF (at 614.172 and 585.368 nm) and Stokes-stepwise line fluorescence (S-SWLF) (at 493.409 and 649.690 nm) can be observed. Because of the relatively important population of the D levels, AS-DLF at 455.403 nm results, after excitation at 614.172 nm. For analytical purposes, the best results are obtained when the DLF at 614.172 nm is observed and pumping is accomplished with 455.403 nm.

Several measurements were carried out for barium with the smaller "Minimate" monochromator, both at the conventional observation height of 20 mm and above the chimney, which extended the height of the plasma by 40 mm. With a slit width of 0.5 mm and a plasma power of 700 W, the detection limits obtained were 5 and 8 ng ml^{-1}, this last figure referring to the measurements carried out above the plasma extension tube.

The detection limit obtained with the 1.29 m monochromator with 0.1-mm slits, 700-W plasma power and 20-mm observation height, was 0.7 ng ml^{-1} [2].

Because of the large power available in the fundamental wavelength of the dye used (Coumarin 450, see Table 1), the transition was highly saturated: in fact, the insertion of a neutral density filter of 10% transmission in the laser beam resulted in a decrease of the fluorescence signal by only 30%.

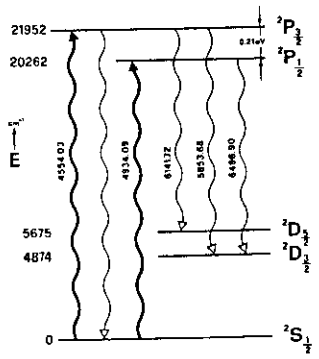

Fig. 6. Schematic partial energy level diagram for the barium ion. Wavelengths are indicated in Angstrom.

Two final remarks were made for barium and are illustrated in Figs 7 and 8. In Fig. 7, it can be seen that, because of the wide spectral bandwidth of the laser in comparison with the ion absorption profile, the laser grating can be scanned over the absorption region, thus allowing to correct for scattering, which in the case shown was due to some laser radiation reflected into the monochromator. For resonance fluorescence work, this is always a possibility. Secondly, as shown in Fig. 8, because of the fact that saturation of the fluorescence is strongly approached, a decrease in the laser power by a factor of 10 will decrease the scattering signal by the same amount but will leave the fluorescence practically unchanged. Note also in this

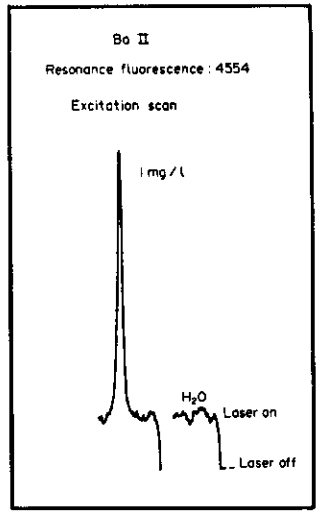

Fig. 7. Scattering correction by scanning the laser throughout the absorption profile of the barium ion in the ICP. The wavelength is indicated in Angstrom.

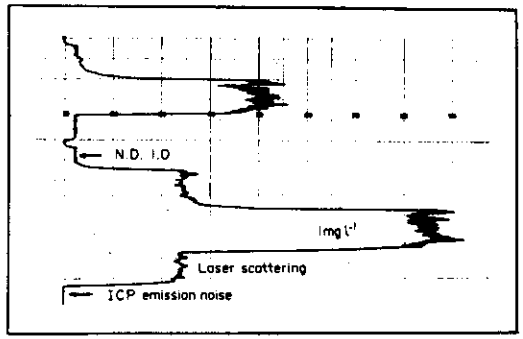

Fig. 8. Scattering correction by taking advantage of the saturation of the fluorescence signal. Figure shows from right to left: ICP emission noise; scattering signal due to laser light into the monochromator; resonance ionic fluorescence of 1 μg ml^{-1} of Ba; scattering level with the laser power decreased $\times$ 10, fluorescence signal with the laser power decreased $\times$ 10.

figure that the ICP emission noise, at the detector/amplifier settings used for 1 $\mu g\,ml^{-1}$ of barium, is practically non-existent.

3.2.4. *Gallium.* Also for gallium, some measurements were performed with the chimney on the plasma torch and the Minimate monochromator at a plasma power of 800 W. The combination of excitation and fluorescence wavelengths at 403.298 and 417.206 nm, i.e. Stokes and anti-Stokes DLF, gave a detection limit of 5 $ng\,ml^{-1}$. The excitation at the u.v. transition of 287.424 nm and the observation of the Stokes DLF at 294.418 together with the thermally assisted Stokes-stepwise line fluorescence (TA-S-SLF) at 294.364 nm, also resulted in a detection limit of 5 $ng\,ml^{-1}$.

The final detection limit reported in Ref. [2] was 1 $ng\,ml^{-1}$, and was obtained with the u.v. excitation by frequency doubling the Rh 590 dye.

Since all the results given here for the elements investigated were obtained without the Fabry–Perot etalon in the laser cavity, it was felt interesting to investigate the resolution capabilities of our laser system in the case of the well known gallium–manganese spectral interference [12]. The results reported below were obtained with the separated air–acetylene flame as atomizer. If the laser is tuned at the gallium resonance line (403.298 nm) and manganese is present in the sample solution, the resonance fluorescence of manganese at 403.307 is also excited, since the wavelength difference with the laser line is only 0.009 nm. With the narrowing etalon in the oscillator cavity, however, the laser spectral bandwidth should be narrower than the wavelength separation. The excitation spectrum shown in Fig. 9 was obtained by first setting the grating at the peak of the line (as observed by monitoring the fluorescence signal) and then *manually* tilting the Fabry–Perot over an entire free spectral range. As seen in the left side of this figure, the two peaks are clearly resolved, the asymmetry and irreproducibility of the tracings being obviously due to the manual scan of the etalon. In these conditions, it was found that with the laser tuned at the gallium peak, only 4.5% of the

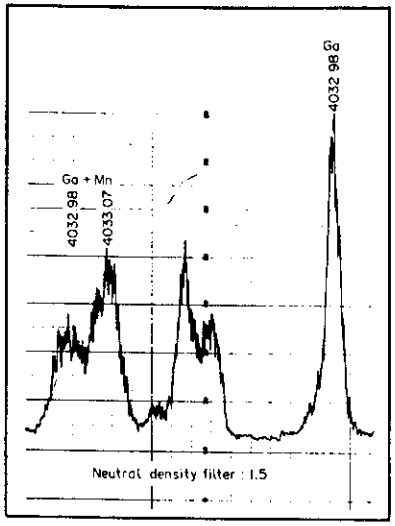

Fig. 9. Excitation scans throughout the gallium and manganese resonance absorption lines. Scan was accomplished by manual tilting of Fabry-Perot etalon in the laser cavity. Wavelengths are given in Angstrom.

[12] S. J. WEEKS, H. HARAGUCHI and J. D. WINEFORDNER, *Anal. Chem.* 50, 360 (1978).

manganese fluorescence was excited. The profile on the right side of Fig. 9 was obtained in the same way but with only gallium atomized in the flame.

It is essential to note that the excitation scans shown were obtained with the laser power decreased by more than a factor of 30 in order to minimize saturation broadening. Indeed, at full laser power, the same experiment repeated resulted in the broad profiles shown in Fig. 10, with no discernible separation of the gallium and manganese peaks.

3.2.5. *Molybdenum.* The series of ionic resonance lines in the region between 201 and 208 nm could not be reached by our laser system. For the atomic lines, there are no suitable DLF transitions with high transition probability values, so that collisionally assisted fluorescence has to be employed.

For the molybdenum ion, with a plasma power of 1 kW, a detection limit of 40 $ng\,ml^{-1}$ was obtained for the combination 287.151 nm (excitation) and 291.192 nm (fluorescence, DLF). It is worth noting that the exciting transition starts from a level lying approximately 1.5 eV above the ground state. AS-DLF could also be used, with a detection limit of 150 $ng\,ml^{-1}$, by exciting at 277.540 nm and measuring at 202.030 nm.

For the molybdenum atom, the only good combination is excitation of the resonance line at 313.259 nm and the measurement of the Stokes-stepwise line fluorescence at 317.035 nm. With these two lines, a detection limit of 5 $ng\,ml^{-1}$ was reported [2].

Of course, resonance fluorescence at 313.259 nm can also be used if scattering can be avoided.

3.2.6. *Lead* This element is particularly attractive in atomic fluorescence with laser excitation both because of the fact that the excitation line at 283.306 nm can be very efficiently reached by frequency doubling the Rh 590 dye and because DLF can be measured at a wavelength (405.783 nm) far away from the exciting one and characterized by a high value of the spontaneous transition probability.

At a plasma power of 800 W and using 2-mm slits with the 1.29-m monochromator, a detection limit of 1 $ng\,ml^{-1}$ was obtained [2].

For this element, an experimental observation was made by directing the laser beam

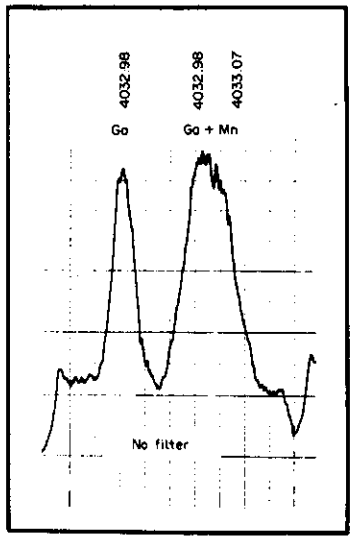

Fig. 10. Same as Fig. 9 but at full laser power. Here, saturation broadening prevents the resolution of the two absorption peaks. Wavelengths are given in Angstrom.

downwards in the ICP axis (see Fig. 2). The fluorescence signal obtained was approximately × 2 larger than that given by the conventional excitation. This configuration seems therefore to warrant further experimental investigation.

3.2.7. *Silicon.* As shown in Fig. 11, many suitable excitation/emission combination are possible in the spectral region 350–253 nm. However, silicon represents a very peculiar example, in which the high population of level $^1D_2$, the high laser power available at 288 nm and the possibility of collecting most of the strong transitions shown in Fig. 11 with a wide monochromator slit, combine together to give the best analytical sensitivity. In fact, with the laser excitation peaked at 286.160 nm and the fluorescence measured at a wavelength setting of a 251.5 nm with a spectral bandwidth sufficiently large to collect the lines at 250.690, 251.432, 251.611, 251.921 and 252.411 nm, a detection limit of 1 ng ml^{-1} was obtained [2].

Figure 12 shows the emission spectrum (A) and the fluorescence spectrum (B) in the same spectral region. The absence of noise in the baseline of the fluorescence spectrum for the same plasma settings and with a wider monochromator slit width is worth stressing.

3.2.8. *Tin.* The two near resonance transitions at 300.914 and 303.412 nm start from a level lying approximately 0.2 eV above the ground level and should then be highly populated in the ICP. Moreover, both lines can be efficiently reached by frequency doubling the Rh 640 dye.

With the laser excitation set at 300.914 nm, the DLF at 317.505 nm observed with a plasma power of 750 W, at an observation height of 20 mm and with a 1-mm monochromator slits, yielded the best detection limit of 3 ng ml^{-1} [2].

The same laser excitation and the observation of the anti-Stokes DLF at 286.333 nm resulted in only a × 2 deterioration of the detection limit (6 ng ml^{-1}). Again, 6 ng ml^{-1} was obtained by exciting at 303.412 nm and measuring the Excited state-Thermally assisted-Stokes fluorescence at 317.505 nm.

3.2.9. *Titanium.* From the relative transition probabilities reported for the titanium ion [13], it appears that the best combination would be given by exciting at 308.802 nm and measuring the Stokes-DLF at 316.852 nm. However, we experienced the same problem reported above for aluminium, i.e. OH fluorescence was excited over a broad spectral range.

Several possibilities were offered by tuning the excitation wavelength at 307.864 nm. In

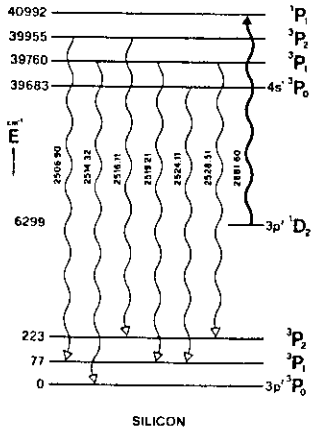

Fig. 11. Schematic partial energy level diagram for the silicon atom. Wavelengths are indicated in Angstrom.

[13] C. H. CORLISS and W. R. BOZMAN, Experimental transition probabilities for spectral lines of seventy elements, NBS Monograph 53. U.S. Government Printing Office, Washington, D.C. (1962).

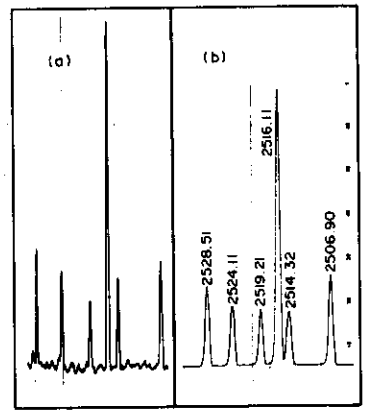

Fig. 12. Emission (a) and fluorescence (b) spectra of 10 μg ml^{-1} of silicon in the ICP. a: Monochromator slit width = 50 μm; b: monochromator slit width, 100 μm; laser excitation set at 288.160 nm. For both scans, the ICP power was 800 W, the observation height 20 mm, and the PMT voltage 1000 V. Wavelengths are indicated in Angstrom.

fact, either directly from the excited level or from nearby levels collisionally coupled with the former level, several fluorescence transitions could be measured. These lines and the corresponding fluorescence process, are collected in Table 3.

With a plasma power of 700 W, at 20 mm above the coil, and with 2-mm slits, a detection limit of 1 ng ml^{-1} was found by measuring at 316.257 + 316.852 nm [2]. By measuring the

Table 3. Fluorescence transitions for the titanium ion in the inductively coupled plasma resulting from excitation at 307.864 nm*

Excitation wavelength (nm) (Transition)† $l \rightarrow u$	Fluorescence wavelength (nm) (Transition)† $l \rightarrow u$	Fluorescence process‡
	308.802 (393–32 767)	E-TA-S-SWLF
	316.177 (984–32 603)	E-S-SWLF
	316.257 (1087–32 698)	E-S-DLF
307.864 (225–32 698)	316.852 (1216–32 767)	E-TA-S-SWLF
	323.452 (393–31 301)	E-S-SWLF
	323.657 (225–31 114)	E-S-SWLF
	323.904 (94–30 959)	E-S-SWLF

* Due to the many transitions reported [13], some weaker lines might also be included in the observed fluorescence signal.

† Energy of levels in cm^{-1}; l = lower level; u = upper level.

‡ Named according to Ref. [10]. E-TA-S-SWLF: Excited state thermally Assisted-Stokes-Stepwise Line Fluorescence; E-S-SWLF: Excited State-Stokes-Stepwise Line Fluorescence; E-S-DLF: Excited state-Stokes-Direct Line Fluorescence.

other transitions reported in Table 3, a × 2–3 degradation in the detection limit was observed.

3.2.10. *Thallium.* Both resonance lines at 276.787 and 377.572 nm could be reached and Stokes-DLF observed at 352.943 and 535.046 nm, respectively.

The detection limit reported for the u.v. combination, with a plasma power of 800 W and 2-mm monochromator slits was 7 ng ml^{-1} [2]. The other combination, for the same plasma settings, resulted in a better detection limit, i.e. 4 ng ml^{-1}. This result can be understood in terms of the difference in the excitation wavelengths, laser power, absorption oscillator strengths, fluorescence quantum efficiency and background emission noise at the measured fluorescence wavelength [1].

3.2.11. *Vanadium.* Resonance fluorescence at 318.398 nm of the vanadium atom could easily be observed by frequency doubling the Rh 640 dye. The detection limit found was 5 ng ml^{-1} but some scattering was inevitably present in the measurement. For the vanadium ion, a very good combination was found by exciting at 268.796 nm and observing the Stokes-DLF at 290.882, with a detection limit of 3 ng ml^{-1} [2].

As already reported in the case of nitrous oxide–acetylene flame [14] a large choice of non-resonance fluorescence transitions for vanadium is possible. This is clearly demonstrated in Fig. 13 in the case of ICP atomization. This figure shows an excitation spectrum of the vanadium atom where the fluorescence monochromator is set at 411.178 nm and the output of the dye laser (BBQ) is slowly scanned in the spectral region 379–391 nm. All the transitions shown are due to thermally assisted and/or stepwise line fluorescence processes, both of the Stokes and anti-Stokes type.

Figure 13 shows also an interesting laser feature. In fact, one can easily identify the spectral range of lasing of the BBQ dye as the region when the broad fluorescence continuum (on the right and left sides of the figure) modifies into a well defined series of laser lines.

3.2.12. *Yttrium.* Both atomic and ionic fluorescence transitions were studied for yttrium. In addition, several measurements were carried out with the Minimate monochromator and the chimney on the torch to obtain the extended plasma.

Atomic fluorescence was excited at the 407.738 nm resonance line and measured either at 416.752 nm (Stokes-DLF) or 412.831 (thermally assisted-Stokes-stepwise line fluorescence), this last one resulting in a stronger fluorescence signal, because of the higher value of the spontaneous transition probability.

Ionic fluorescence measured at 321.669 nm and excited at 319.562 nm (excited state-Stokes-DLF) gave a detection limit of 30 ng ml^{-1}. With the laser excitation set at 508.742 nm, i.e. a transition whose lower level lies approximately 1 eV above the ground level, several

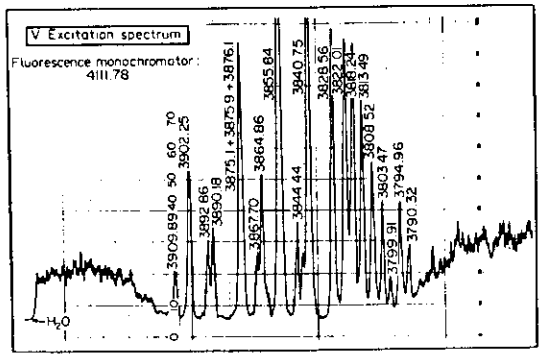

Fig. 13. Excitation spectrum of the vanadium atom in the plasma. Fluorescence monochromator: 411.178 nm; laser scan: 379–391 nm. Wavelengths are indicated in Angstrom.

[14] M. A. BOLSHOV, A. V. ZYBIN and I. I. SHIRENKINA, *Spectrochim. Acta* 36B, 1143 (1981).

analytically useful fluorescence transitions were observed (see Figs 14 and 15). By parking the monochromator at 371.030 nm (excited state-anti Stokes DLF), a detection limit of 7 ng ml^{-1} was obtained with the extended plasma and the Minimate monochromator.

With the 1.29-m monochromator, a plasma power of 1 kW and at an observation height of 20 mm, the detection limit for the same excitation/fluorescence combination was found to be 0.6 ng ml^{-1} [2]. These results, as well as those already reported for barium, demonstrate that there is no advantage in using either the extension tube or the higher luminosity monochromator.

3.2..3. *Zirconium.* A multitude of ionic lines suitable for excitation because of their high absorption oscillator strength and the small value of the lower energy level, are available [13]

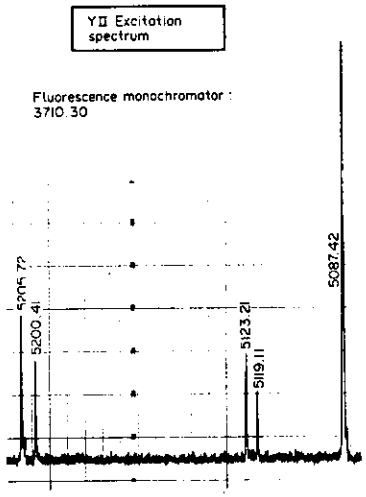

Fig. 14. Excitation spectrum of the yttrium ion in the plasma. Fluorescence monochromator: 371.030 nm; laser scan: 508–525 nm. Wavelengths are indicated in Angstrom.

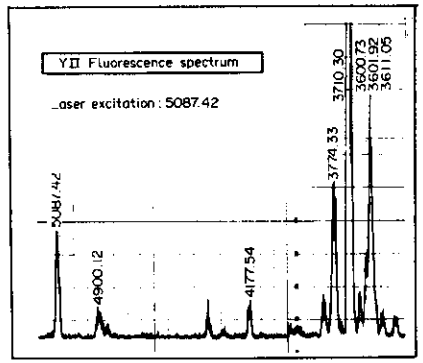

Fig. 15. Fluorescence spectrum of the yttrium ion in the plasma. Laser excitation: 508.742 nm; monochromator scan: 360–509 nm. Wavelengths are indicated in Angstrom.

and therefore the determination of their optimum combination will take a long time. Table 4 collects the transitions tested as well as the detection limits obtained.

The best detection limit of 3 ng ml^{-1} [2] was achieved by exciting with a transition whose lower level is approximately 1 eV above the ground level and measuring the strong fluorescence at 256.887 + 257.139 nm with 1-mm slits.

3.2.14. *Uranium.* As for zirconium, quite a number of ionic lines of uranium should be suitable for excitation with accompanying strong emission of collisionally assisted as well as direct line fluorescence [13].

Our interest in uranium fluorescence was prompted by the possibility of evaluating its isotopic ratio by scanning the spectrally narrow laser beam over the atom/ion absorption profile while monitoring the resulting fluorescence signal. Disappointedly, no significant fluorescence was observed for all the lines possessing a useful isotopic shift. As shown in Fig. 16, when the laser excitation was tuned either at 385.958 or 409.014 nm, practically no

Table 4. Fluorescence transitions and detection limits for the zirconium ion in the inductively coupled plasma*

Excitation wavelength (nm) (Transition)† $l \rightarrow u$	Fluorescence wavelength (nm) (Transition)† $l \rightarrow u$	Fluorescence process‡	Detection limit (ng ml^{-1})
273.486 (35-36 869)	297.805 (3300–36 869)	E-S-DLF	16
	346.994 (8058–36 869)	E-S-DLF	12
284.458 (8056–43 202)	258.340 (4506–43 202)	E-AS-DLF	35
	298.780 (9743–43 202)	E-S-DLF	350
305.484 (8153–40 878)	346.302 (11 984–40 853)	E-S-SWLF	60
	350.548 (12 360–40 878)	E-S-DLF	30
	374.598 (14 190–40 878)	E-S-DLF	65
309.923 (0–32 257)	336.782 (2572–32 257)	S-DLF	40
	339.198 (1323–30 796)	S-SWLF	12
310.658 (8058–40 239)	256.887 (1323–40 239)	E-AS-DLF	
	+ 257.139 (763–39 640)	+ E-AS-SWLF	3
313.348 (7736–39 640)	257.139 (763–39 640)	E-AS-DLF	
	+ 256.887 (1323–40 239)	+ E-TA-AS-SWLF	12

* Due to many transitions reported [13], some weaker lines might also be included in the observed fluorescence signal.

† Energy of levels in cm^{-1}; l = lower level; u = upper level.

‡ Named according to Ref. [10]. The acronyms have been defined in the captions of Table 3 except for the following: E-AS-DLF: Excited state-Anti-Stokes-Direct Line Fluorescence; S-DLF: Stokes-Direct Line Fluorescence; S-SWLF: Stokes-Stepwise Line Fluorescence; E-AS-SWLF: Excited state-Anti Stokes-Stepwise Line Fluorescence; E-TA-AS-SWLF: Excited state-Thermally Assisted-Anti-Stokes-Stepwise Line Fluorescence.

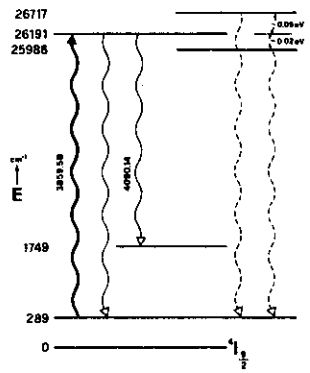

Fig. 16. Schematic partial energy level diagram for the uranium ion. Wavelengths are indicated in Angstrom.

fluorescence (or extremely weak) could be observed at 378.284 and 389.036 nm (dashed transitions in the figure), i.e. from two levels lying approximately 0.05 and 0.02 eV, respectively, from the level reached by the laser radiation. At present, we have no explanation for this peculiar behavior.

However, by tuning the laser at 409.014 nm and measuring the anti-Stokes direct line fluorescence at 385.958 nm, a detection limit of 20 ng ml^{-1} was obtained. It is worth mentioning that this detection limit was achieved with only 50 kW of laser peak power, due to a severe degradation of the dye (DPS).

3.3. *Air–acetylene flame and carbon rod as atom reservoirs*

As stated before, no systematic investigation was carried out for these two atomizers, except for the elements lead and thallium, because of the interest of their determination in biological fluids such as blood and urine.

Table 5 collects the results obtained for these elements in both the separated air–acetylene flame and the modified carbon rod atomizer. The frequency doubled laser beam size was optimized with the variable beam expander (see Fig. 1) in order to fill the aperture of the small 0.1-m monochromator. The ellipsoidal mirror behind the flame was also retained.

The detection limit given in Table 5 for lead in the air–acetylene flame (0.02 ng ml^{-1}) was sufficient to allow its direct determination in blood, thus avoiding the time consuming electrothermal atomization [3]. On the other hand using the carbon rod, and with 10 μl of sample solution, the absolute detection limit was found to be 6 fg. This value, while confirming the results of 1.5 fg (for 60 μl) published by BOLSHOV *et al.* [14] and of 5 fg

Table 5. Detection limits for lead and thallium atomized in the separated air–acetylene flame and in the carbon rod

Element	Excitation wavelength (nm)	Fluorescence wavelength (nm)	Detection limit (ng ml^{-1}) Flame	Carbon rod*
Pb	283.306	405.783	0.02	6×10^{-4}
Tl	276.787	352.943	0.8	0.01

* 10-μl injection volume. The detection limit was calculated by evaluating the noise in the blank signal at the fluorescence wavelength due to the injection of 10 μl of distilled water in the atomizer. The laser was operated at 50 Hz and the boxcar gate time constant was set at 1 μs.

reported by TILCH *et al.* [15], was not the limiting value which could be achieved for our system. In fact, "environmental fluorescence" excited by the u.v. laser light could not be completely prevented from entering the monochromator and reaching the detector. However, this can be avoided with further patience and careful positioning of light traps and baffles. For the sake of curiosity, if this limiting noise is eliminated, the detection limit for lead would decrease to a value of 8.6×10^{-6} ng ml^{-1} with a corresponding absolute detection of 8.6×10^{-17} g.

4. DISCUSSION

For the sake of clarity, we would like to summarize here the most important outcomes of our work, even though some of the following statements have already been made or properly stressed before [1, 2].

4.1. *Advantages of the ICP as atom/ion reservoir*

These advantages are as follows.

(i) As for conventional atomic emission measurements with the ICP, its high temperature and electron concentration results in relative freedom from chemical and ionization interferences.

(ii) The peculiar characteristic of the ICP that elements are readily ionized results in a wide choice of analytical line combinations, e.g. for Ba, Ti, U, V, Y and Zr the best sensitivity is obtained with ionic lines, while for Al, B, Ga, Mo, Pb, Si, Sn and Tl the best results are obtained with atomic lines.

(iii) Many transitions are suitable for excitation, not only the resonance lines of the elements. There is a high population of energy levels up to 1 eV in the ICP. The excitation of the Y II transition at 508.743 nm, with its lower energy level near 1 eV, serves as a good example.

(iv) Collisionally assisted fluorescences gives very strong signals in many cases, e.g. the excitation of Si at 288.158 nm and the measurement of stepwise line fluorescence of the group of lines between 250.690 and 252.851 nm. This is due to a high frequency of collisions at the elevated temperature of the ICP.

(v) Non-resonance fluorescence yields extremely good detection limits in most cases, due to the wide choice of analytical line pairs. This means that the classical scattering problem of atomic fluorescence is eliminated.

(vi) In several cases, the quantum efficiency in the ICP is high due to the argon atmosphere, resulting in smaller loss of analytical signal compared to flames as reservoirs [16, 17].

4.2. *Advantages of high power pulsed laser as excitation source*

These advantages are as follows.

(i) Owing to the short duration of the laser pulse, high temperature atom reservoirs can be efficiently used, since the background emission signal from the atom reservoir during the pulse is relatively small, with the result that the fluorescence to background emission ratio is high.

(ii) Because of such high fluorescence to emission ratio, a monochromator with good resolving power and consequently, moderate light throughout, as that described in most of our measurements, can be used. This can be beneficial for cases such as boron where it is required that the 249.678 and 249.773 nm lines be separated.

(iii) The analytical signal is weakly dependent on the laser fluctuations, due to the saturation of the transitions when pumped by a high power laser beam [1]. In all cases investigated, the pumped transitions above 260 nm were saturated to a considerable degree.

(iv) The most important advantage of a pulsed dye laser is of course its tunability over a wide wavelength range through the use of frequency doubling and mixing techniques.

[15] J. TILCH, H. J. PAETZOLD, H. FALK and K. P. SCHMIDT, Analytiktreffen 1982, Atomspektroskopie, Neubrandenburg (DDR), 8–12 November 1982, Abstract N DV 55.
[16] H. UCHIDA, M. A. KOSINSKI, N. OMENETTO and J. D. WINEFORDNER, *Spectrochim. Acta* **38B**, 529 (1983).
[17] H. UCHIDA, M. A. KOSINSKI, N. OMENETTO and J. D. WINEFORDNER, *Spectrochim. Acta* **39B**, 63 (1984).

4.3. *Advantages of the combined system: pulsed laser with ICP reservoir*

These advantages are as follows.

(i) Good sensitivity and detection limits.

(ii) Extremely high selectivity. With non-resonance fluorescence measurements there is virtually no chance of spectral interference, as explained in the case of boron fluorescence. This implies that the wavelength combination giving the best detection limit can always be used in analytical work, whereas the wavelengths yielding the best detection limits cannot be always used in emission ICP measurements, where spectral interferences often prescribe the use of less sensitive lines.

(iii) When the sensitivity is not the major goal, the atomic fluorescence technique offers the possibility of collecting the signal from a small volume of the plasma, e.g. 1 mm^3, enabling the analyst to select an analytical zone of homogeneous temperature and one most free of interference effects. In conventional ICP emission, line of sight measurements have to be done, light being thus collected from a whole range of plasma conditions.

4.4. *Disadvantages of the technique*

The disadvantages are as follows.

(i) The laser excited atomic fluorescence technique is, almost by definition, a single element technique since only a single transition of the analyte atoms is excited. Indeed, from this stem the most important advantages of freedom from spectral interferences (in contrast with all emission techniques where all atoms, including major and matrix elements, are excited to a very large number of energy levels), and of high sensitivity as a result of the fact that all the excitation energy is pumped into this single transition while all other atoms are left undisturbed.

(ii) The complexity and high cost of the equipment. The fact that different dyes are needed for different wavelength regions and these dyes have to be renewed as a result of degradation are serious obstacles to routine measurements. As stressed before, the eight cell dye laser [4] which was used in this study did facilitate change from one dye to another considerably, so that in our system the degradation problem actually was the only real obstacle.

5. CONCLUSIONS

The development of pulsed dye lasers tunable over a wavelength range from 220 nm to the near infrared has come to the stage where it can be used with success as primary excitation source for analytical atomic fluorescence measurements. The atomic fluorescence mode of measurement offers enhanced sensitivity and improved detection limits when used in conjunction with conventional atom reservoirs such as flames, carbon furnace and the ICP, compared to the use of these same reservoirs or sources in atomic absorption or atomic emission mode. In addition, the utmost in spectral selectivity is obtained with this technique when non resonance fluorescence is employed. This will not always be possible with use of low temperature atom reservoirs like flames or graphite furnaces, but seems to be feasible for the majority of elements when the high temperature ICP is used.

Further developments and refinements of the commercially available dye laser systems are needed to make things easier for the analyst, such as fast replacement of dyes, more power in the low u.v. region (220–260 nm) and reliable extension of the range to lower wavelengths.

With regards to the atom reservoir, a high temperature source like the ICP is the choice for high accuracy and good sensitivity. The development of a simpler and more versatile atom reservoir ($T \sim 5000$K) deserves the attention of spectroscopists in this field.

Acknowledgements—H. G. C. HUMAN would like to thank the Joint Research Center authorities and in particular the Education Training Service for the grant of a visiting scientist fellowship.

Direct Determination of Lead in Blood by Laser-excited Flame Atomic-Fluorescence Spectrometry

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A simple method for the determination of lead in blood by atomic-fluorescence spectrometry is described in which the sample is diluted with Triton-X (1+10). The sample is then nebulised directly into an argon-separated air - acetylene flame burning on a circular, home-made, capillary burner. Aqueous standards can be used for calibration purposes. The direct line fluorescence of lead at 405.8 nm is measured after excitation at 283.3 nm provided by a frequency doubled pulsed tunable dye laser pumped by a XeCl excimer laser, thus avoiding any scattering due to the matrix. The laser peak power was approximately 40 kW at the UV wavelength and the fluorescence was highly saturated even when the beam size was expanded in the flame to *ca.* 15 mm diameter. By diluting 0.1 ml of blood to 1 ml and using discrete sampling in the flame, the detection limit was found to be 4 ng ml^{-1} and can be decreased considerably by taking a larger volume of blood. Several blood samples, as well as quality control samples, were analysed and the results found to be in very close agreement with those provided by the well established Delves cup atomic-absorption, graphite furnace atomic-absorption and anodic-stripping voltammetry methods.

Keywords: *Lead determination; laser-excited flame atomic-fluorescence spectrometry; blood*

The determination of lead in blood by atomic-absorption, -emission and -fluorescence spectrometry is well documented. In most instances one has to resort to electrothermal atomisation and/or to the well established Delves cup procedures[1] in order to achieve the necessary sensitivity. Understandably, the use of flame atomisation with direct aspiration of the blood samples allows a rapidity of analysis that is certainly greater than that given by any other technique of comparable sensitivity.[2]

To our knowledge, the most sensitive use of flame atomic fluorescence for the direct determination of lead in blood was reported by Human and Norval,[3] who used a boosted hollow-cathode lamp as a primary irradiation source. Stokes direct line fluorescence could be measured, after excitation at 283.3 nm, without any scattering problem because the fluorescence wavelength at 405.8 nm was removed from the source with a liquid filter, *i.e.*, a 500 g l^{-1} solution of nickel sulphate hexahydrate. The blood samples were diluted 20-fold and aspirated into an oxygen - argon - hydrogen flame sheathed with another external argon stream. Human and Norval[3] reported a detection limit of 24 ng ml^{-1} of lead in blood by taking into account, as the criterion for its evaluation, the standard deviation of the background plus the signal. As a consequence, their detection limit should still be lowered when only the noise in the background is considered.

Ottaway[4] used emission, absorption and fluorescence measurements with both flame and electrothermal atomisers for the determination of several elements in blood. The direct determination of lead in blood by flame atomic fluorescence was carried out with a specially dedicated instrument utilising electrodeless discharge lamps as excitation sources, a xenon arc for the correction of scattering, a double monochromator to reject the stray light and a photon counting detection system.[2] However, a detection limit of 60 ng ml^{-1} and a determination limit of 125 ng ml^{-1} were reported, stating that their method, although suitable for rapid screening of samples of interest in occupational or environmental exposure surveys, was "unsuitable for the precise measurement of blood levels in much of the unexposed population."

In a recent investigation carried out in our laboratory on the general analytical usefulness of an excimer laser-pumped tunable dye laser system as primary excitation source for atomic and ionic fluorescence in flames, furnaces and inductively coupled plasmas as atomisers,[5,6] it was found that the direct line fluorescence of lead in a separated air - acetylene flame gave an aqueous detection limit of 0.02 ng ml^{-1}. It was therefore felt that the direct determination of this element in blood at 10-fold dilution could easily be feasible, providing a quick and reliable analytical procedure that would be capable of a detection limit of 0.2 ng ml^{-1}. However, the total measuring time needed to achieve such a detection limit was approximately 45 s, which would clearly require at least 10 ml of solution at the usual nebulisation uptake rates. Because of the limited availability of blood samples, our investigation was carried out with 100 µl of blood.

The aim of this paper is to present the experimental details of our investigation together with some preliminary results obtained on several quality control blood samples, which had already been analysed by anodic-stripping voltammetry, graphite furnace atomic-absorption and Delves cup atomic-absorption methods.[7]

Experimental

Instrumentation

The excitation source was a tunable dye laser pumped by an excimer laser. The excimer laser (Model EMG-102, Lambda Physik, Göttingen, FRG) was operated with XeCl at 308 nm and was capable of providing 157 mJ per pulse of approximately 12 ns duration at a repetition rate of 1 Hz. This rate could be varied up to 100 pulses per second but a maximum value of 10 Hz was used in our work. The dye laser was manufactured by Jobin Yvon Instruments (Longjumeau, France) and consisted of the eight-cell oscillator - amplifier configuration described by Bos.[8] The Rhodamine 590 dye, dissolved in high-purity methanol, was circulated throughout the quartz cell and transversely pumped by the excimer laser. After amplification, the dye beam was directed through a KDP (potassium dihydrogen phosphate) crystal where frequency doubling occurred with approximately 10% efficiency. The output at 280 nm, separated from the fundamental beam by means of a band pass wavelength filter, was then expanded 10 times with a variable beam expander (Oriel, Stamford, CT, USA). The average power reaching the atomiser was measured at a 10-Hz repetition rate with a volume absorbing disc calorimeter (Model 38-1101, Scientech, Boulder, CO, USA). Typical values found with fresh dye solution were 40 mW in the fundamental and, therefore, *ca.* 4 mW in the UV output. With a pulse width of *ca.* 5 ns, this corresponds to a peak power of *ca.* 80 kW in the frequency doubled beam. However, after beam expansion, an approximately 2-fold loss occurred so that the excitation irradiance at the flame was not greater than 40 kW cm^{-2}. The dye laser spectral band width was measured by slowly scanning the grating in the oscillator cavity while monitoring the fluorescence in the flame. At 285 nm, the full width at half maximum of the laser was found to be 0.012 nm with a 3000 lines mm^{-1} grating.[6]

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The samples were nebulised in an argon-separated air - acetylene flame burning on a home-made Meker-type capillary burner of 16 mm diameter fitted on a conventional pre-mixing chamber with pneumatic nebulisation. The fluorescence was collected with a small, high-luminosity monochromator (Model H-10, Jobin Yvon) and no condensing optics were used between the flame and the monochromator slit, the flame - slit distance being calculated so as to fill the monochromator aperture. An ellipsoidal mirror was placed behind the flame[9] in order to increase the solid angle of collection of the fluorescence signal and consequently the signal to noise ratio. This was possible because the flame background emission noise was significantly reduced by the argon shielding.

The fluorescence signal was measured by a wide response photomultiplier (Type R 928S, Hamamatsu, Japan) with a built-in pre-amplifier (Jobin Yvon). The resulting pulse, of *ca.* 70 ns half width, was fed into a gated integrator and boxcar averager (Model 162-165, PAR EG&G, Princeton, NJ, USA) with a gate width of 50 ns and a gate time constant of 1–10 µs. The boxcar was triggered by a synchronous pulse provided by the excimer power supply and was operated in the exponential averaging mode (see under Results and Discussion).

Reagents and Sample Preparation

All reagents were of the highest purity available and doubly distilled water was used to dilute the standard solutions suitably. All disposable syringes and glassware were carefully cleaned overnight with nitric acid. Thoroughly mixed blood samples were prepared in duplicate by diluting the original sample with 0.1% Triton-X solution and distilled water.

For discrete sampling in the flame, a PTFE cup directly attached to the nebuliser capillary was tested and the nebuliser uptake rate adjusted to a reduced value. With 1 + 10 dilution, no correction was necessary for the slow uptake rate of the blood compared with aqueous standards.[2]

Results and Discussion

Because of the excellent sensitivity obtained in pure aqueous solution, a 1+10 dilution of the blood sample was considered suitable and sufficient to neglect the above-mentioned correction factor. On the other hand, it was necessary to investigate if 1 ml of diluted blood would be enough for repeated flame nebulisations and data processing.

For discrete nebulisation obtained by introducing up to 0.5 ml in the conventional PTFE sampling cup, it is essential to consider the over-all time constant of the detection system with respect to the nebuliser uptake rate. For *ca.* 9 ml min^{-1} uptake rate, the entire sample is used in *ca.* 4 s. For the exponential averaging mode of operation of the boxcar, if the time constant of the gate is set at 10 µs and the gate width at 50 ns, the observed time constant is 1.3 s at a laser repetition rate of 10 Hz.[10] The steady-state signal level will then be reached after 6.5 s, *i.e.*, after five observed time constants. The measuring time is therefore too long and more sample is needed to attain the true fluorescence signal. For continuous sample introduction into the flame, the true signal will be reached even with 1 ml of sample solution, but only one measurement would then be possible. The solution to this problem, without increasing the volume of blood, is either to decrease the time constant of the gate or to increase the repetition frequency of the laser. The last choice would obviously be the best, as in this instance the number of pulses averaged by the boxcar, and consequently the signal to noise ratio, does not change.

These considerations are borne out experimentally and the results are shown in Figs. 1 and 2. Fig. 1 shows the fluorescence peaks obtained by discrete nebulisation of diluted blood spiked with aqueous lead solutions. As clearly seen, the height of the third peak is sometimes unpredictable, indicating that the sample volume was insufficient. The signals were obtained with the laser frequency set at 10 Hz and the gate time constant at 10 µs. By changing this last value to 1 µs, the noise in the base line increased, as indicated by arrows A and B. The wider second peak shown for the addition of 40 ng ml^{-1} was due to the complete aspiration of 1 ml of sample solution.

Fig. 2 shows the same fluorescence peaks obtained at higher amplification settings and for a 1-µs gate time constant. The sample peaks correspond to a lead concentration of 8.5 ng ml^{-1} and are characterised by a signal to root mean square noise ratio of 65, *i.e.*, by a relative standard deviation of *ca.* 2%. This results in a detection limit for signal to noise ratio of 0.4 or 4 ng ml^{-1} in the original blood.

It is clearly evident from Fig. 2, but also discernible in Fig. 1, that some laser-induced noise is present at the direct line fluorescence transition of lead. In fact, both the level of the background and its associated noise increase when the laser beam traverses the flame, as indicated by the arrows in Fig. 2. This was not due to flame scattering from the blood matrix but to some environmental fluorescence (from mirror holders,

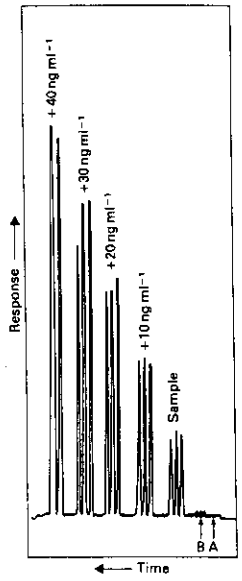

Fig. 1. Recorder tracings of the fluorescence peaks obtained for discrete nebulisation of diluted blood samples. (The concentrations in blood are ×10 higher.) A, Background noise at 10 µs gate time constant; B, background noise at 1 µs gate time constant; laser repetition rate, 10 Hz

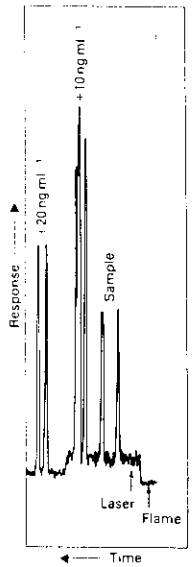

Fig. 2. Recorder tracings of the fluorescence peaks obtained for aqueous nebulisation of diluted blood samples. (The concentrations in blood are ×10 higher.) Gate time constant, 1 μs; and laser repetition rate, 10 Hz. For the addition of 20 ng ml⁻¹, the sensitivity was reduced 5-fold.

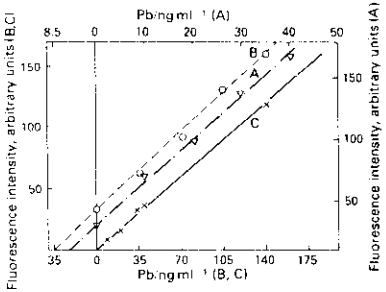

Fig. 3. Calibration graphs for aqueous lead solutions and for two standard blood solutions. A, "White" blood standard; certified content, 8 μg per 100 ml. B, "Blue" blood standard; certified content, 6 μg per 100 ml. C, Aqueous lead standards, to be compared with graph B only.

optical benches, light traps, etc.) occurring at 405.8 nm and excited by the frequency doubled UV laser output at 283.3 nm. With care and patience, this cause of noise can be eliminated, thus still improving the precision of the determination and increasing the limit of detection.

In addition to its rapidity of analysis, the use of the air - acetylene flame should allow the analytical determination to be carried out by direct comparison with an aqueous calibration graph, as chemical interferences due to the matrix should be negligible.[5] This is clearly borne out in Fig. 3, which shows the calibration graph obtained for aqueous solutions (with Triton-X added) and two standard additions

Table 1. Comparison between the lead values obtained by laser-excited flame fluorescence and AAS for several blood samples

	Pb value/μg per 100 ml		
		AAS†	
Sample code*	This work	ETA	DC
Pool	18	17	17
Blue	35	36	36
White	8.5	8	8
O	4.2	3.7	3.3
2/C	70	72	72
B.O	40	41	42
2/18	11	12	13
2	37	39	41
20/A	3	3.4	3.8
1/C	35	40	41
81627	23	22	22

* Samples were kindly provided by W. Leyendecker of the JRC, Ispra.

† AAS, atomic-absorption spectrometry with: ETA, electrothermal atomisation; and DC, Delves cup atomic absorption.

graphs for two well characterised quality control samples.[7] As seen from the slopes of the graphs obtained, the direct evaluation *versus* aqueous standards seems to be amply justified.

Several blood samples, whose lead contents had already been analysed by other methods,[7] were tested for accuracy with our laser-excited fluorescence technique. A 1-ml volume of diluted blood solution was completely aspirated into the air - acetylene flame and the laser repetition rate was maintained at 10 Hz. The results obtained are collected in Table 1 where it can be seen that the agreement between the three methods is excellent.

Two practical problems are worth mentioning here if routine work is envisaged. Firstly, the dye solution degrades under UV irradiation, more so if the repetition rate is increased, and therefore the excitation power decreases considerably (*ca.* 50%) after prolonged use of the dye. Because saturation (and therefore independence upon laser fluctuations) must be approached over a large flame volume, this problem needs careful consideration and frequent checks with a suitable standard solution. Secondly, the excitation frequency of the spectrally narrow dye laser output, as well as the tuning of the frequency doubling crystal, can vary with time giving a consequent reduction of the fluorescence signal. In both instances, a ratioing technique, realised by a two-channel operation of the boxcar, would therefore be advisable.

Conclusions

The laser-excited flame atomic fluorescence method described here is capable of determining lead in blood by directly aspirating the diluted blood solution into a separated air - acetylene flame, with great freedom from chemical interferences and scattering problems. Calibration with aqueous lead solutions is possible and a detection limit of 4 ng ml⁻¹ can be achieved with 0.1 ml of blood. If the sample volume originally available can be increased, say, to 0.5 ml and still diluted 10-fold, the possibility of increasing the gate time constant of the boxcar as well as the repetition frequency of the laser would certainly reduce this limit and approach that obtained for aqueous solutions thus providing great sensitivity combined with the very large dynamic range characteristic of the fluorescence technique.

The accuracy of the determination was shown to be very good compared with the average results obtained by other well established methods such as Delves cup atomic-absorption and graphite furnace atomic-absorption. The precision of the determination, shown as a relative standard deviation of 2.5% for the tracings in Fig. 2, at a concentration of 8.5 ng ml⁻¹, should not be taken as the precision of the entire analytical procedure. Indeed, the errors such as contamination and/or incomplete recovery, inherent in the handling of the blood samples prior to the fluorescence measurements, are certainly the limiting factors for the over-all precision and must be carefully considered in each analysis.[7]

The remarkable sensitivity obtained for lead even with flame atomisation was firstly due to the fact that a large excitation volume, obtained by expanding the laser beam in the flame, could be saturated because of the high laser power, with the corresponding measurement of the maximum available fluorescence signal, and secondly to the possibility of varying the laser repetition rate and the gate time constant in order to optimise the signal to noise ratio. However, in order to exploit fully these benefits a larger volume of blood solution is needed.

Finally, it is worth noting here that the laser-excited fluorescence detection limits obtained in our laboratory for flame as well as inductively plasma atomisation[6] indicate that this technique can certainly be extended to the direct determination of other elements of interest in biological fluids.

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Laser-excited atomic fluorescence in a pulsed glow discharge*

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Abstract— A pulsed demountable glow discharge has been used as an atom cell for laser excited atomic fluorescence. Lead atoms are sputtered from the surface of copper and graphite cathodes and are excited by a pulsed frequency-doubled dye laser after the discharge is switched off. The combination of a "dark" atom cell with non-resonance atomic fluorescence leads to a very low background signal. The detection limit for lead in copper is 0.1 μg/g and for lead in aqueous solutions (5 μl) deposited on graphite electrodes is 20 pg.

INTRODUCTION

CATHODIC sputtering within a low pressure rare gas discharge is a convenient means of producing an atomic vapor directly from a solid sample for emission [1, 2] absorption [3] or fluorescence [4, 5] spectrometry. In the case of atomic fluorescence, it is particularly suitable because it provides an atomic vapor diluted in a low-pressure inert atmosphere, an ideal low-quenching medium for the fluorescence process. Furthermore, absorption lines are narrow due to the lack of pressure broadening and chemical interferences due to compound formation are virtually non-existent. Direct vaporization from the solid sample is attractive when it is desirable to detect trace quantities without further sample preparation and dilution and when a rapid analysis is required.

Earlier work with a pulsed glow discharge has shown that atom populations sputtered from the cathode remain available for excitation for times on the order of a few ms after the discharge has been extinguished [6]. Thus, the glow discharge can be operated in such a way as to produce a stable ground state atom population and a resultant atomic fluorescence free from background emission.

EXPERIMENTAL

The glow discharge cell used in this work is shown schematically in Fig. 1. It is similar in design to the one used in a previous experiment [6] but has been reduced in overall dimensions and the water-cooled cathode holder has been modified to accept a 6.35-mm diameter sample rod. The circuit used to shunt the discharge off is discussed in the previous publication [6]. Briefly, a high voltage VMOS power FET (Motorola MTMIN100) is triggered by a signal generator (Wavetek Model 805) to shunt a 720 Ω resistor across the discharge causing it to go dark within 0.5 μs. A laboratory constructed variable delay circuit triggers the laser 300 μs after the discharge is extinguished, and the discharge is allowed to re-ignite 200 μs later. The discharge is operated at 20 Hz which is the optimum repetition frequency for the dye laser. In previous studies [6], the discharge was shunted off for times up to 10 ms in order to observe the behavior of the decaying atom population. In the present work, a shorter time (500 μs) was chosen to improve the overall stability of the discharge. The intensity of the fluorescence signal was the same with

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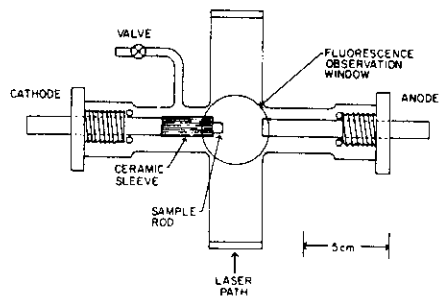

Fig. 1. Schematic drawing of the glow discharge cell.

the discharge operating continuously indicating that no significant loss of atom population occurs during the 500 μs that the discharge was off. The background noise, however increased 10–100 × when the discharge was not shunted off prior to the fluorescence measurements.

The non-resonance fluorescence signal is detected at 90° to the laser beam path from a region extending from approximately 3 to 6 mm in front of the cathode surface. Laser excitation is provided by a frequency doubled nitrogen pumped dye laser (Molectron Models UV-24 and DL-II) tuned to the 283.31-nm lead transition. The laser has a spectral line width of 0.015 nm (FWHM) and a pulse width of 5 ns with a typical pulse energy of 5 μJ. The laser is unfocussed with a beam area of approximately 15 mm². The fluorescence radiation at 405.78 nm is collected with *f*/2 fused silica optics (1:1 imaging) and detected through a 0.5-m monochromator with a spectral bandpass of 8 nm (Spex Model 1870) by a Hamamatsu R1414 photomultiplier tube. The laser beam traverses the discharge parallel to the spectrometer slit and the area of the beam roughly approximates the dimensions of the atom cloud produced from the cathode. A long-pass sharp cut filter (Corion LG-350, 350 nm cut-off) placed in front of the slit ensures that no scattered laser radiation reaches the detector. The photomultiplier signal is terminated with a 1000 Ω load resistor, amplified by a wideband amplifier (Evans, Model 4163, DC-10 MHz) and processed by a boxcar averager (Stanford Research Systems, Model SR 250). The photocurrent pulse resulting from the laser induced fluorescence is stretched to 100 ns (FWHM) by the 1000 Ω load resistor and sampled with a boxcar gate of 30 ns. The boxcar is triggered in the conventional way by a laboratory-constructed photodiode pickoff at the laser. Figure 2 shows a block diagram of the entire experimental set-up.

Two different types of samples were examined in this work. Aqueous solutions of lead (prepared by dissolving lead nitrate) were introduced to the discharge by drying in air a 5-μl aliquot on the end face of spectroscopically pure graphite electrode (6.35 mm dia. × 103 mm length). Copper rods (NBS Standard Reference Materials No. 494–500) of the same dimensions which were certified for lead concentration over the range 0.4–128 μg/g were also used. In either case, the rods slip-fit into a water-cooled brass sample holder and were insulated with a 12.7 mm dia. × 35.0 mm long ceramic sleeve which confined the negative glow region of the discharge (and consequently the sputtering process) to the tip of the sample rod. A stainless steel anode of 12.7 mm dia. was positioned 4.0 cm from the cathode face producing a simple planar geometry glow discharge with no positive column and a thin anode glow. Both the anode and cathode holder were held in place by threaded glass vacuum fittings (Ace Glass Co.) and were easily

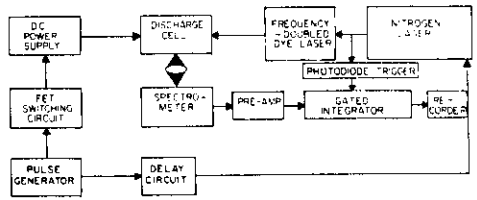

Fig. 2. Block diagram of the experimental system.

removed for cleaning or sample exchange. In order to achieve a reproducible atom population within the discharge cell, a consistent pumping and flushing procedure was adopted which involved evacuation to 13 Pa (0.1 torr), pressurizing to 5 psi with argon, evacuation to 13 Pa again and finally, filling to the operating pressure, usually 900–1000 Pa (7–8 torr). The entire process required ~ 6 min and resulted in a fluorescence signal reproducible to within 1–2%. A single rotary vacuum pump was used; fill gas pressure was monitored with a capacitance manometer and regulated with precision values. Upon ignition the discharge produced an abnormally large fluorescence signal which decayed over a period of several minutes to a constant and reproducible level. Figure 3 shows a typical trace of the fluorescence signal from a copper cathode sample (NBS No. 494) containing 26.5 μg/g lead. The discharge was routinely operated at 600 V (measured across the discharge) and at currents of 40–50 mA. The graphite electrodes required a larger ballast resistor in series with the discharge (6200 Ω) and a higher power supply voltage in order to maintain 600 V across the discharge. For either type of electrode a minimum of 550 V was required across the discharge in order for the discharge to reliably re-ignite after being switched off.

Results and Discussion

Figure 4 shows the combined results of 12 separate determinations of the analytical curve for lead in copper over the range of concentrations present in the NBS SRM sample rods.

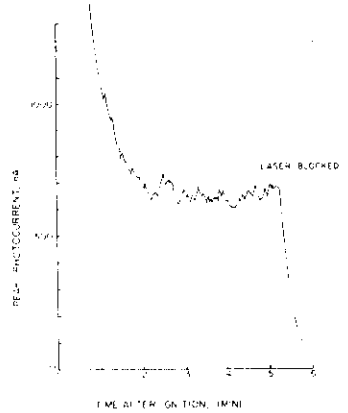

Fig. 3. Fluorescence signal obtained from a copper rod containing 26.5 μg/g Pb.

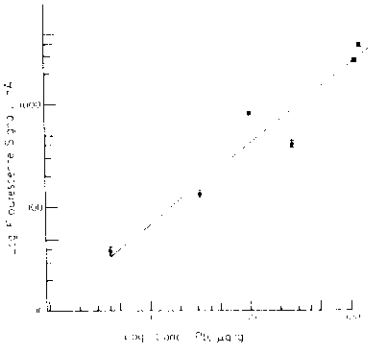

Fig. 4. Analytical curve for lead in NBS copper Standard Reference Materials No. 494–500.

Prior to use, the rods were cleaned by the procedure recommended by the NBS: rinsed in 1 : 1 nitric acid followed by a rinse in 1 : 1 hydrochloric acid, a rinse with distilled water, and air dried on filter paper.

It was not possible to obtain a measurement of the true blank signal because a copper cathode known to be free of lead was unavailable. Therefore, a measurement was made of the signal with the laser blocked or with the laser tuned off the lead wavelength. In either case, the resulting signal and its accompaning noise is due only to randomly occurring dark current pulses falling within the 30 ns gate of the boxcar (standard deviation ~ 0.2 nA) and to radio-frequency interference picked up from the firing of the nitrogen laser (standard deviation ~ 1.3 nA). These standard deviations are determined from 16 measurements with an instrumental time constant of 15 s. The slope of the analytical curve is 27 nA per μg/g Pb. The detection limit at 3 times the standard deviation of the background is therefore 0.1 μg/g Pb. The discharge is fully extinguished at the time the laser fires and scatter from the laser beam is completely eliminated by the sharp-cut filter and monochromator.

Two points on the analytical curve (at 10 and 26.5 μg/g) deviate reproducibly with respect to the other four. At this time, there is no clear explanation of these anomalous points. All six points on the analytical curve exhibit relative standard deviations of 8–20%. The unlikely possibility of a non-resonance spectral interference was examined and eliminated as an explanation. The possibility that the two cathodes had been interchanged was eliminated as an explanation by performing separate analysis by atomic absorption which verified the NBS certification values.

Samples of these two electrodes (~ 0.5 g) were also dissolved in nitric acid and analysed by drying a 5-μl aliquot on a graphite rod and introducing it as the cathode in the glow discharge. Under these conditions, the NBS certification values are also verified and the fluorescence intensities for the two samples lie in the correct respective positions on the analytical curve. The log–log slope of the analytical curve in Fig. 4 is also inexplicably low (0.8), and the correlation coefficient for the linear regression fit is rather poor ($r^2 = 0.92$). At this time, no explanation of these results is possible.

Figure 5 shows the analytical curve which results when dried aqueous solutions of lead are sputtered from graphite cathodes. The behavior of the discharge (with respect to background noise and signal levels) is similar to that obtained with the copper samples except that the analytical curve has the expected log–log slope of 1.0 and a much better correlation coefficient for the linear regression fit ($r^2 = 0.996$). The slope is 183 nA ng^{-1} and the background

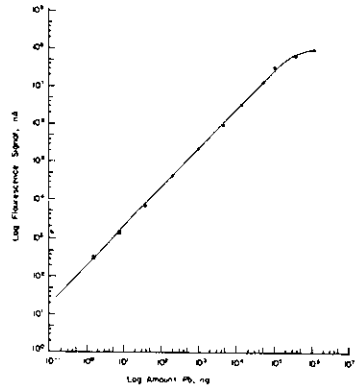

Fig. 5. Analytical curve for aqueous lead solutions deposited on graphite rods (sample volume = 5 μl).

standard deviation is 1.3 nA. The detection limit at 3 times the standard deviation of the background is therefore 20 pg pb. As with the copper samples, the limiting background noise is predominately radio-frequency pick-up from the firing of the nitrogen laser.

In conclusion, a pulsed glow discharge has been shown to provide a stable, reproducible low-background atom resevoir for laser-excited atomic fluorescence determinations.

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