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**LASER-EXCITED ATOMIC
FLUORESCENCE SPECTROPHOTOMETRY:
A feasibility study on
constructing a
spectrophotometer**

by

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MANAGEMENT PERSPECTIVE

The determination of very low level trace metals in environmental samples has been a problematic task for analysts. Existing methods often produce unsatisfactory results, as evidenced by abundant "less-than" values frequently reported by environmental laboratories.

The use of lasers can greatly increase the resolution and sensitivity of conventional spectroscopic techniques, and thereby effectively minimize the problems related to conventional equipment. Progress in laser technology has led to the rejuvenation of classical spectroscopy, because laser light is by far superior to light from other sources in terms of brightness, spectral purity, directionality and in the way it can be produced in extremely intense and short pulses. By using laser light, significant improvement in the sensitivity is expected. Some recent publications related to laser-excited atomic fluorescence spectroscopy (LEAFS) promise femtogram detection of trace metals. The development and applications of LEAF to the field of environmental analytical chemistry should result in considerable improvements with respect to effectiveness, efficiency and economy of environmental laboratories.

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PERSPECTIVE GESTION

Le dosage de teneurs très faibles en métaux traces dans des échantillons environnementaux a constitué jusqu'ici une tâche problématique pour les analystes, les méthodes existantes donnant souvent des résultats insatisfaisants. Le grand nombre de valeurs inférieures à la valeur réelle signalées par les laboratoires effectuant ce genre de dosages en est un indice évident.

Il est possible, grâce à l'emploi de lasers, d'augmenter la résolution et la sensibilité des techniques spectroscopiques classiques, donc de réduire efficacement au minimum les problèmes posés par les appareils usuels. Les progrès réalisés dans le domaine du laser ont entraîné un renouvellement de la spectroscopie classique; en effet, la brillance, la pureté spectrale et la directionnalité de la lumière laser ainsi que la possibilité de produire des impulsions extrêmement intenses et courtes dépassent de loin ce qui est permis avec un autre type de lumière. L'emploi de lumière laser laisse entrevoir la possibilité d'une amélioration significative de la sensibilité des méthodes. D'après des publications récentes dans le domaine de la spectroscopie de fluorescence atomique au laser excité (LEAFS), il deviendrait possible de détecter des traces métalliques de l'ordre du femtogramme. Le développement de la LEAF et son application dans le domaine de la chimie analytique environnementale devrait entraîner une amélioration considérable de l'efficacité et de la rentabilité des laboratoires effectuant l'analyse d'échantillons environnementaux.

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ABSTRACT

This report describes a successful feasibility study on the development of a laser - excited atomic fluorescence spectrophotometer (LEAFS). A tuned pulsed laser light was used as the excitation source for the gas phase lead atoms generated in the graphite furnace. From the sensitivity observed in this preliminary study, it is very clear that low- or sub-ppt detection limit for lead can be easily achieved. To our knowledge, it is the first working LEAFS built in Canada.

RÉSUMÉ

Ce rapport est une description d'une étude de faisabilité réussie portant sur le développement d'un spectrophotomètre de fluorescence atomique à laser excité (LEAFS). On s'est servi de lumière laser pulsée accordée pour exciter les atomes gazeux de plomb produits dans le four graphite de l'appareil. Cette étude préliminaire a permis d'observer une sensibilité indiquant de façon très évidente qu'il sera facilement possible, pour ce métal, de parvenir à une limite de détection de l'ordre de quelques ppt, voire encore moins. À notre connaissance, c'est là le premier LEAFS fonctionnel construit au Canada.

INTRODUCTION

The determination of very low level trace metals in environmental samples has been a difficult task for analysts. Existing methods generate unsatisfactory results, as evidenced by abundant "less-than" values reported by environmental laboratories. Recently, some publications related to laser-excited atomic fluorescence spectroscopy (LEAFS) promise ultra-sensitivity, down to femtogram detection of trace metals¹⁻³. This would be an ideal technique for ultratrace analyses of environmental samples. To increase reliability of very low level results, we decided to obtain and use a LEAF spectrophotometer for the development of relevant analytical methods. Because there is presently no commercial instrument on the market and only very limited information is available in the literature, a complete design, construction and assembly of the LEAFS prototype was carried out and is described in this report.

Since our laboratory has no lasers nor optics-related equipments, we utilized the services of the Ontario Laser and Lightwave Research Center (located in University of Toronto campus). We took this route with two purposes in mind: 1) to familiarize ourselves with lasers and related equipments and 2) to study the feasibility of the LEAFS, i.e. to build a laser spectrophotometer (to a first approximation) and to observe a hands-on signal, even that of a 1 ppm of an element of interest, for example lead. This report describes the successful achievement of the two goals. We observed

signals of not only 1 ppm, but also those of much lower concentrations. To our knowledge, this is the first working LEAF spectrophotometer built in Canada.

EXPERIMENTAL

Equipment. Table 1 lists the modules and instruments forming the make-up of the spectrophotometer, their specification and conditions used.

A modification to the commercial graphite furnace was made. The graphite tube and the left graphite ring was pierced through (2 mm diameter) at right angle to, and below, the sample port so that the path of the laser light is perpendicular to the tube axis (rather than along the axis).

Monochromator scanning and dye laser tuning. Before working with Pb lines, we used a HeNe laser (theoretical wavelength 632.8nm) to check the performance of the monochromator. The wavelength scanning gave the most intense light at the exit slit at 634.5nm, which we considered acceptable.

The monochromator was next scanned with the Electrodeless Discharge Lamp (EDL) Pb lamp using the setup shown in Fig. 1, giving maximum peak heights at 406.60 nm. Fixing this wavelength, the dye laser

was tuned to the Pb absorption line by directing part of the beam into the EDL lamp and observing the resultant fluorescence line (Fig. 2). The dye laser was scanned from 279 to 286 nm, and the peak maximized at 283.62 nm. In turn the latter wavelength was used to repeak the monochromator scan, and the process continued until optimized wavelengths were obtained. These wavelengths, giving maximum peakheights, were 406.65nm on the monochromator and 283.61nm on the dye laser (Fig.3) (compared to theoretical values of 405.78nm for Pb fluorescence line and 283.30nm for Pb absorption line, respectively). Figure 4 shows the synthesized experimental setup used to analyse Pb standards.

Standards. One thousand (1000) ppm Pb reference standard (from Fisher Scientific) was diluted to 1000, 100, 10 and 1 ppb working standards, using the 18 MΩ Milli-Q water and Seastar ultrapur HNO₃. All standards contained 0.2% HNO₃.

RESULTS AND DISCUSSION

The laser, furnace and interference - filter pinhole (Fig. 4) was aligned using the strong emission from a strip of fluorescent card inserted into the graphite tube through the sample port. The use of pinhole helped block out visible and near UV light. It was found possible to use a beam splitter to permit simultaneous monitoring of the reference peak (generated by the reference and tuning

channel) and the analyte peak (generated by the other channel during sample analysis) (Fig.4).

Figure 5 shows the peaks of the background, blank (0.2 % HNO_3 in Milli-Q water), and 10 pg Pb standard with maximum attenuation on the recorder, i.e. the peak height can't be made any smaller under the conditions used. Very high signal to noise ratio (20:1) indicates that the sensitivity can be improved. It is clear that the detection limit could easily reach the femtogram range with refinement of experimental setup. For example, since the residence time of the "hot" Pb atoms is very short (μs range) in an effective volume of only $\approx .03 \text{ cm}^3$, a laser with a high pulse repetition rate ($>10 \text{ Hz}$) will ensure a more adequate sampling of atoms and will improve the sensitivity further.

The fluorescence signal is, on logarithmic scales, linearly dependent on the excitation intensity until near optical saturation. There, the fluorescence signal begins to slope down and then reaches the plateau (saturation), where the signal remains constant with increase of excitation intensity⁴. The use of a neutral density filter indicated we were working in the linear region (non-saturation), i.e. we were not in the optimal region where maximum sensitivity could have been achieved. This region, which is ideal for LEAFS, corresponds to that excitation intensity where the signal just reaches the plateau (i.e. where it maximizes) and where the scatter signal (noise) minimizes^{4,2}.

The atomization temperatures tested were 2000, 1500, and 1000°C. One thousand degree C produced acceptable responses while minimizing the background signal. (Similar responses were observed when the monochromator was used in place of the filter and pinhole in Fig. 4). The responses for 1500 and 2000°C were higher but so were the background signals. The atomization temperature needs to be optimized along with an interference filter with narrower bandwidth, say 10 nm, instead of the 50 nm FWHM bandwidth used.

For ultra-sensitive work, the overall optical setup needs a more appropriate laboratory facility and finer alignment capability. For example the monochromator and the photomultiplierII (Fig.4) would require proper XYZ- tables for fine tuning (rather than hand-tuning).

The voltage for photomultiplierII was only 500 volts to generate a sensitivity shown in Fig.5. The voltage can be raised to increase the sensitivity further. To obtain proper data acquisition and subsequent quantitation, a PC with appropriate software and interface with the boxcar would be required.

The tuning process (Fig. 2) was developed to take advantage of the relatively high power of an EDL lamp compared to a hollow cathode lamp. It was found possible to use a commercial EDL lead lamp to tune the dye laser. Without an EDL lamp we would have to build an inhouse lamp² or use a separate flame atomic absorption

spectrometer³. Tuning the dye laser proved to be quite elusive. Accurate optical alignment coupled with very slow scanning and proper "tracking" of the second harmonic generator was a prerequisite.

CONCLUSION

The feasibility study on the construction of a laser-excited atomic fluorescence spectrophotometer for trace metal analysis was successfully carried out. To our knowledge, it is the first working LEAF spectrophotometer in Canada. Judging from the sensitivity observed in this preliminary study, it is very clear that low- or sub-ppt detection limit for lead can be easily achieved. We are assembling the various components of the spectrophotometer in our laboratory and should have a working prototype by the end of the fiscal year.

ACKNOWLEDGMENT

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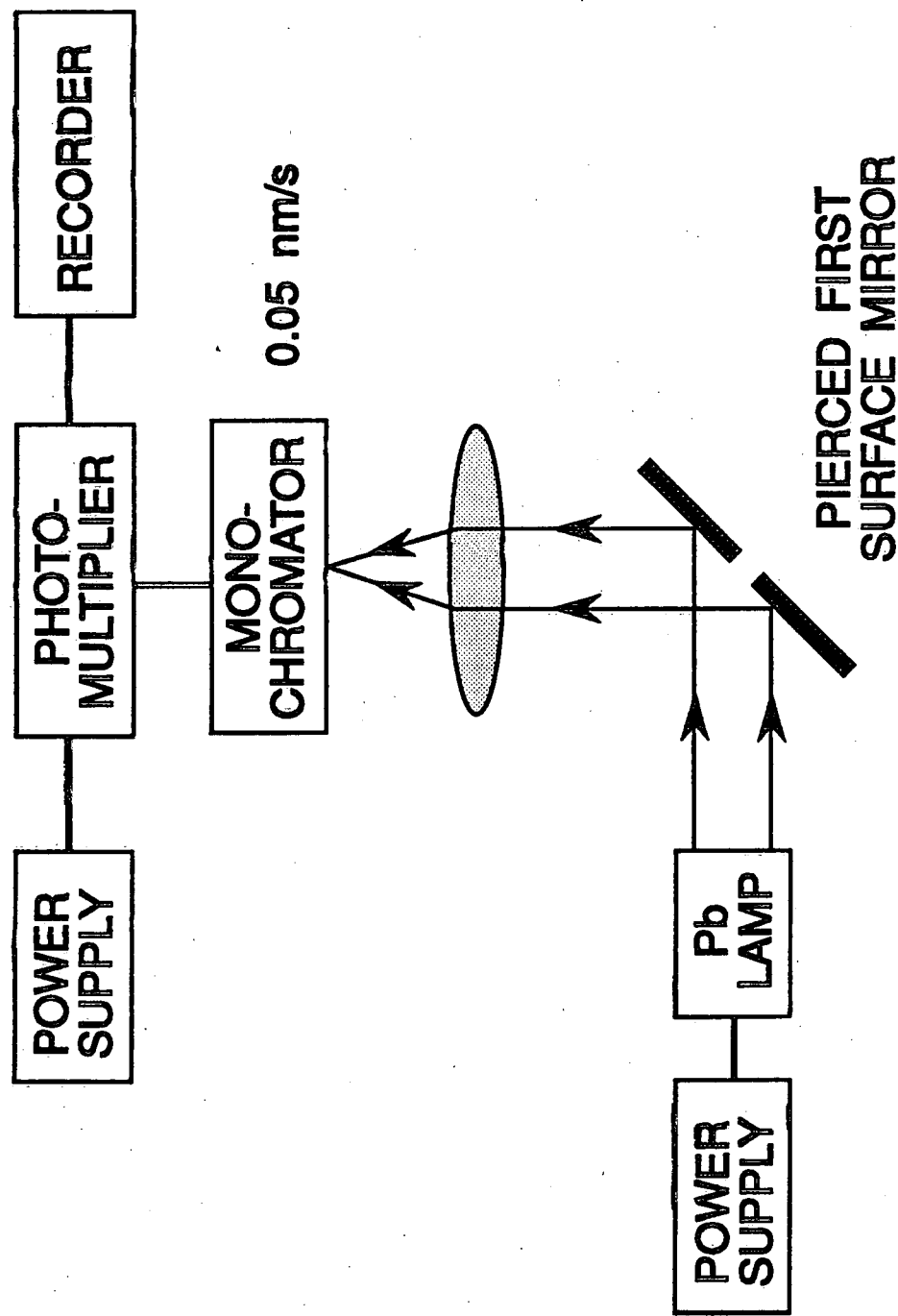
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TABLE 1. EQUIPMENT SPECIFICATIONS AND CONDITIONS USED

PULSED Nd:YAG LASER	Qanta-Ray DCR-3 (Spectra Physics)
Energy / pulse	400 mJ at 532 nm
Pulse width	5-7 nm at 532 nm (7-9 at 1064)
Pulse repetition rate	10 Hz
PULSED DYE-LASER	Quanta-Ray PDL-2 (Spectra Physics)
Tuning range	380-920 nm
for Rhodamine 590	553-577 nm
Spectral width	0.2 / cm
(with etalon)	0.05 / cm
Pulse duration	< 7 ns
Pulse energy	90 mJ
SECOND HARMONIC GENERATOR	Autotracker II (Inrad, Inc.)
Wavelength range	217 - 470 nm
Output stability	± 1%
Pulse energy	up to 6 mJ
Control	Control display module (manual ,auto)
scanning rate	0.025 nm / sec / Hz (.1 nm / sec max.)
UV harmonic separator	Inrad (m / n 752 - 104)
UV energy output	~ 1.3 mJ
LEAD LAMP	EDL lamp (power supply 10 watts)
ELECTROTHERMAL ATOMIZER	Perkin-Elmer HGA 2100
Dry, char, atomization temperature	120, 500, 1000 - 2000°C
Sample volume	10 uL
MONOCHROMATOR	GCA / McPherson Instr., EU-700-56
Aperture ratio	f / 6.8 at 200 nm
Focal Length	0.35 m
Reciprocal line dispersion	2 nm / mm
PHOTOMULTIPLIER I	IP28 (power supply set at 800 volts
PHOTOMULTIPLIER II	Products for research, PR1405 SHRF
	IP28 (power supply set at 500 volts)
BOXCAR INTEGRATOR	SR 250 (Stanford Research Systems)
Gate width	50 uS (multiplier 1); 100 (mult. 3)
OSCILLOSCOPE	Iwatsu Electronics, SS-5706 (30 Mhz)
CHART RECORDER	BBC Goertz Metrawatt SE120

**Figure 1. CALIBRATION OF THE SPECTROMETER FOR THE
EXPERIMENTAL Pb ATOMIC FLUORESCENCE
WAVELENGTH - 406.60 nm**



**Figure 2. DYE LASER TUNING SET-UP FOR EXPERIMENTAL
Pb ABSORPTION WAVELENGTH - 283.61 NM**

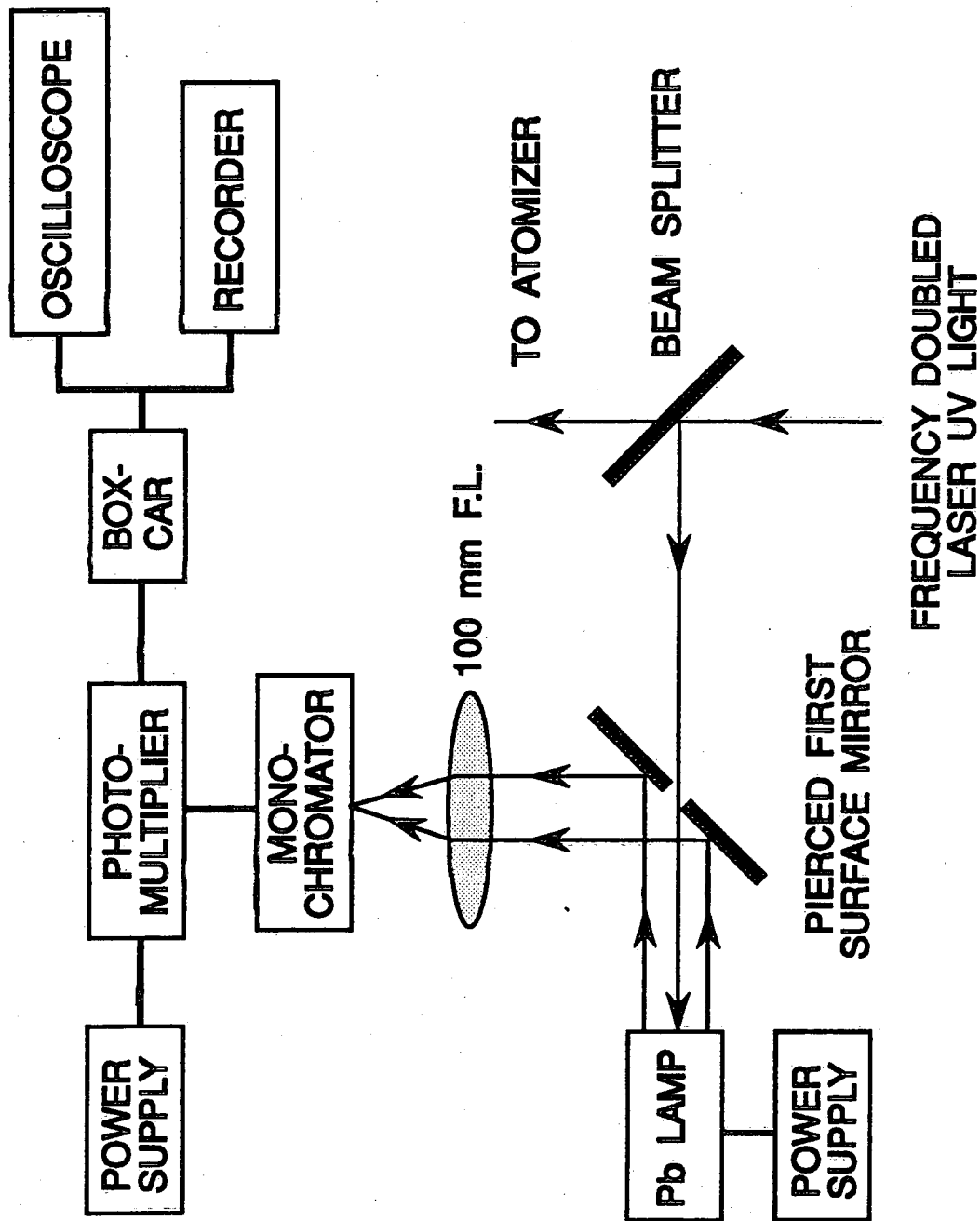
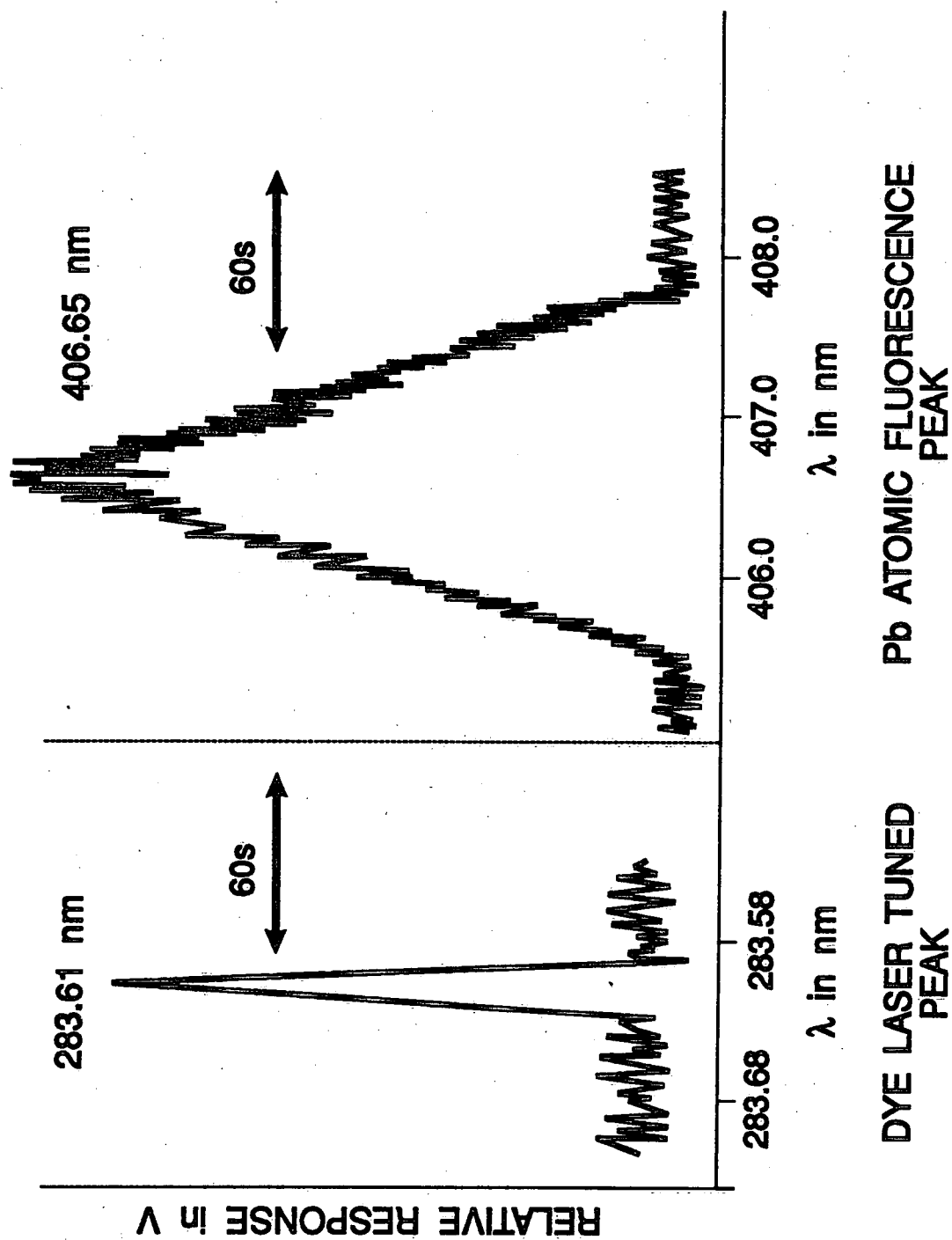


Figure 3. CALIBRATION AND TUNING PEAKS FOR Pb



**Figure 4. BLOCK SCHEMATICS OF LASER-EXCITED
ATOMIC FLUORESCENCE SPECTROMETER**

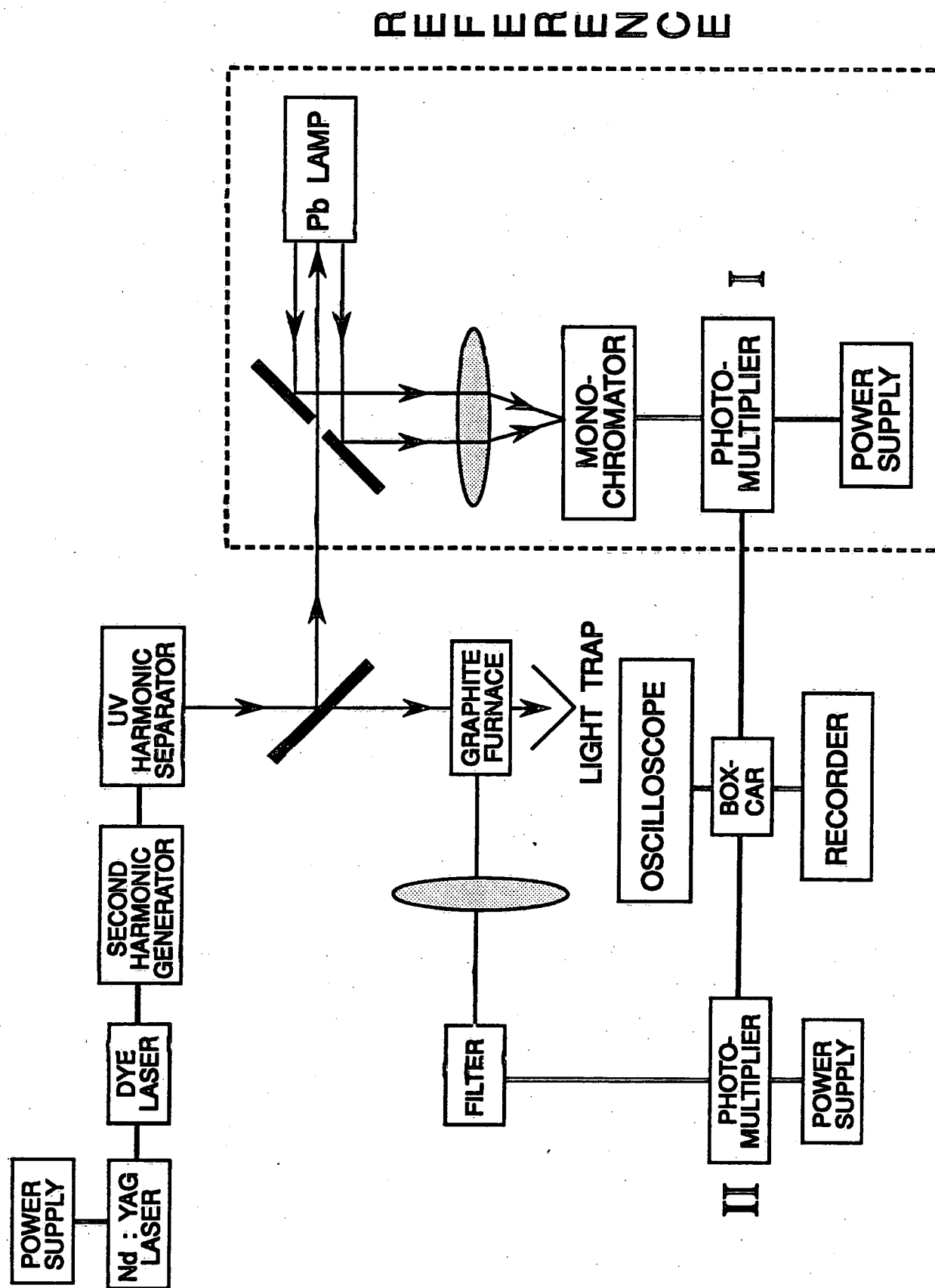


Figure 5. LEAFS RESPONSE TO 10 pg OF LEAD

