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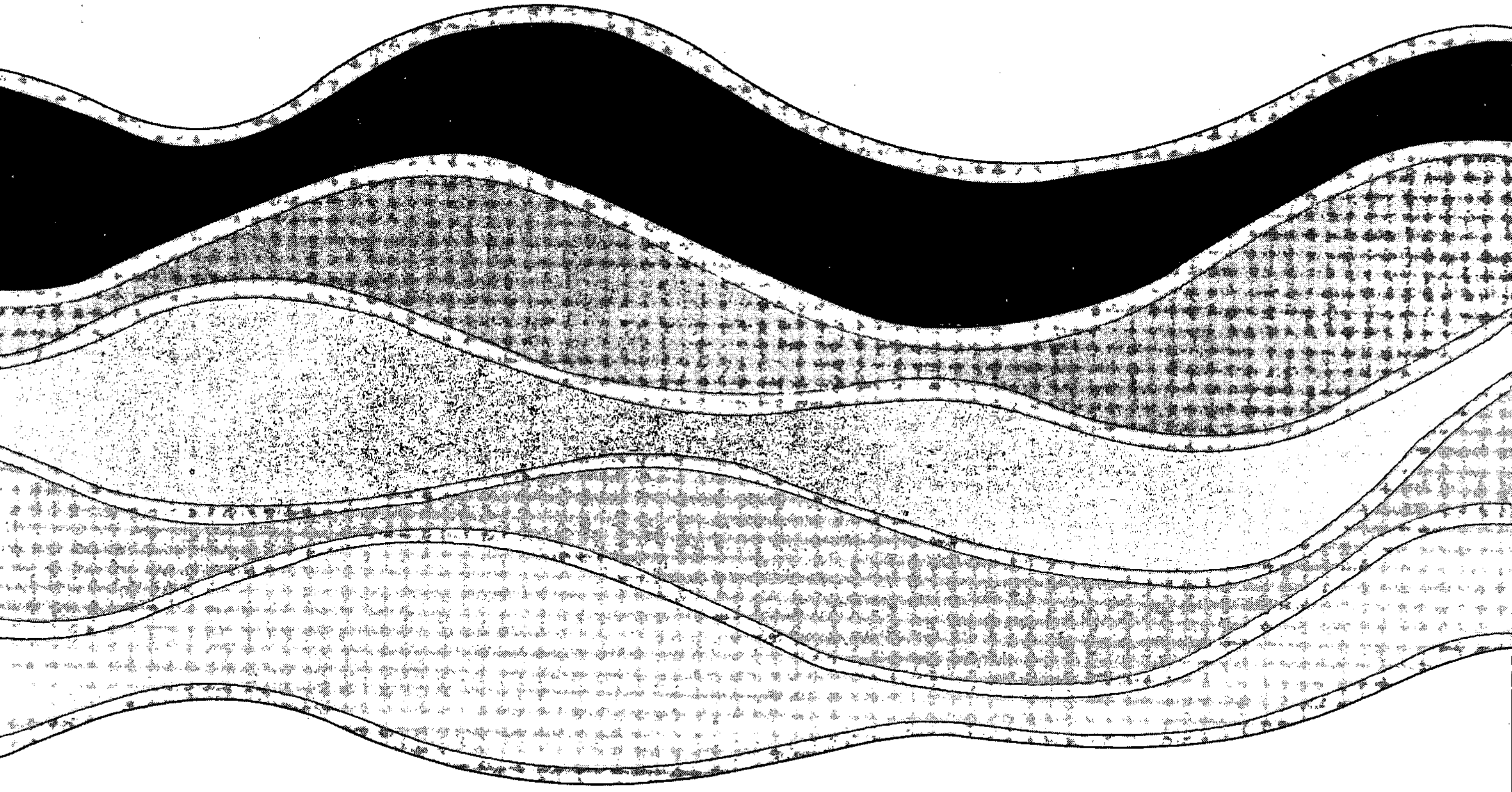

LASER SPECTROSCOPY. Part II* - COPPER VAPOR LASER-BASED ATOMIC FLUORESCENCE SPECTROMETER

V. Cheam, R. Desrosiers, I. Sekerka and J. Lechner

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* Part I is reference 11

MANAGEMENT PERSPECTIVE

The development of "New technologies" and the increase in "Analytical capabilities" are an integral part of the Canada's Green Plan for the "Great Lakes Prevention Initiative" and for "Preserving the Integrity of the Canadian Artic". To adequately meet these challenges, NWRI has embarked on the development of novel instruments and methods; namely Laser-Excited Atomic Fluorescence Spectrometers (LEAFS), new method for easily tuning lasers to specific wavelengths, and analytical methods using LEAFS for direct analysis of environmental samples. This report details the technical aspects underlining the construction of a Copper Vapor Laser - based LEAFS, particularly the configuration and manipulation of lasers, optics and electronics required to improve the sensitivity and to simplify the overall operation. The described LEAFS is an ultrasensitive instrument unmatched by any conventional instrument. The report also serves as a simple but adequate reference for those scientists who want to build a LEAFS for their own research.

Since there is no LEAFS available commercially, one of our goals is to commercialize it in the near future. This goal is realistic given the fact that laser technology and hi-tech instruments are progressing rapidly.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Le développement de «nouvelles technologies» et l'accroissement des «capacités analytiques» font partie intégrante du Plan vert du Canada, et notamment de l'«Initiative de prévention pour les Grands Lacs» et de la «Préservation de l'intégrité de l'Arctique canadien». Pour répondre efficacement à ces défis, l'INRE s'est engagé dans le développement de nouveaux instruments et méthodes, comme le spectromètre de fluorescence atomique avec excitation par laser (LEAFS), une nouvelle méthode permettant de syntoniser facilement des lasers à des longueurs d'onde spécifiques, et des méthodes analytiques utilisant le LEAFS pour l'analyse directe des échantillons environnementaux. Le présent rapport décrit en détail tous les aspects techniques ayant conduit à la mise au point du LEAFS à base de laser à vapeur de cuivre - particulièrement la configuration et la manipulation des lasers et des dispositifs optiques et électroniques nécessaires pour améliorer la sensibilité et simplifier l'utilisation. Le LEAFS décrit est un instrument ultrasensible, surpassant tous les appareils classiques. Le rapport sert également de référence simple mais suffisante pour les scientifiques qui veulent se doter d'un LEAFS pour leurs propres recherches.

Étant donné qu'il n'existe aucun LEAFS sur le marché, l'un de nos objectifs est de le commercialiser dans un proche avenir. Cet objectif est réaliste si on tient compte du fait que la technologie du laser et les appareils de haute technicité progressent rapidement.

ABSTRACT

This report documents the continuing progress of the research and development work on Laser-Excited Atomic Fluorescence Spectrometry (LEAFS) undertaken at NWRI. It deals with a Copper Vapor Laser - based spectrometer and details the technical aspects underlining the design of LEAFS, particularly the configuration and manipulation of lasers, optics and electronics required to improve sensitivity and to simplify operation. The sensitivity obtained with this new LEAFS is 100 times better than the first one we built earlier [11].

RÉSUMÉ

Le présent rapport traite des progrès permanents en matière de recherche et de développement dans le domaine des spectromètres de fluorescence atomique avec excitation par laser (LEAFS) à l'INRE. Il porte plus précisément sur un spectromètre à base de laser à vapeur de cuivre et donne en détail tous les aspects techniques ayant permis la mise au point du LEAFS, particulièrement la configuration et la manipulation des lasers et des dispositifs optiques et électroniques nécessaires pour améliorer la sensibilité et simplifier l'utilisation. La sensibilité obtenue à l'aide de ce nouveau LEAFS est 100 fois supérieure à celle du premier que nous avions mis au point précédemment.

INTRODUCTION

As laser technology is rapidly improving, so are laser-based instruments. The classical atomic fluorescence spectrometry, which had been practically forgotten since the appearance of AAS in mid-1950, has abundantly benefited from this rapid laser progress and has become a topic of intense interest in scientific community [1-12].

The determination of very low levels of heavy metals in environmental samples with existing methods often leads to unsatisfactory results. Ultrasensitive techniques are needed for this type of analysis. Spectroscopy using a laser light source is the most promising technology given the increased resolution and sensitivity that can be achieved over other methods. Among various spectroscopic techniques, Laser-Excited Atomic Fluorescence Spectrometry (LEAFS) utilizing graphite furnace atomizer is the method of choice due to its potential of single atom detection.

This report, the second one in a series, documents the continuing progress of the research and development work on Laser-Excited Atomic Fluorescence Spectrometry (LEAFS) undertaken at NWRI. The first report (Part I) dealt with the feasibility study on constructing a LEAFS based on an Nd:YAG- pumped dye laser, in collaboration with the Ontario Laser and Lightvawe Research Centre located at the University of Toronto [11]. Even though this Nd:YAG-based LEAFS was successfully built and had excellent sensitivity, it was essentially the University's property and it was cost-ineffective to go there and use it regularly to develop methods for analysis of environmental samples. Furthermore, based on literature, it would be advantageous to utilize a pumping laser with higher repetition rate such as a metal vapor laser. This report (Part II) details the various manipulations of a copper vapor laser-pumped dye laser, optics and electronics to improve the sensitivity, to simplify the LEAFS operation and to serve as a simple but adequate reference for those scientists wishing to build a LEAFS for their own research. This new LEAFS is located in the CCIW complex and is the first one in Canada which has been succesfully applied to the analysis of environmental samples [2, 13].

LASERS AND OPTICS

A Copper Vapor Laser (MLT20, Metalaser Technologies) was chosen over an Nd-YAG laser (11) or other lasers because of its high repetition rate (4-10 kHz), which is advantageous as it generates a larger number of fluorescence pulses during the atomization time, thus resulting in better sensitivity. This laser simultanously emits a green light (510.6 nm) and a yellow light (578.2 nm), with a ratio of ~2:1 during normal operation at 6 kHz. The green light is filtered through via a dichroic beamsplitter and used to pump a dye laser (DL-13, Laser Photonics). The built-in oscillator was found to be very unstable causing severe Thyrathron instability and laser malfunction. To rectify this we used an external HP3311A function generator set at 6 kHz to trigger the Copper Vapor Laser (CVL).

A fluorescent organic dye (Rhodamine 6G dye in chloride form) was used in the dye laser to provide a tunable range of working wavelengths of about 550 nm to 590 nm, which can be frequency-doubled by a second harmonic generator (Autotracker II, Inrad Inc.) to give UV light required for atomic spectroscopy of heavy metals. Due to the high laser "reprate" (6 kHz) and low pulse energy, we found it was necessary to use an intracavity polarization rotator in front of the oscillator dye cell (to increase polarization by a factor of about 100) and an achromat to focus the light onto the Second Harmonic Generator' s crystal in order to generate the UV light. This radiation passes through a Perkin Elmer model HGA 2100 graphite furnace where it is absorbed by metal atoms. The light fluoresced by the excited atoms is collected from the furnace using a pierced mirror placed in front of the furnace. Two plano convex lenses focus the fluorescent light through a 10 nm bandpass dielectric filter onto the entrance slit of a Schoffel GM250 monochromator. This radiation is dispersed by the grating monochromator and sensed by a Thorn EMI 9813 photomultiplier mounted at the exit slit. The signal is measured by an EG&G model 4121 "boxcar" gated integrator. The resultant averaged measurement is further averaged and stored by a PC AT based data acquistion system to be discussed below in detail in ELECTRONICS section.

Having set the lasers up, it is imperative that the dye laser be tuned to the correct spectral line of the element of interest. Without proper tuning, the atomic transition will not take place adequately to achieve saturation of the excited state. Without saturation, fewer atoms are excited and subsequently fluoresce, resulting in lower signal to noise ratio and poorer detection limit. Since the CVL pulse energy is much lower than the Nd:YAG's, it was advantageous to have the tuning setup behind the graphite furnace, not in front of it as previously done via beamsplitted UV light (11). The UV radiation passes through the furnace to a Perkin Elmer EDL lamp used as atom source for tuning the dye laser to the correct spectral line of the element. With this configuration, the entire UV light is dedicated to LEAFS operations (particularly useful for those requiring low irradiance light) as well as for tuning process. The linewidth of the induced fluorescence was found to be 0.003nm based on the manufacturer's dial settings and was also verified to be 0.003 nm using a Burleigh wavemeter model WA-4500. The description and discussion on tuning has been detailed elsewhere (1). We have found that during several hours of operation the dye laser may drift by 3pm from the original centre wavelength. This is an appreciable fraction of the atomic absorption linewidth and without re-tuning the sensitivity is significantly reduced.

ELECTRONICS

a) Overview

The basis of the detection system is an EG&G model 4121 "boxcar" integrator. The boxcar is a gated integrator with averaging performed by a low pass filter. An idealized laser fluorescence pulse train consists of an array of rectangular pulses which individually look similar to railway boxcars- hence the name boxcar integrator or boxcar averager. The boxcar reduces noise by integrating each pulse and then averaging the integrated values. Because of its synchronization with the laser, the boxcar is "on" only when a signal is present. A voltmeter on the other hand is always "on" even when no laser pulses are present. During these periods the voltmeter is susceptible to noise. This is why a boxcar offers much reduced noise in comparison to a simple detector. The boxcar isn't perfect however. Only a small number of gate widths (durations) are available on the boxcar making exact matching with the signal duration difficult. Also synchronous noise which occurs exactly at the gate interval cannot be removed by the boxcar. As well, noise or background which occurs during the gate open period is not reduced by the boxcar under normal operation except through the integration and averaging process.

b) Photomultiplier interconnections

The photomultiplier (PMT) was mounted in the standard 300 mm long B2F/RFI uncooled housing provided by Thorn EMI. This included EMI's standard voltage divider, magnetic shield, RF shield and room for the gating circuit mentioned in section c) below. After its failure, the gating circuit was removed. A ferrite bead was placed over the signal line to see if this had any effect on signal noise characteristics. No improvement was noted. The PMT was connected via a coaxial cable to the boxcar's 1 Mohm input, onto which a BNC Tee connector had been mounted; at the end of this T a 10 kohm termination resistance was installed. This arrangement effectively stretched the 5 ns pulses to $1\mu s$ pulses because of the 100 pF distributed cable capacitance and the 10 kohm load. Loads of 1 and 10 kohm were tried; the 10 kohm was found to give better results. Because of impedance mismatch between the 10 kohm termination and the nominal 50 ohm line, multiple ringing oscillations were evident on the oscilloscope. This was expected and is of little consequence since this ringing is averaged out by the boxcar. The proper 50 ohm termination for minimal ringing was used only with osciloscope measurements. The advantage of pulse stretching is that timing jitter relative to signal duration is reduced and signal durations can be matched to gate width settings on the boxcar. Additionally, since the PMT is a current source, an increase in the load resistance increases the voltage level to more convenient levels. However it does make fluorescent lifetime measurements impossible.

c) Delay and Power-on Width for PMT Gated Power Supply

In our early work a Thorn EMI model GB1001B gating circuit was used to control the Thorn EMI model 9813B-QA photomultiplier. Gating of the PMT is a simple method to reduce background. If the PMT is powered on only during the duration of the received fluorescent pulses, one has in effect a crude synchronous detector which rejects incoherent signals. However, the gating board has a response time much slower than the laser. Thus if the gating board were triggered directly by the laser pulse, the laser pulse would have passed by long before the gating board turned on the PMT. A circuit was therefore built to synchronize the gating board with the previous laser pulse. A simple delay circuit using a 74HC4538 was used (see Figure 1 for the schematic). An optoisolator (not shown on this schematic) was used to isolate the circuitry from the laser trigger. The optoisolator inverted the trigger signal from the laser external oscillator as shown by the timing waveform on Figure 1. The first half of the 74HC4538 was triggered by the falling edge of this optoisolator pulse. An adjustable delay created by turning a front panel mounted potentiometer allows synchronization of the PMT power-on with the laser pulse . Up to 200 μs of delay could be created. Since the repetition rate of the laser is 6 kHz, which corresponds to 166 μs between pulses, this was more than sufficient.

The duration of the power-on period was set by the second half of the 74HC4538 and could be adjusted from 100 ns to 10 μs. The power-on period was limited by the original gating circuit itself. The manufacturer's specification was for a minimum 2 μs "on" period with a 0.1% duty cycle. We used a 2 μs period but the 6 kHz laser repetition rate imposed a 1.2% duty cycle. This circuit was used for a short period but was discontinued after the Thorn EMI gating circuit failed. We suspect that the cause of the failure was the large duty cycle. A faster gating circuit with a larger duty cycle is presently under construction and test. For most of our work, however, no gating circuitry was used. Instead a circuit was designed and built to make use of the boxcar baseline subtraction feature. This is described in section d) below.

d) Boxcar Triggering Electronics and Baseline Subtraction Technique

The copper vapor laser was externally triggered by an HP model 3311A function generator. This was found to give improved stability over the internal oscillator of the copper vapor laser. The external oscillator also provided synchronization of the detection electronic system to the laser pulse.

A fast optoisolator (U4 in Figure 2) was used to isolate the detection system trigger from the copper vapor laser. A ferrite bead (L1 of Figure 2) was used between the function generator and the optoisolator to reduce laser power supply induced noise. The optoisolator output was used to trigger two EG&G model 4121 boxcar signal averagers -- one for LEAF measurement and one for tuning. These averagers were used principally in what EG&G refer to as their "baseline 2" mode. In this mode two samples are taken one of the signal and one of the background and the difference is transferred to the averager. This mode requires twice as many triggers as in the uncorrected normal mode. It also requires a logic signal which sets the boxcar's "baseline I/O" line low to take a "baseline" sample and high to take a "regular" sample. Figure 3 shows the overall interconnections for LEAF "baseline 2" mode of operation.

To generate the appropriate signals a circuit shown in Figure 2 was used. Figure 4 is the timing diagram. The rising edge of the optoisolator output (timing diagram line 2) triggered one half of the 74HC4538 monostable. This produced a 50 μs wide pulse. This pulse output (1Q of U1 on the schematic, line 3 of the timing diagram) was passed to the second half of the 74HC4538. The falling edge of 1Q triggered a 10 μs pulse (2Q of U1 on the schematic, line 4 of the timing diagram). The inverse of this signal (2Qbar, line 5 of the timing diagram) was used to toggle the "baseline I/O" line on the boxcar located on the boxcar rear panel. The 2Q level was delayed by 150ns (U2 pin4, line 7 of the timing diagram) to allow the "baseline I/O" signal to stabilize. This was then "anded" with the 1Q signal (U3 pin 3, line 8 on the timing diagram). This was buffered by Schmitt trigger output drivers to form the boxcar trigger (U2 pin12, line 9 on the timing diagram). This signal formed one of the outputs of the logic box and was sent to the input of an EG&G 4144 delay generator where it was delayed by 215 ns. The signal was then directed to the boxcar trigger inputs (line 10 on the timing diagram). Most of this additional 215 ns was due to delays in the laser thyratron triggering circuit. It was determined by monitoring the laser pulse (line 11 on the timing diagram) and making sure that it coincided with the boxcar gate monitor (line 12 of the timing diagram). Thus a 12 kHz trigger output together with an output line which controlled the boxcar "baseline I/O" was produced by a 6 kHz trigger input. The net result was that when the external oscillator produced a pulse to trigger the laser, a pulse was formed which triggered a boxcar "signal" measurement. Fifty microseconds later a further pulse triggered a "baseline" measurement. Every fluorescent pulse had a baseline measurement subtracted from it. This was particularly useful with the measurement of lead (Pb) in a graphite furnace. For this element it appears that furnace blackbody stray radiation is one of the principal limiting factors in the determination of detection limit.

The 6 kHz repetition rate permitted accurate background correction under the rapid rise and fall in the blackbody radiation during atomization. However unlike Zeeman background correction for example, this baseline subtraction technique can not by itself reduce laser stray radiation or window fluorescence which may also be contributing factors to the limit of detection. It does not reduce random shot noise and Johnson noise caused by the PMT and the electronics which may occur during the boxcar gate period. Only the integration and averaging processes reduce these noises. We found this external triggering quite stable, making it unnecessary to trigger directly off the laser pulse using a photodiode. The boxcar which was used for tuning was operated in the "normal" mode since there was no varying background to subtract. The trigggering was identical however.

e) Atomization sampling period

A simple monostable circuit was built to control the atomization sampling period (Figure 5). The Perkin Elmer model 2100 graphite furnace power supply generates a trigger on atomization. This signal is located at terminal board TB303 on the side of the Perkin Elmer power supply. It is buffered and passed to a 74HC4538 which forms a pulse. The pulse duration is adjustable using a front panel mounted potentiometer, which allows the setting of atomization sampling periods from 0 to 10 seconds. This does not control the furnace firing period. It does control the period during which the data acquisition system collects data. This makes it easy for data acquisition software to determine start and stops. It is also a useful technique to get rid of secondary peaks caused by chlorides for example.

f) **Signal inverter**

An analog and digital I/O board (model CIO-AD08, Computer Boards Inc.) was connected to the PC AT bus and used for data acquisition and control. The board has either a ±5V, a ±10V or a 0 to 10V range but not a 0 to -10V range. Since a negative high voltage powered the photomultiplier, the boxcar output ranged from 0 to -10V. In order to maximize the resolution it was preferable not to use the ±10V range which would have sacrificed one bit or 2.5 mV resolution. Thus an integrated circuit opamp OP07CP was used to build an inverter with a nominal gain of -1. This was coupled to the I/O board set at the 0 to 10V range (Figure 6).

g) **Software**

Initially we used the boxcar software provided by EG&G Princeton Applied Research. It served us well for several months but with increasing use limitations in the software became evident. Data rates were limited by the IEEE-488 bus software. We could not trigger the data acquisition from an external source. Averaging of the data within a single scan was not possible. Integration and peak detection were also not possible. A data acquisition, analysis and presentation program was therefore written. The program was coded in "C" using Borland Turbo C++ with graphics extensions provided by Scientific Endeavors "GraphiC v. 6.0". The program controls the Computer Boards Inc.

CIO-AD08 data acquisition board (ADC). This board acquires samples at 1Khz rate under software control. Twenty of these samples are acquired and averaged for each point giving an effective 50 Hz data rate. Multiple averaging is done to reduce analog to digital conversion noise. Up to 5,000 of these points are collected while the program is waiting for an atomization trigger signal. Once the trigger is sensed, the program acquires data until the atomization trigger signal returns to a logical low. The program then computes the following: 1) The 50 points i.e 2.5 seconds worth of data prior to the atomization trigger are averaged to form a baseline signal. This corrects for ADC and boxcar offsets. This is called "base". 2) The peak signal during the atomization is called "peak". The "base" signal is subtracted to form "peak-base". 3) A cumulative sum of all the points measured during the atomization period is computed. This is a crude integration, which is termed "csum". 4) The baseline value "base" is multiplied by the same number of points in the computation of "csum". This is called "cbase" and is subtracted from the cumulative sum "csum" to form "csum-cbase". The values "peak-base", "csum-base" ,"base", "cbase" plus any comments are displayed on the screen, printed and stored.

All the data points used to compute the above values are stored in a separate file. These data points may be viewed graphically by selecting a function key. A computer mouse may then be used to zoom in on particular portions of the plot. The plot may be dumped to a printer or to a file as a Postscript file for manipulation by data presentation software such as for example Corel Draw. To analyse the next sample, the program prompts the user to continue or to end the session. The number of points stored is presently limited to 6,000 points. This is about 50 analyses which is a typical 2-hours run. The graphical data may be viewed after the session using the programs "Play" and "Replay". "Play" is used to view the run of data which was last taken. No file name prompts are requested. "Replay" is used to view any of the previous files. It requests a file name. Usually data are stored with the file name bearing the SI date format e.g. 920622_1 refers to the first file on June 22,1992.

THE SPECTROMETER AND ITS PERFORMANCE

Figure 7 shows the schematic of the complete CVL- based LEAFS system and Table 1 gives the various instruments forming part of the spectrometer. Figure 8 shows the sharp, well-spaced fluorescence peaks for many samples including low ppt standards. This is a marked improvement in sensitivity, data acquisition and presentation over the first system [11]. This LEAFS was successfully applied to the determination of Pb in the Great Lakes waters [2, 13].

FUTURE RESEARCH

As the research on LEAFS development continues and intensifies, the simplicity, cost-effectiveness (without compromising sensitivity) and applicability to environmental analysis are our primary goals. . It will be made more user friendly and more suitable for routine application. To further increase sensitivity, the light loss as well as background and blank signals must be minimized. The use of 1nm narrow bandpass filter or a CCD array detector instead of a monochromator will be attempted. To further improve cost-effectiveness, a LEAFS should be smaller, more compact with equal or better perfomance and ultimately with multi-element capability.

REFERENCES

1. V. Cheam, R. Desrosiers, J. Lechner and I. Sekerka, Microchem. J., in press in Microchemical Journal.

2. V. Cheam, J. Lechner, I. Sekerka, R. Desrosiers, J. Nriagu and G.Lawson,Anal. . Chim. Acta, 269 (1992) 129.

3. M. A. Bolshov, V.G. Kolosnikow, S.N. Rudnev, C.L.Boutron, U. Gorlach, and C.C. Patterson, J. Anal. Atom. Spectrometry, 7 (1992) 99.

4. M.A. Bolshov, C.F. Boutron, F.M. Ducroz, U. Gorlach, O.N. Kompanetz, S.N. Rudniev and B. Hutch, Anal. Chim. Acta, 251 (1991) 169.

5. J.B. Womack, E.M. Gessler and J.D. Winefordner, Spectrochim. Acta, 46B (1991) 301.

6. D.J. Butcher, R.L. Irwin, J. Takahashi, G. Su, G-T. Wei and R.G. Michel, Appl. Spectroscopy, 44 (1990) 1521.

7. H. Falk, H.-J. Paetzold, K.P. Schmidt and J. Tilch, Spectrochim. Acta, 43B (1988) 1101.

8. B.W. Smith, J.B. Womack, N. Omenetto, J.D. Winefordner, Appl. Spectroscopy, 43 (1989) 873.

9. G.-T. Wei, J.P. Dougherty, F.R. Preli, R.G. Michel, J. Anal. Atomic Spectrometry, 5 (1990) 249.

10. M.A. Bolshov, C.L. Boutron and A.V. Zybin, Anal. Chem., 61 (1989) 1758.

11. V. Cheam, I. Sekerka and R. Desrosiers, National Water Research Institute Contribution No. 90-128, Burlington, 1990, pp. 1-13.

12. V.M. Apatin, B.V. Arkhangel'skii, M.A. Bolshov, V.V. Ermolov, V.G. Koloshnikov, O.N. Kompanetz, N.I. Kuznetsov, E.L. Mikhailov, V.S. Shishkovskii and C.F.Boutron, Spectrochim. Acta, 44B (1989) 253.

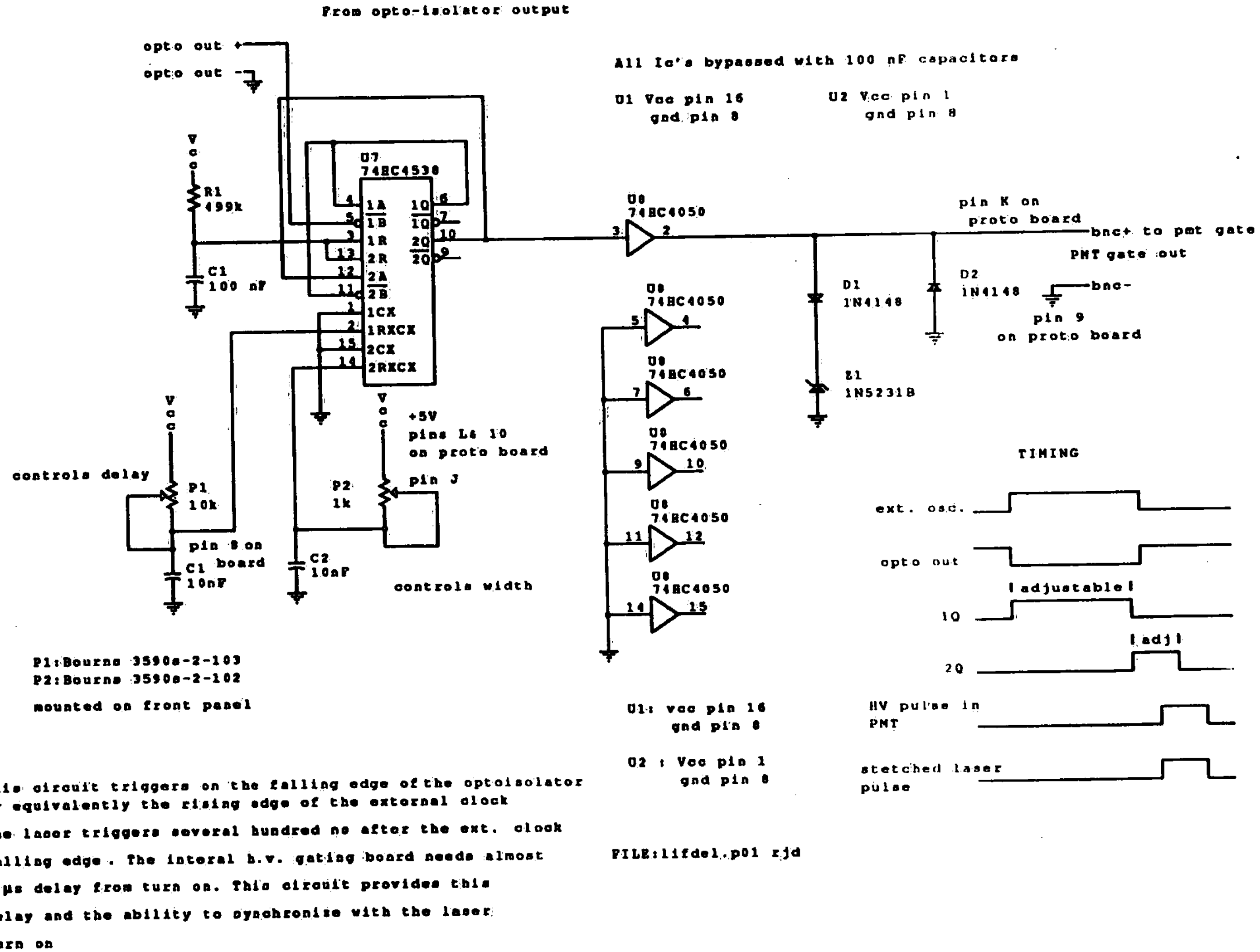
13. V. Cheam, J. Lechner, I. Sekerka, R. Desrosiers, Application of Laser-Excited Atomic Fluorescence Spectrometer to the determination of Lead in environmental samples by direct analysis, Presented at the 22nd International Roland Frei Memorial Symposium on Environmental Analytical Chemistry, at Dormund, Germany, June 9-12, (1992) P62.

TABLE 1. Equipment and Operating conditions

COPPER VAPOR LASER	MLT20 (Metalaser Technologies)
Pulse width	24 ns
Power input, Power output*	3.6 kW, 6 W
OSCILLATOR/ FNCTION GENERATOR	HP 3311A
INTERFACE BOX	In-house built
DELAY GENERATOR	4144, EG&G PAR (delay = 215 ns)
DYE LASER	DL-13 (Laser Photonics)
Dye: Rhodamine 6G	0.2g/L (4.2 x 10^{-4} mole/L)
Setting for maximum fluorescence	283.3 nm (for Pb)
SECOND HARMONIC GENERATOR	Autotracker II (Inrad Inc.)
Crystal	KDP-B
VISIBLE LIGHT FILTER	UG5, 4mm (Schott Glass Technology)
ELECTROTHERMAL ATOMIZER	Perkin-Elmer HGA 2100
Graphite Tube	8x28 mm
Dry, char, atomization	120, 500, 1800-2100C; 40, 40, 5 sec.
Sample injection, Internal gas flow	10-25 μL, Stopped flow (Interrupt)
NARROW BANDPASS FILTER	Melles Griot (405.7±5nm)
MONOCHROMATOR I	Schoeffel GM 250, 0.25m
Aperture ratio	f/3.6
Slit width	0.8 mm
PHOTOMULTIPLIER I	Thorn EMI 9813
Voltage setting (Power Supply)	1.7-2.4 kV (Thorn EMI type PM28B)

BOXCAR AVERAGER (Software) Gate width, Operation mode	4121B, EG&G PAR (in-house software) 1 μs, Baseline 2 mode
A to D CONVERTER	4161A, EG&G PAR
LEAD LAMP	EDL lamp, 10W (Perkin Elmer)
MONOCHROMATOR II Aperture ratio Slit width	GCA/ McPherson, EU-700-56, 0.35m f/6.8 at 200nm 0.3 mm
PHOTOMULTIPLIER II Voltage setting (Power Supply)	1P28 0.9 kV (Hamamatsu C956-04)
BOXCAR AVERAGER	4121B, EG&G PAR
MULTIMETER	HP 3468A
ENERGY METER Power range	Scientech 36-0201 200 mV 0.1mW - 25W

* With time the power output decreases; this value is less than half the value measured when copper metal was freshly loaded.



This circuit triggers on the falling edge of the optoisolator or equivalently the rising edge of the external clock

The laser triggers several hundred ns after the ext. clock falling edge. The interal h.v. gating board needs almost 1 µs delay from turn on. This circuit provides this delay and the ability to synchronise with the laser turn on

Figure 1. Delay and pulse width circuit for LEAFS PMT gated power supply

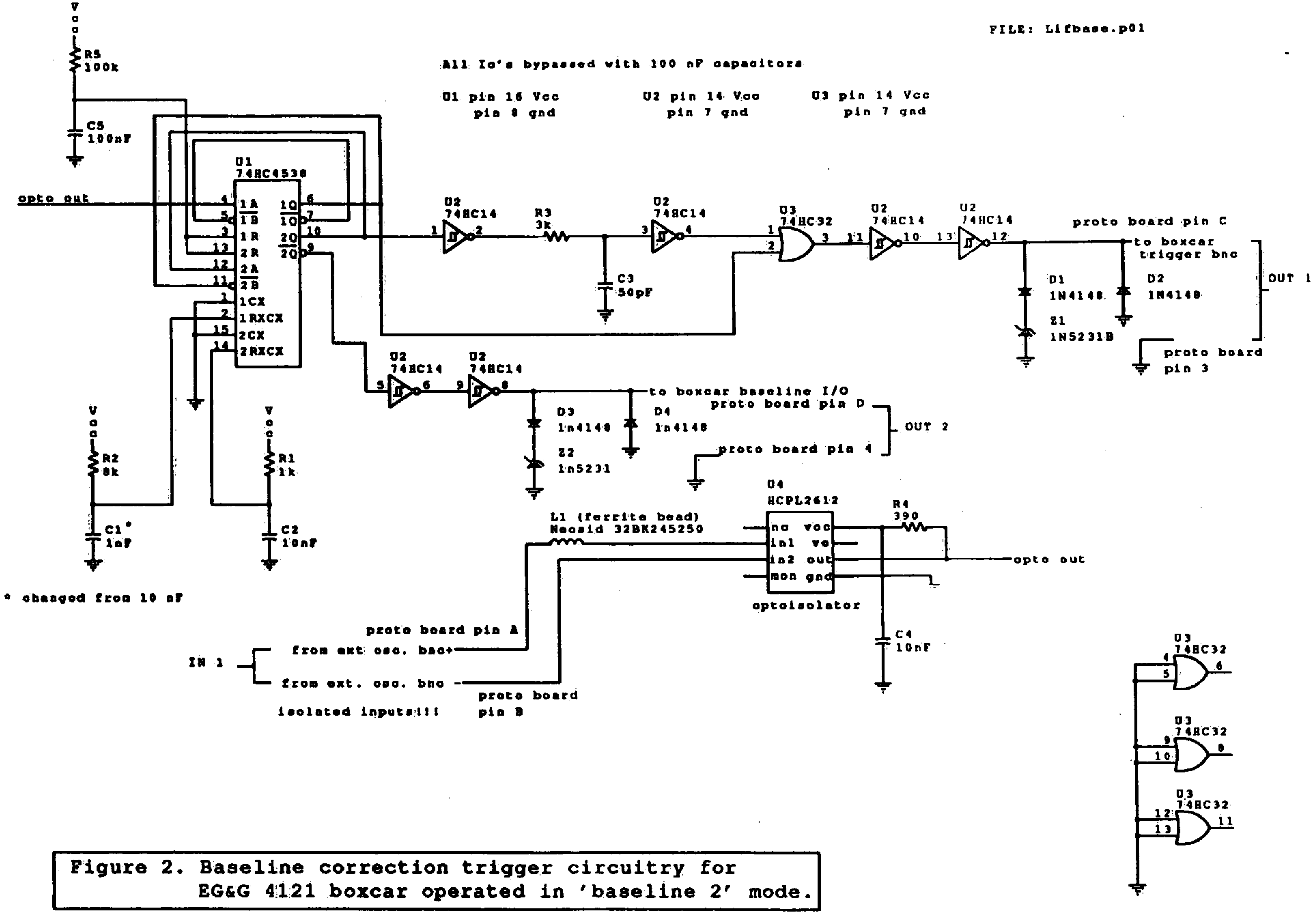


Figure 2. Baseline correction trigger circuitry for EG&G 4121 boxcar operated in 'baseline 2' mode.

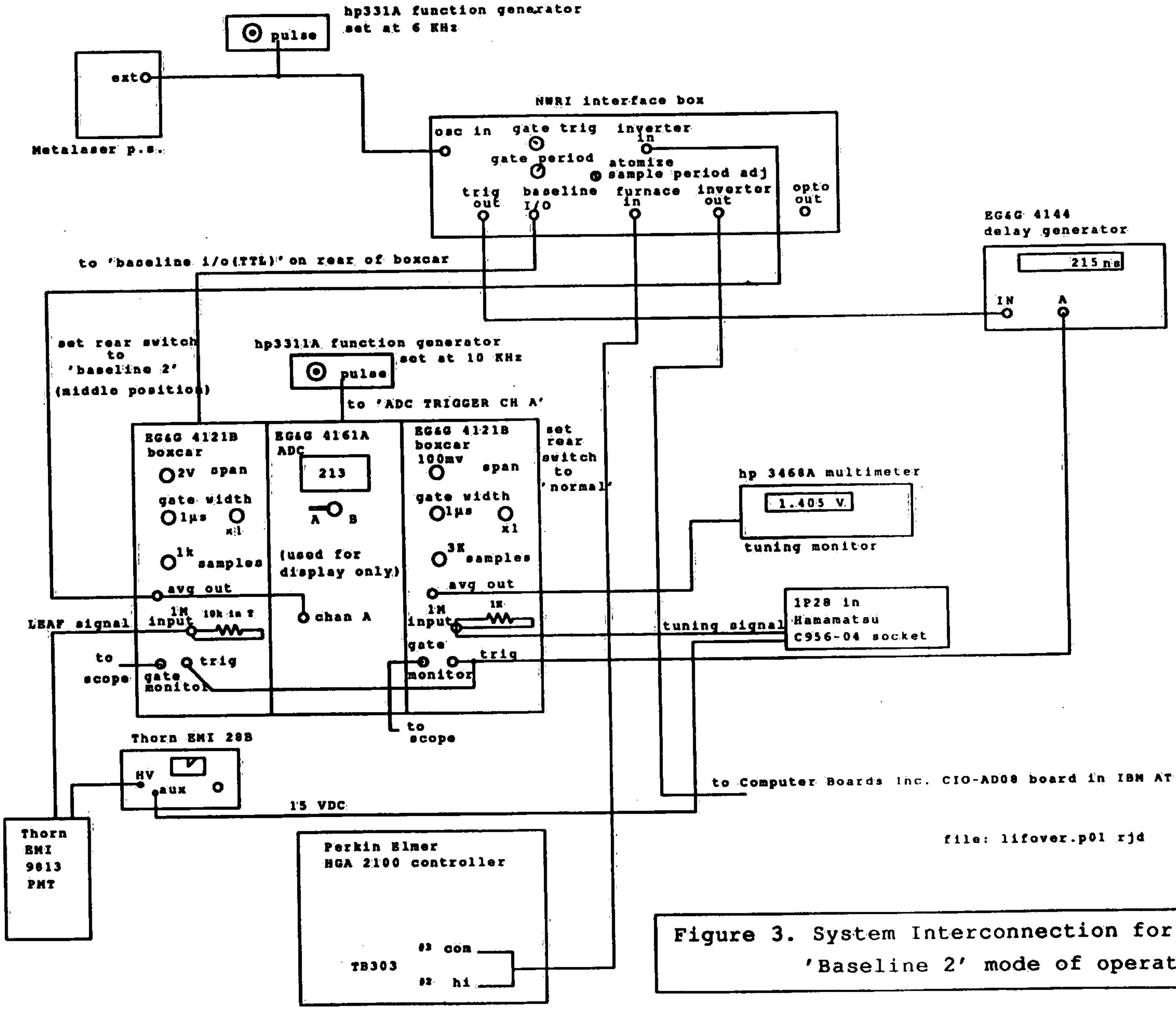


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Figure 3. System Interconnection for LEAFS
'Baseline 2' mode of operation

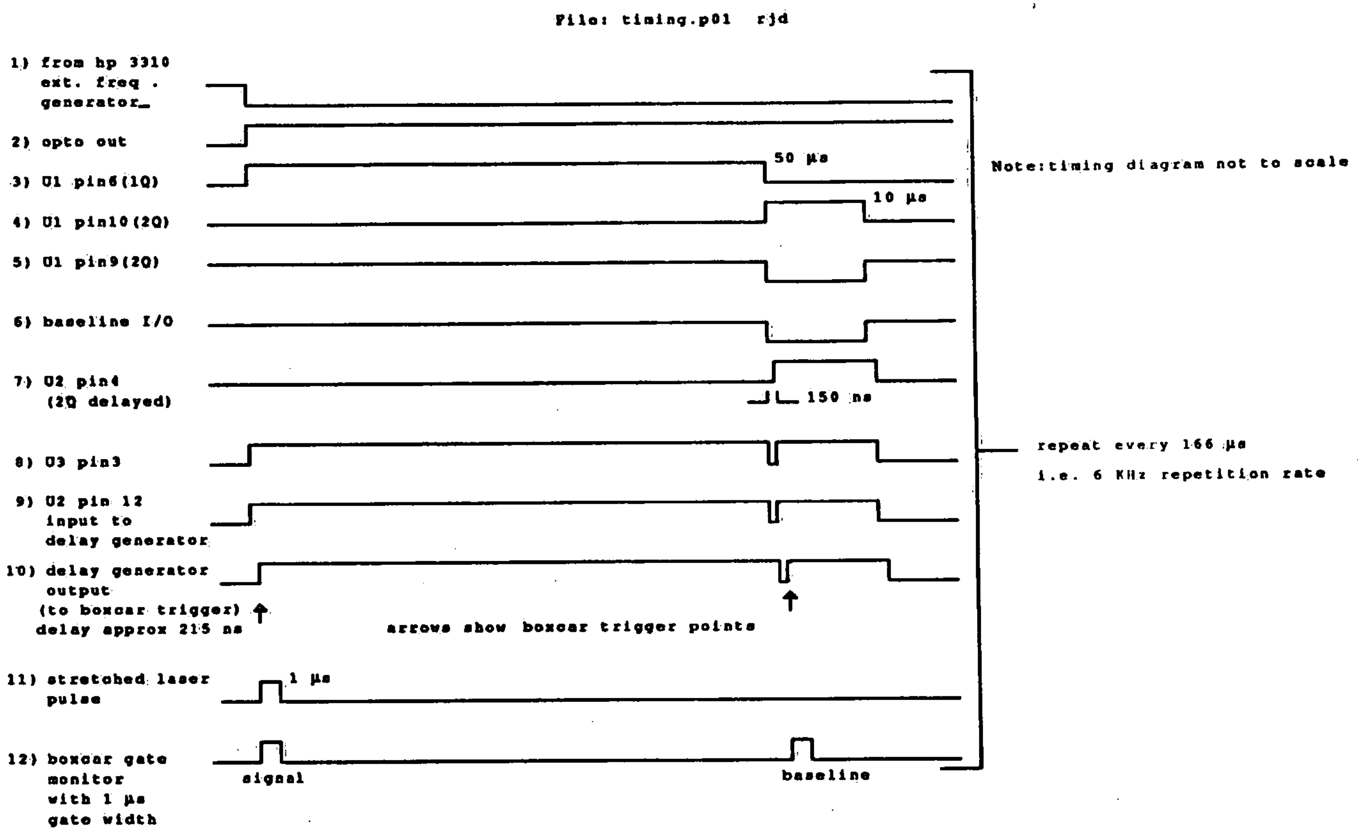


Figure 4. Timing Diagram for 'Baseline 2' baseline Correction circuitry

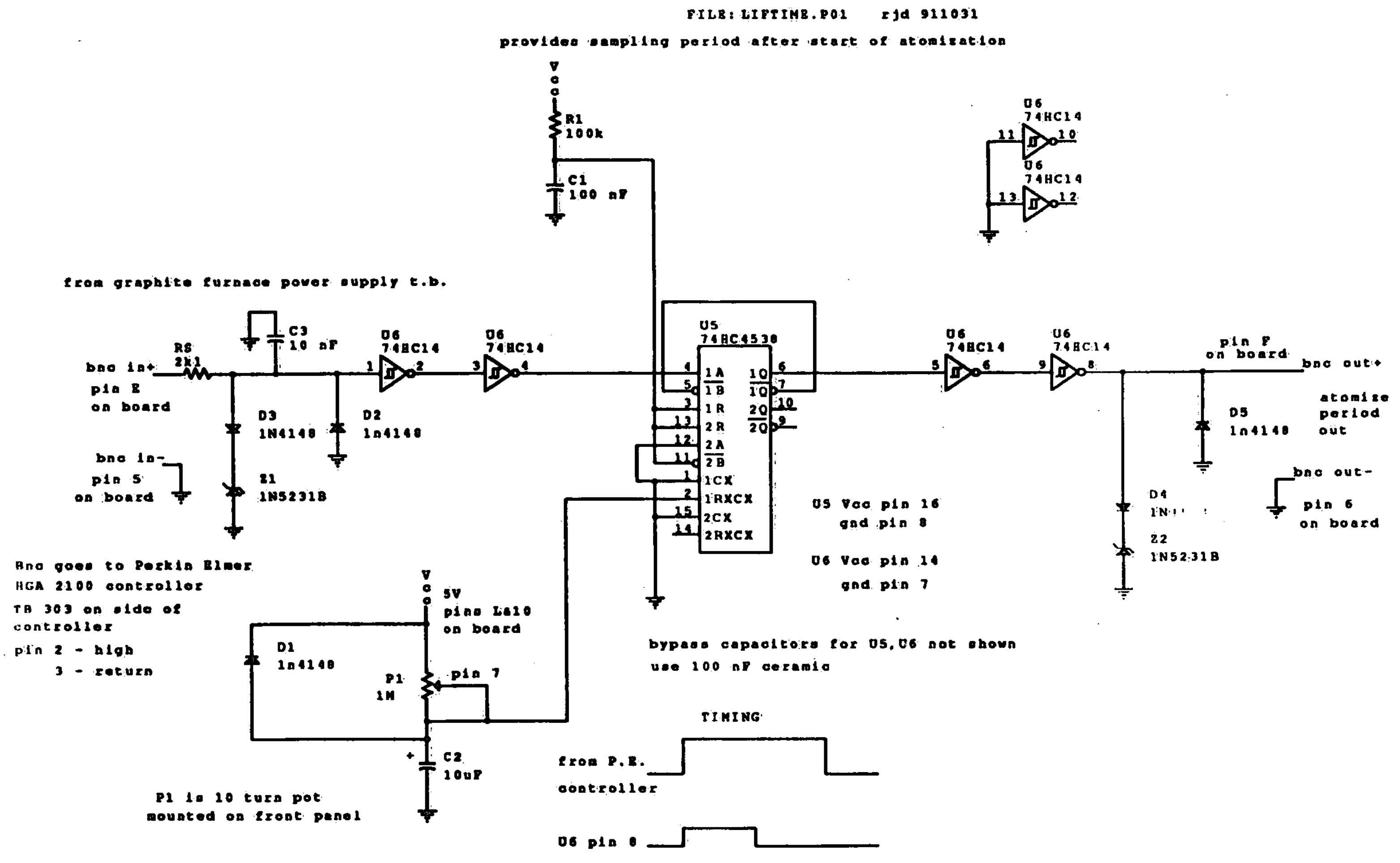


Figure 5. Atomization sampling period circuit

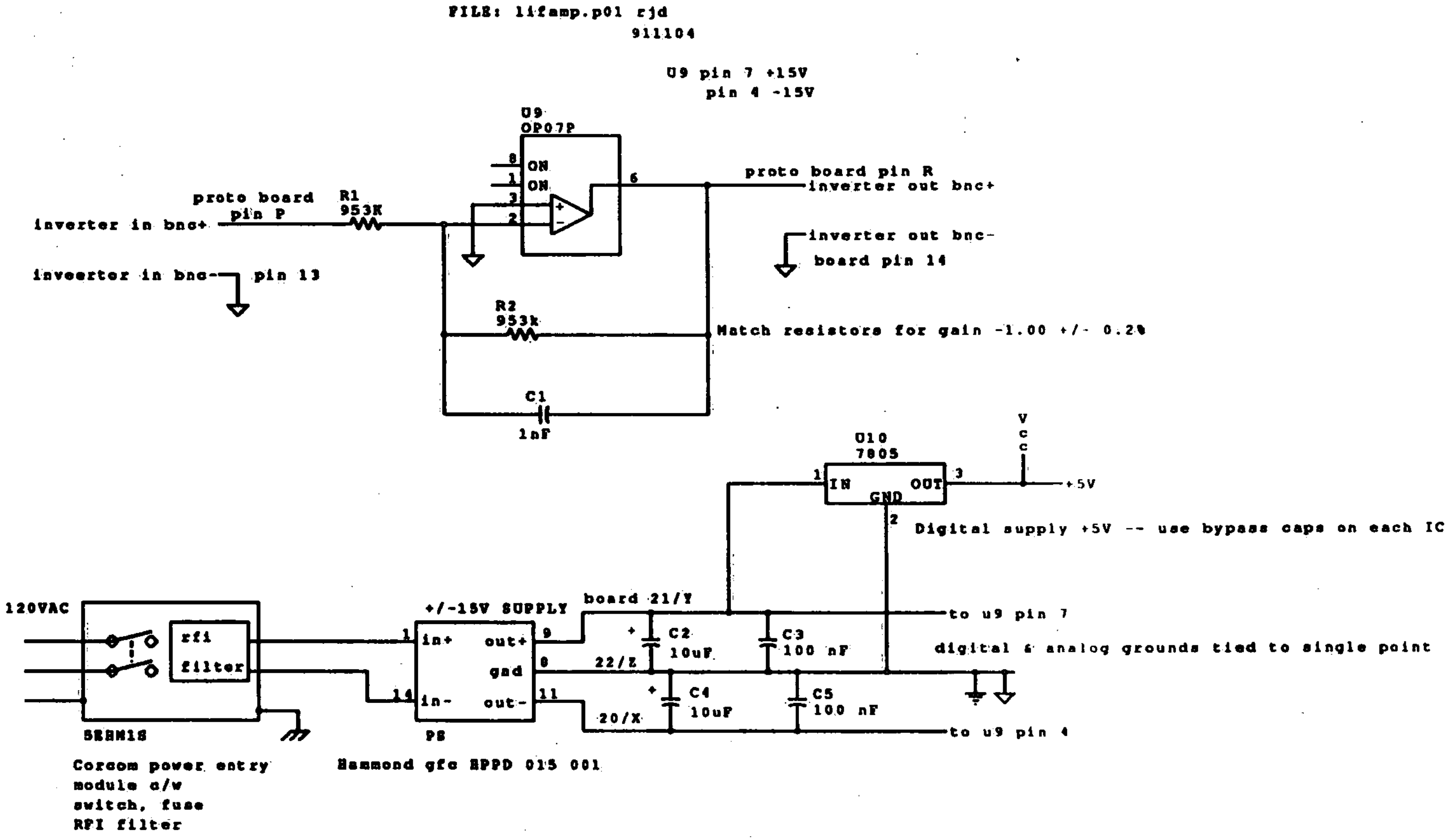


Figure 6. Boxcar signal inverter

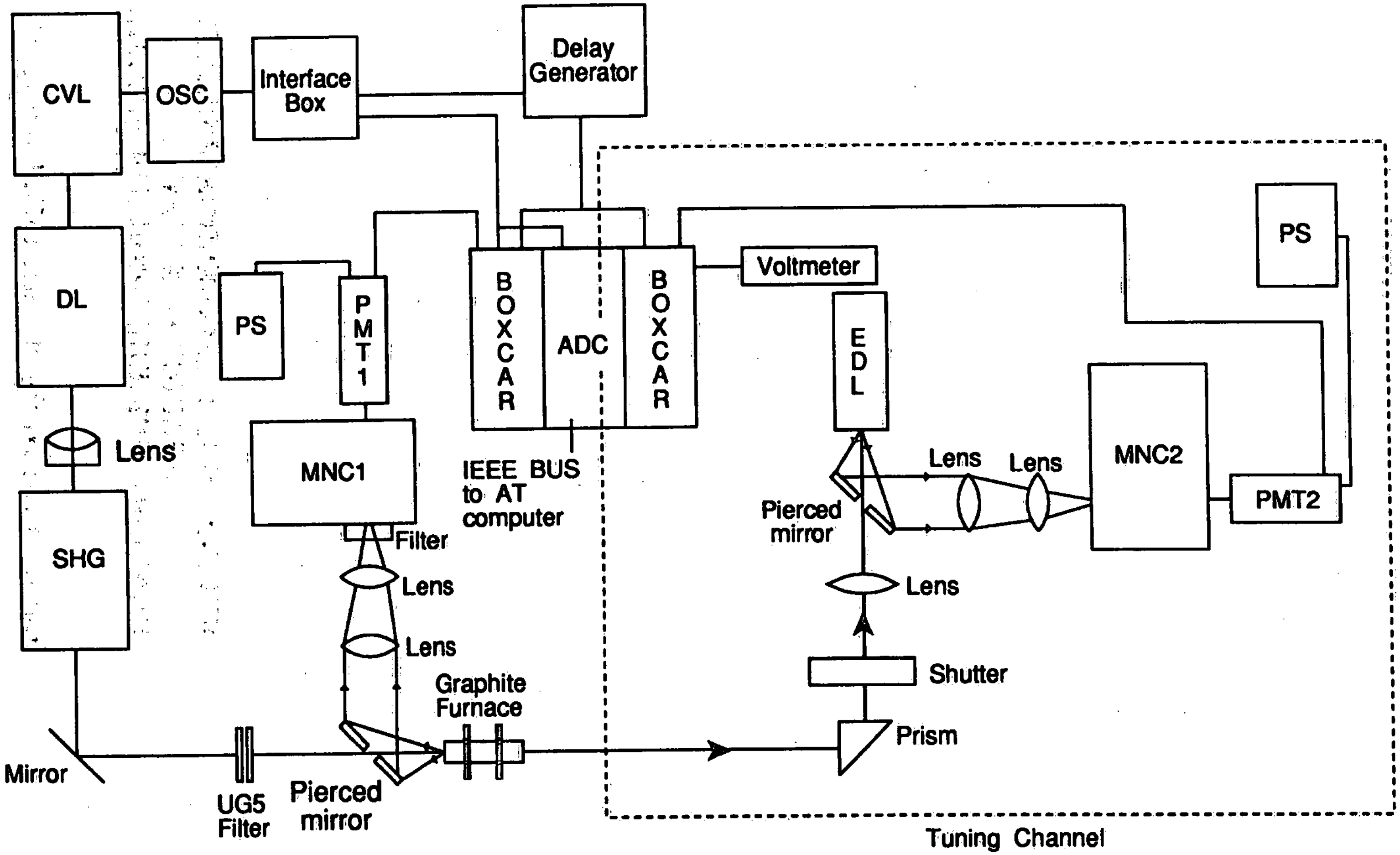


Figure7. LEAFS System Schematic

CVL=copper vapour laser DL=dye laser SHG=second harmonic generator
MNC=monochromator PS=power supply PMT=photomultiplier
ELD=electrodeless discharge lamp ADC=analog to digital converter
OSC=Oscillator

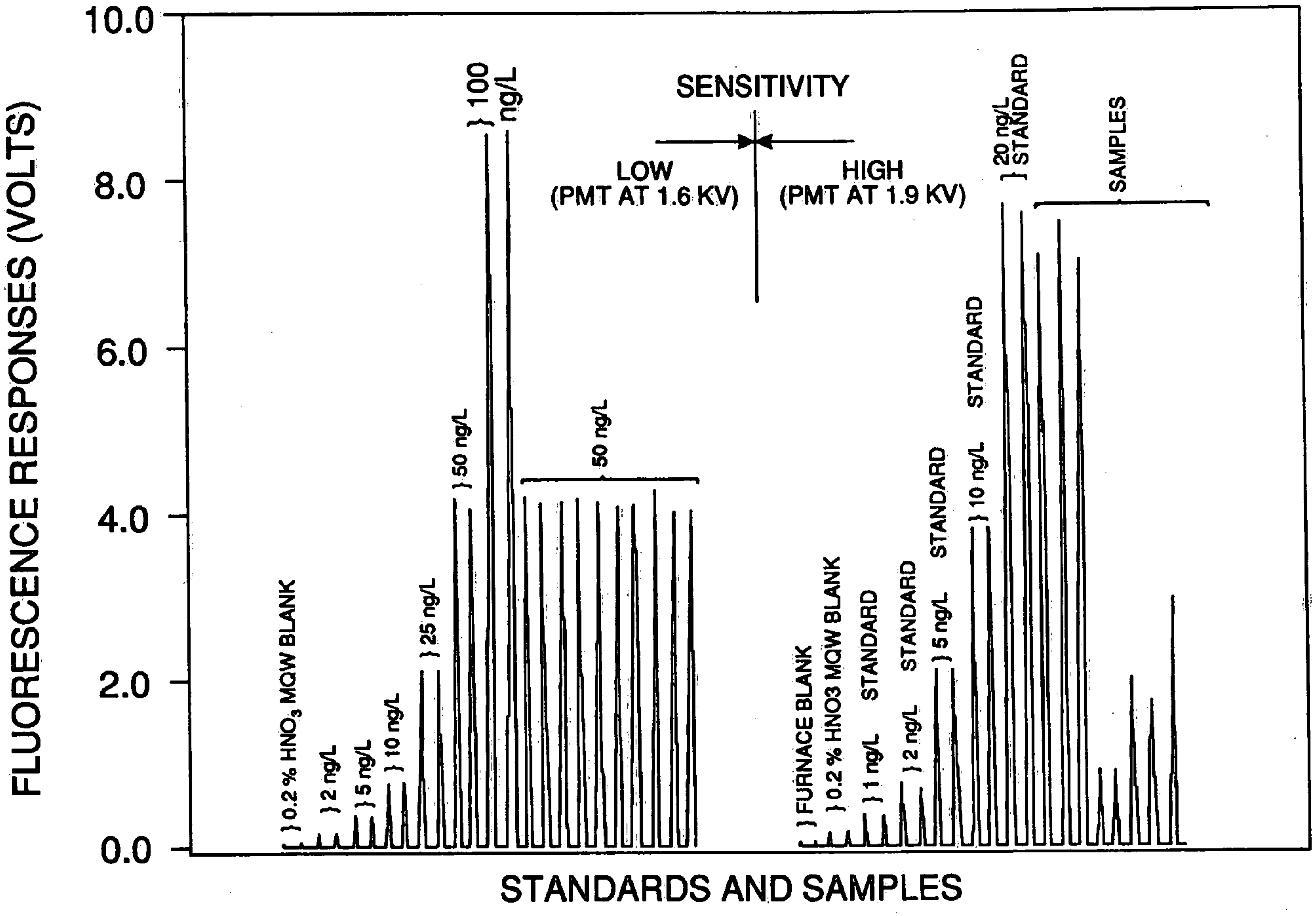
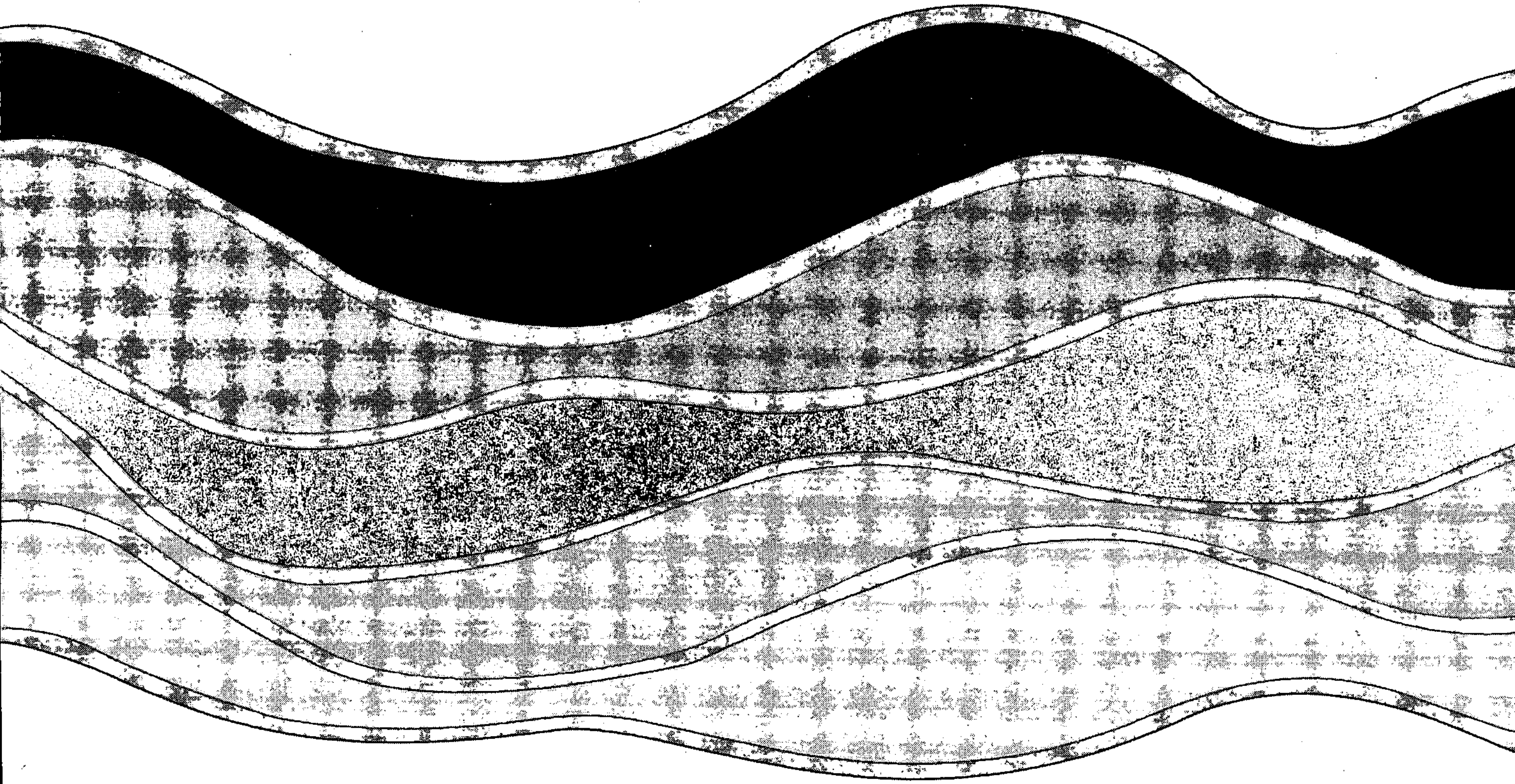


Figure 8. Typical fluorescence responses for standards and samples containing Pb (20µL injection)



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