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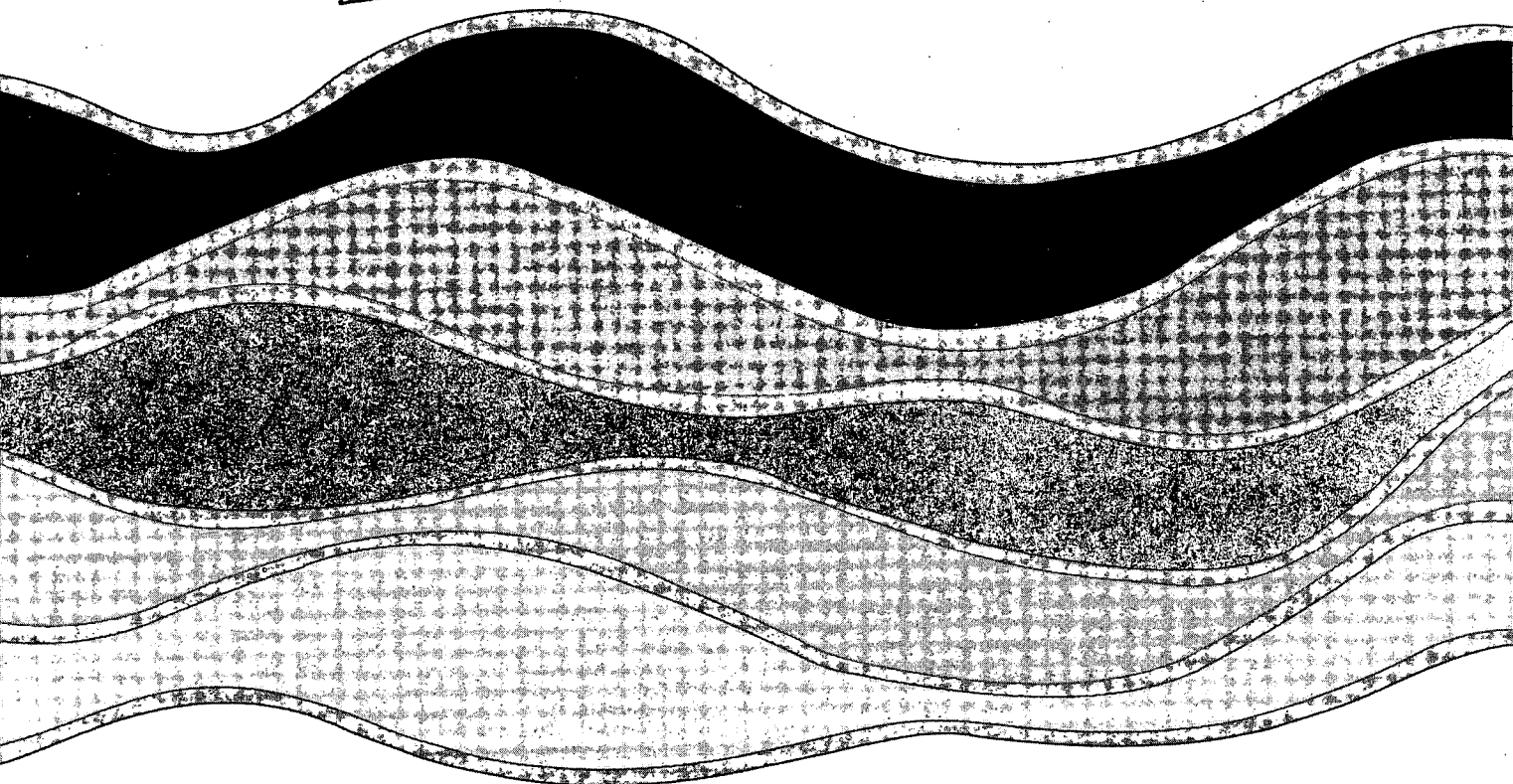
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MANAGEMENT PERSPECTIVE

Toxic metals such as Hg, Pb, Cd and their compounds are serious cumulative body poisons. The determination of very low levels of heavy metals in environmental samples with existing methods often leads to unsatisfactory results. 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) is the method of choice due to its potential of single atom detection.

A copper vapor laser-based LEAFS and an ultrasensitive method have been successfully developed and applied to direct determination of Pb in Great Lakes water samples. The generation of analytical data is simple, time-saving and avoids the possibility of accumulating contamination since the preconcentration steps are no longer necessary. This is the first time that direct analyses of such samples have ever been successfully performed. Existing methods require these samples to be preconcentrated ($\approx$200 times) before they can be analysed.

The results from 14 sampling sites indicate Pb level in Lake Ontario of less than 25 ppt, which is much less than the average value of 300 ppt reported for this lake up to year 1986.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Des métaux lourds comme le Hg, le Pb, le Cd et leurs composés sont des poisons corporels cumulatifs dangereux. Les méthodes existantes utilisées pour le dosage de très faibles concentrations de métaux lourds dans des échantillons prélevés dans l'environnement produisent souvent des résultats insatisfaisants. La spectroscopie utilisant une source lumineuse au laser est la technique la plus prometteuse étant donné le pouvoir de résolution accru et la plus grande sensibilité qui peuvent être obtenus par rapport à d'autres méthodes. Parmi les différentes techniques de spectroscopie, la spectrométrie à fluorescence atomique à excitation laser (LEAFS) est la méthode privilégiée en raison de son pouvoir de détection d'un seul atome.

Une méthode LEAFS fondée sur un laser à vapeur de cuivre et une méthode ultrasensible ont été mises au point et appliquées au dosage direct du Pb dans des échantillons d'eau des Grands Lacs. La production de données analytiques est simple, permet de sauver du temps et empêche l'accumulation possible de contaminants puisque des étapes de pré-concentration ne sont plus nécessaires. C'est la première fois que des analyses directes d'échantillons de cette nature sont effectuées avec succès. Les méthodes existantes exigent une préconcentration de ces échantillons (facteur $\approx$ 200) avant de les analyser.

Les résultats montrent une teneur en Pb dans le lac Ontario inférieure à 25 p.p.10^9, ce qui est beaucoup moins que la valeur moyenne de 300 p.p.10^9 signalée jusqu'en 1986 pour ce lac.

ABSTRACT

A copper vapor laser - pumped dye laser has been used in the development of a Laser-Excited Atomic Fluorescence Spectrometer (LEAFS) which was optimized to give low ppt sensitivity. Using the spectrometer, a method has been developed for direct analysis of Pb in Great Lakes water samples. This is the first time that direct analyses of such samples have ever been successfully performed. Existing methods require these samples to be preconcentrated ($\approx$200 times) before they can be analysed. The following performance characteristics were achieved by the LEAFS method: satisfactory recoveries (within 3%) of 2 certified reference materials, a relative standard deviation of 4.9% at 10 ppt level, fifty three spike recoveries within 100$\pm$10%, and a working detection limit of 0.4 ppt at 25 μL injection volume (10 fg absolute). The 18-megaohm water used was found to contain less than 0.9 ppt Pb.

Keywords: LEAFS; Laser-excited atomic fluorescence spectrometry; Lead determination; Lead level in the Great Lakes waters; Direct analysis.

RÉSUMÉ

La combinaison du laser à vapeur de cuivre et du laser à colorant pompé a été utilisée pour mettre au point un spectromètre à fluorescence atomique à excitation laser (LEAFS) qui a été optimisé pour donner une sensibilité à de faibles teneurs (p.p.10^9). Au moyen de ce spectromètre, on a élaboré une méthode pour l'analyse directe du plomb (Pb) dans des échantillons d'eau des Grands Lacs. C'est la première fois que des analyses directes d'échantillons de cette nature sont effectuées avec succès. Les méthodes existantes exigent une préconcentration des échantillons (facteur $\approx$ 200) avant de les analyser. Les caractéristiques de rendement suivantes ont été atteintes par la méthode LEAFS : récupérations satisfaisantes (à 3 % près) de 2 matériaux de référence certifiés, un écart type relatif de 4,9 % pour une teneur de 10 p.p.10^9, cinquante trois récupérations d'échantillons enrichis à près de 100 ± 10 %, et une limite de détection pratique de 0,4 p.p.10^9 pour un volume d'injection de 25 μl (10 fg absolu). L'eau 18-mégaohm utilisée contenait moins de 0,9 p.p.10^9 de Pb.

Mots-clés : LEAFS; spectrométrie à fluorescence atomique à excitation laser; dosage du plomb; teneur en plomb dans l'eau des Grands Lacs; analyse directe.

INTRODUCTION

The determination of lead in water is of great importance because of the well documented toxicity of lead in the aquatic environment and the entire ecosystem. Electrothermal atomic absorption spectrometry is commonly used for this determination. The problem of the method is that severe interferences attributed to the matrix effect are usually encountered. The methods have been the subject of debate and dissatisfaction among environmental scientists for many years. Existing graphite furnace AAS or ICP require sample preconcentration ($\approx$200 times) by such procedure as solvent extraction/backextraction or evaporation. These procedures not only are time consuming and labour intensive but also are prone to accumulate contamination and tend to give biased high results. For accurate determination of ultratrace amounts, there is an obvious need to develop a very sensitive technique and an effective method to alleviate these problems. Based on literature and our own experiences, Laser-Excited Atomic Fluorescence Spectrometry (LEAFS) should meet these challenges.

Even though LEAFS has been shown to be an ultrasensitive technique for metals analysis [1-8], it has not become popular among analysts due to its commercial unavailability. It will be seen that a LEAF spectrometer can be built to provide adequate sensitivity to avoid preconcentration steps, and that it can be used for efficient, direct analysis of environmental samples.

This paper describes the development of a copper vapor laser-based LEAF spectrometer and of a method for direct analysis of Great Lakes water samples. It briefly addresses Pb levels in the Great Lakes vis-a-vis historical data. To our knowledge, this is the first time that direct analyses of such samples have ever been successfully performed.

EXPERIMENTAL

LEAF spectrometer setup

Figure 1 shows the block diagram of the LEAFS system. An external oscillator set at 6 kHz was used to trigger a 20 Watt copper vapor laser (CVL) since the built-in oscillator was unstable and caused laser malfunction. The CVL green light (511nm) was used to pump a Rhodamine 6G dye laser (DL). The light from this laser was focussed towards the frequency doubler, which converts part of the visible to UV light. The conversion factor was about 2%. The UV light was then directed through the open ends of the graphite tube of a graphite furnace through a pierced mirror and focussed into the Pb electrodeless discharge lamp (EDL) for tuning process [9]. The Stokes direct line fluorescence light (405.78nm) emitted by the excited atoms in the graphite furnace was then reflected by the mirror and focussed towards the monochromator through a narrow bandpass filter ±5nm. The signal from the monochromator was amplified, stored, and monitored in digital form. The equipment and operating conditions are given in Table 1.

The tuning process using an EDL lamp and a pierced mirror has been discussed in detail elsewhere [8,9] and is schematically shown in Figure 1 as tuning channel. The linewidth of the induced fluorescence was calculated to be 0.003 nm based on the dye laser specifications and corresponding potentiometric measurements. (It should be noted that tuning can be done without the monochromator II/ PMT and boxcar system by using the spectrometer setup for LEAFS, but this method of tuning is no longer independent from LEAFS experiments). To avoid self-reversal phenomenon (2 maxima with a local minimum response), the lamp must be in line with the incoming laser beam and it was found that it was better to focus the laser beam towards the front rather than the middle of the lamp.

Cleaning procedure, Great Lakes waters collection

The rigorous cleaning procedure, which takes over a week and consists of using many agents from soap, acetone, concentrated HCl and HNO$_3$,... and Milli-Q-Water, is described elsewhere [10] and was used to clean all relevant labware. Surface water samples were collected using a raft rod sampler, whereas the depth samples were collected using Go-flo bottles. The samples were immediately brought to the mobile clean laboratory (class 100) equipped with such facilities as clean suit, clean polyethylene gloves, clean plasticware/glassware, and Milli-Q-Water system. Each sample was immediately filtered through 0.4 μm filter into a clean bottle and then acidified to 0.2% nitric acid (Seastar). All samples were collected in the summer of 1991 from various stations in Lakes Ontario, Erie and Superior.

Chemicals, sample preparation and injection

Pure water (18MΩ), referred to as MQW, was obtained from Milli-Q-Water system (Waters) installed in a class 100 clean laboratory. Ultrahigh purity nitric acid (Seastar) with a specified Pb content of 40 ppt was used. Standards and spikes were prepared in the class 100 clean room using precleaned glassware and plasticware and the 0.2% HNO$_3$ MQW blank. Pb standards were prepared from a commercial AAS 1000 ppm standard by sequential dilution with MQW blank. The plastic micropipette tips were soaked in 0.4% acid for several days and each tip was rinsed a dozen times with the solution of interest before use. In spite of very careful sample handling during sample injection into the furnace, some contamination from the surrounding air is expected since the LEAF spectrometer is located in an ordinary laboratory.

RESULTS AND DISCUSSION

Optimization

The Thorn EMI photomultiplier (PMT) originally had a gating board to operate as a gating PMT but the board ceased to function after a brief period of use, probably due to the high repetition rate (6 kHz) we were using, which exceeded the manufacturer's recommended duty cycle. Therefore we removed the gating board, used DC excitation instead to power the PMT and relied on the background substraction method. A logics circuitry of 6 kHz frequency was built and installed to permit the boxcar to substract the baseline from the output signal after every laser pulse, thereby significantly improving the sensitivity. With the boxcar set at $1\mu s$ gate width, at 1000 samples averaged and at baseline mode, the delay of 215 ns gave the best boxcar responses. The delay range of 0-305 ns was tested.

The PMT excitation voltage giving the best signal to blank ratio was 2300 volts as can be seen in Figure 2. The working range was 1.7-2.4 kvolts, the lower end being used for more concentrated samples and the higher end for lower levels samples. The voltage most often used was 2100 V. A ferrite bead was installed in the PMT signal line to reduce the noise but was found to make no improvement.

The atomization temperature ranged from 1800 to 2200°C but the temperature giving optimal recoveries of SLRS-2 (a certified reference material to be discussed below) was 2000-2200°C. The chosen temperature was 2100°C, because 2200°C tended to give overlapping analyte and furnace black body radiation responses, resulting in less accurate quantitation. The slit width of 1.5 mm was found to give optimal responses.

Power output from the dye laser as low as 0.14 watts was found sufficient to perform LEAFS experiments. Of course this is far from attaining optical saturation but

the benefit of operating at lower power resulted in extended operating life time for the CVL before the replacement of copper inside laser tube became necessary. In fact we had 700 hours of operation, twice the time quoted by the manufacturer, before we added new copper ingots.

Samples Analysis

The sample injection volume can range from 10 to 50 μL, but the response is not linear as it slightly shifts downward with volume increase (Fig. 3). Ten to twenty five μL were most often used. Typical fluorescence responses for Pb standards and natural water samples are shown in Figure 4. The arrow in the figure indicates a spurious peak, which occurs about 5-10% of the time; this is probably due to buildup of residues around the graphite tube sample hole falling into the tube during manual injection. An automated injection system will probably help alleviate this and make the method more adaptable to routine use.

A LEAF calibration curve for Pb standards in 0.2% HNO_3 matrix is shown in Figure 5. It is an integrated curve comprising the 0.2-50 ppt range and the 100-1000 ppt range. For the lower concentration range normal instrument sensitivity was used; for the high range lower sensitivity was used so the responses (peakheights in mV) were in measurable scale and were then multiplied by a common factor so they would be in scale with the lower (0.2-50 ppt) range.

Twenty six values of the blank (0.2% acidified MQW) were monitored during a period of two months giving a median value of 0.9 ppt, a mean value of 0.94±0.21 ppt, and extreme values of 0.6 and 1.4 ppt. The blank includes contributions from the MQW itself, 0.2% acid, furnace blank (blackbody radiation) straylight from various scattering processes, surrounding air and electronic noise. Thus the MQW itself should contain less

than 0.9 ppt Pb. A value of 0.28 ppt was reported by Apatin et. al. for the Grenoble ultrapure water [11].

Performance characteristics

Ten replicate analyses of a 10 ppt standard gave an average fluorescence response of 413.3 mV with an RSD of 4.9%. Table 2 shows the results of accuracy tests using two Certified Reference Materials and six values derived from the Multiple Standard Addition Technique [12-13] applied to six different Great Lake water samples-- 2 from each of Lake Ontario, Lake Superior and Lake Erie (different stations, different depths). For each of these samples, three distinct levels of Pb standard were added and the recoveries calculated. In total, fifty three such determinations of recoveries were made and are summarized in Table 3, showing recoveries well within 100±10%.

The working detection limit was defined as twice the standard deviation obtained from replicate analyses of a concentration at least 5 times greater than the lowest concentration which can be distinguished from the blank signal, in this case 0.2 ppt [14]. We made replicate analyses of 2 and 5 ppt (10 and 25 times greater than 0.2) and the resulting pooled standard deviation [15] times 2 was 0.37 ppt. This is for all practical purpose equal to twice the standard deviation of the blank (0.42 ppt) as discussed above. The working detection limit was then taken as 0.4 ppt (10 fg Pb with $25\mu L$ injection).

Concentration of Lead in Lake Ontario

The results summarized in Table 4 show that the Pb concentration in the samples from 2 stations at 4 different depths is lower than 25 ppt. Table 5 shows the results for a profile of another station (LO-33) down to 130 metre deep (near bottom

sediment) and indicates that the Pb level starts at around 18 ppt (surface sample), decreases to about 8 ppt at 100 metre deep, but increases to 18 ppt at the deepest sampling site. The results from the 14 sampling sites (Tables 4-5) indicate Pb levels less than 25 ppt, which is much smaller than the average value of 300 ppt reported for Lake Ontario up to year 1986 [16]. The relative magnitude of these data can be visualized in Figure 6. Our finding of low Pb level agrees with that reported by Flegal et.al. who used a preconcentration-GFAAS technique and cleanroom practices [17]. The high levels of Pb reported previously were likely caused by the combination of contamination and insensitive methods used.

CONCLUSION

A copper vapor laser-based LEAFS and a method have been successfully developed and applied to the determination of Pb in Great Lakes waters by direct analysis.

The preconcentration steps required by the conventional methods are no longer necessary. The generation of analytical data is simple, time-saving and avoids the possibility of accumulating contamination and of producing biased high results. It appears that Pb level in Lake Ontario is much lower than the average value of 300 ppt reported for this lake up to year 1986.

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TABLE 1

Equipment and Operating Conditions

COPPER VAPOR LASER
    Pulse width
    Power input, Power output*
	MLT20 (Metalaser Technologies)
	24 ns
	3.6 kW, 6 W

OSCILLATOR/ FUNCTION GENERATOR	HP 3311A
INTERFACE BOX	In-house built
DELAY GENERATOR	4144, EG&G PAR (delay = 215 ns)

DYE LASER
    Dye: Rhodamine 6G
    Setting for maximum fluorescence
	DL-13 (Laser Photonics)
	0.2g/L (4.2×10^{-4} mole/L)
	280.60 - 280.61

SECOND HARMONIC GENERATOR Crystal	Autotracker II (Inrad Inc.) KDP-B
VISIBLE LIGHT FILTER	UG5, 4mm (Schott Glass Technolog.)
ELECTROTHERMAL ATOMIZER Graphite Tube Dry, char, atomization Sample injection, Internal gas flow	Perkin-Elmer HGA 2100 8x28 mm 120, 500, 2100°C; 40, 40, 5 sec. 10-25 µL, Stopped flow (Interrupt)
NARROW BANDPASS FILTER, 404.7±5nm	Melles Griot

MONOCHROMATOR I
    Aperture ratio
    Slit width
	Schoeffel GM 250, 0.25m
	f/3.6
	1.5 mm

PHOTOMULTIPLIER I Voltage setting	Thorn EMI 9813 1.7-2.4 kV
BOXCAR AVERAGER (Software) Gate width, Operation mode	4121B, EG&G PAR (4162, EG&G PAR) 1µS, Baseline 2
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
	1 mm

PHOTOMULTIPLIER II Voltage setting	Thorn EMI 9798B 0.9 kV
BOXCAR AVERAGER	4121B, EG&G PAR
MULTIMETER	HP 3468A
ENERGY METER Power range	Scientex 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.

TABLE 2

Results of Accuracy Tests

SAMPLE	ORIGIN	Certified,ppt	[a]MSA, ppt	[b]Found, ppt
SRM 1643c	[c]NIST	[*]35.3±0.9	N.A.	36.4±1.5
SLRS-2	[d]NRC	129±11	N.A.	125.3±10.8
[e]LO-79-19m	LAKE ONTARIO	N.A.	12.45	11.85±0.54
LO-87-20m	LAKE ONTARIO	N.A.	22.85	23.14±1.63
LS-2-12m	LAKE SUPERIOR	N.A.	25.75	25.46±0.78
LS-125-175m	LAKE SUPERIOR	N.A.	2.75	2.58±0.21
LE-23-50m	LAKE ERIE	N.A.	44.83	44.86±2.39
LE-54-6m	LAKE ERIE	N.A.	18.97	18.22±2.53

[a] MSA = Results from Multiple Standard Addition technique, field blank
    included

[b] Direct determination, field blank included for lake samples

[*] 1000 times dilution

[c] NIST = National Institute of Science and Technology

[d] NRC = National Research Council of Canada

[e] LO-79-19m = Lake Ontario - Station79 - 19 metre deep; the same meaning
    stands for the other 5 samples.

N.A. = not applicable

TABLE 3

Summary of % recoveries made on six different Great Lakes samples

(3 levels of additions for each sample)

SAMPLE	% RECOVERIES	No. Determtn
LO-79-19m	102±5	17
LO-87-20m	101±10	10
LS-2-12m	100±3	8
LS-125-175m	97±8	6
LE-23-50m	101±2	6
LE-54-6m	106±4	6

TABLE 4

Results (blank included) for two other Lake Ontario stations

SAMPLE[*]	RESULTS, ppt
LO-87-field blank	4.78±1.16
LO-87-0m	18.40±3.51
LO-87-10m	26.01±1.66
LO-87-20m	23.14±1.63
LO-87-35m	16.49±3.36
LO-79-field blank 1	2.79±0.04
LO-79-field blank 2	3.52±0.25
LO-79-field blank 3	3.32±0.04
LO-79-2m	12.54±1.95
LO-79-10m	11.54±0.53
LO-79-19m	11.85±0.54

[*] m = depth in metre

TABLE 5

Results (blank included) for a depth profile of a Lake Ontario station (LO-33)

SAMPLE	RESULTS, ppt
Field blank 1	1.46±0.08
Field blank 2	2.24±0.08
Field blank 3	1.29±0.16
0 metre depth	18.71±1.25
10 metre depth	15.49±1.28
25 metre depth	18.26±0.97
50 metre depth	9.50±0.39
75 metre depth	8.76±0.03
100 metre depth	8.23±0.47
130 metre depth	18.29±0.25
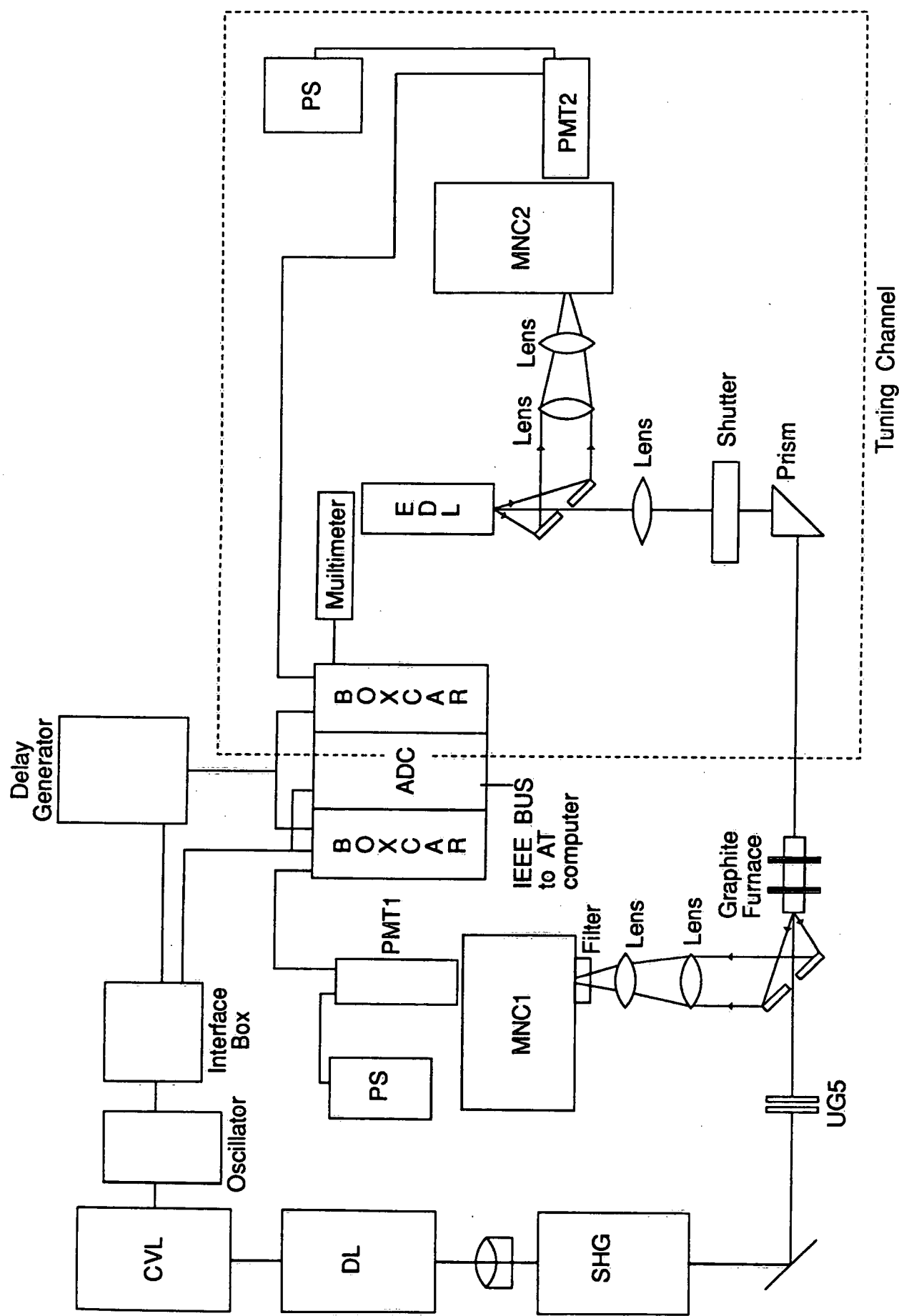
Figure 1   LEAFS System Schematic

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

STANDARD / BLANK RATIO

PMT VOLTAGE

5ppt / WATER BLANK
5 ppt / FURNACE BLANK
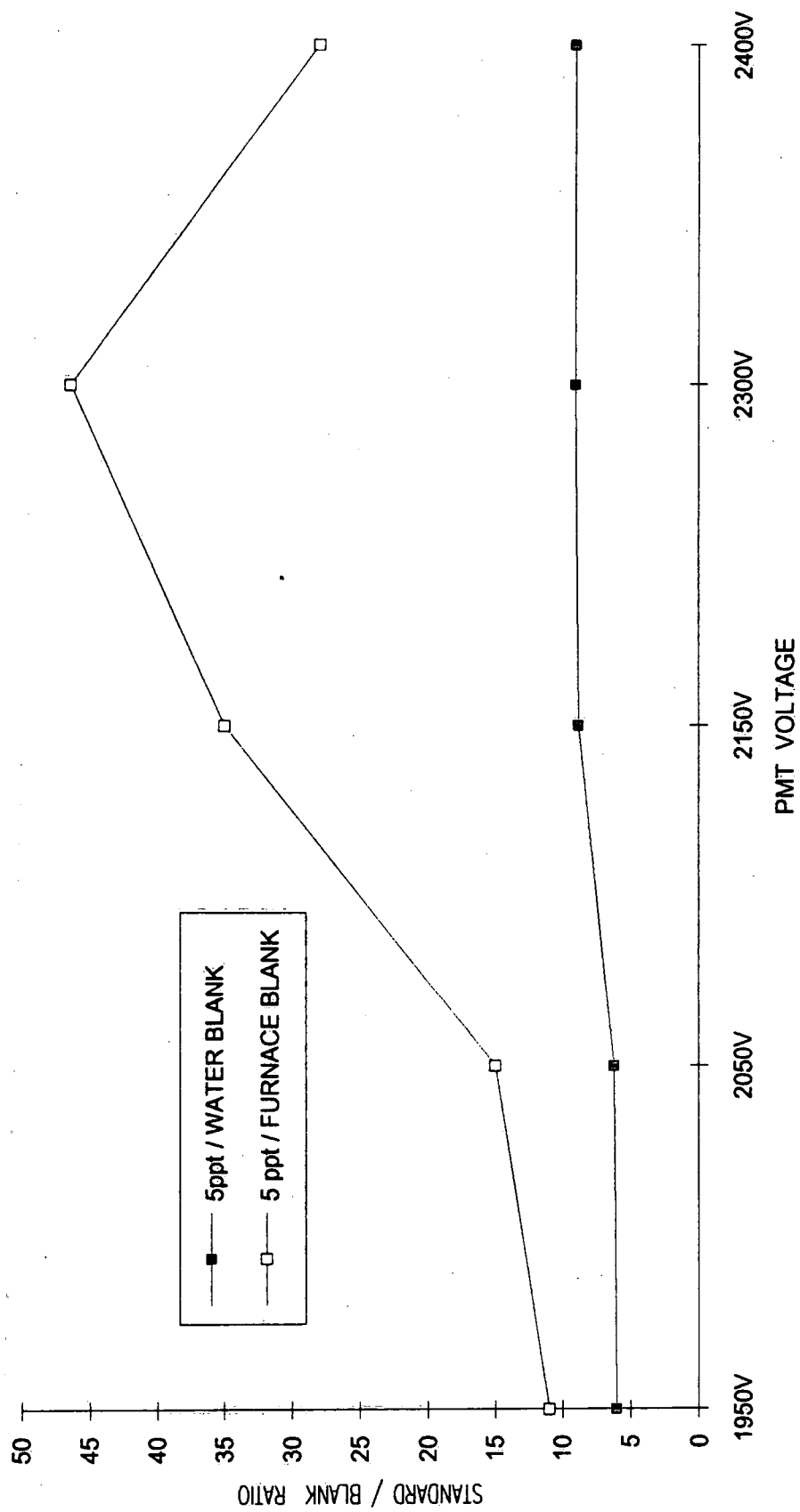
FIGURE 2. VOLTAGE DEPENDENCE OF SIGNAL / BLANK RATIOS FOR A 5 ppt STANDARD

INJECTION VOLUME, μL
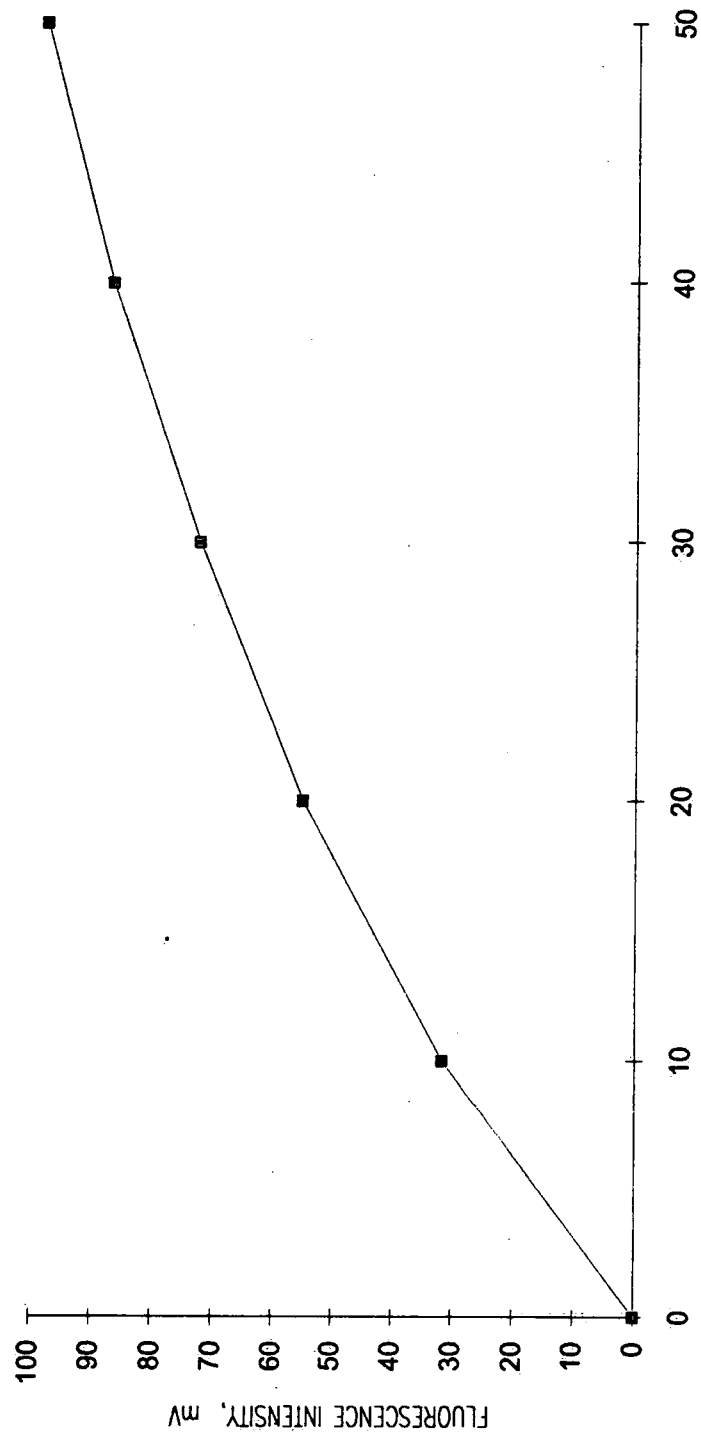
FIGURE 3. SIGNAL (mV) DEPENDENCE ON INJECTION VOLUME
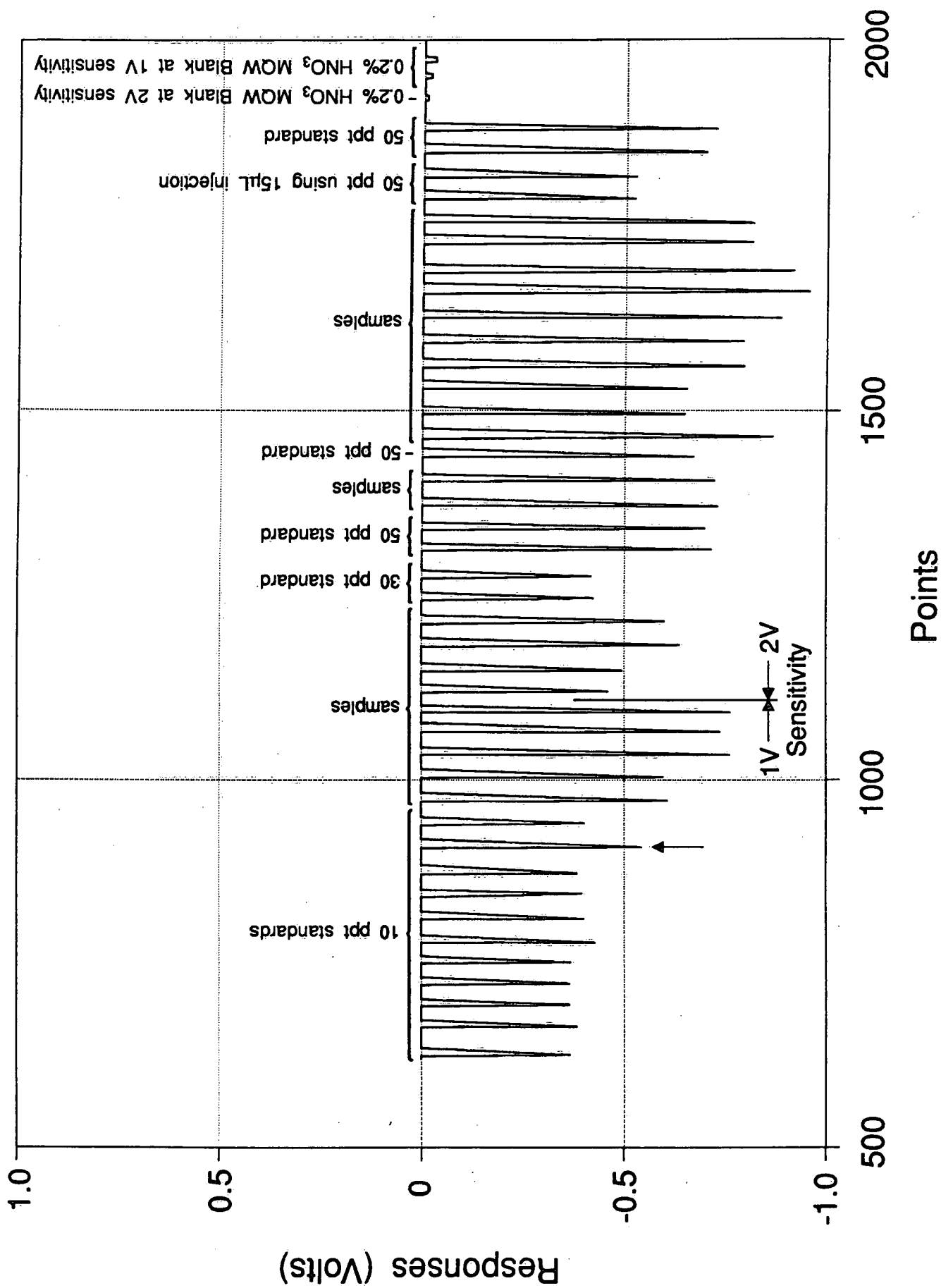
Figure 4. Typical fluoresence responses for standards and samples containing Pb (20µL injection)
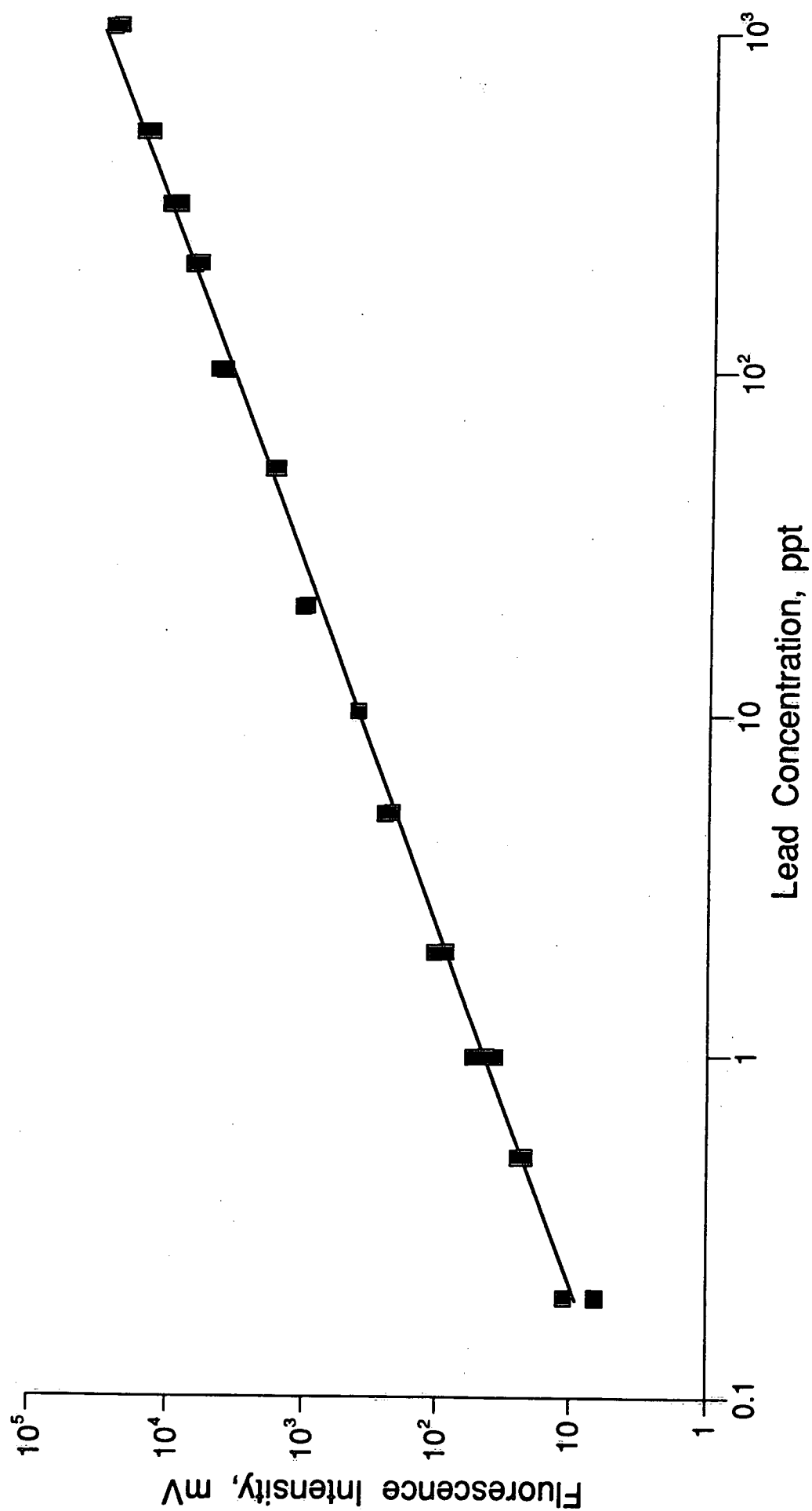
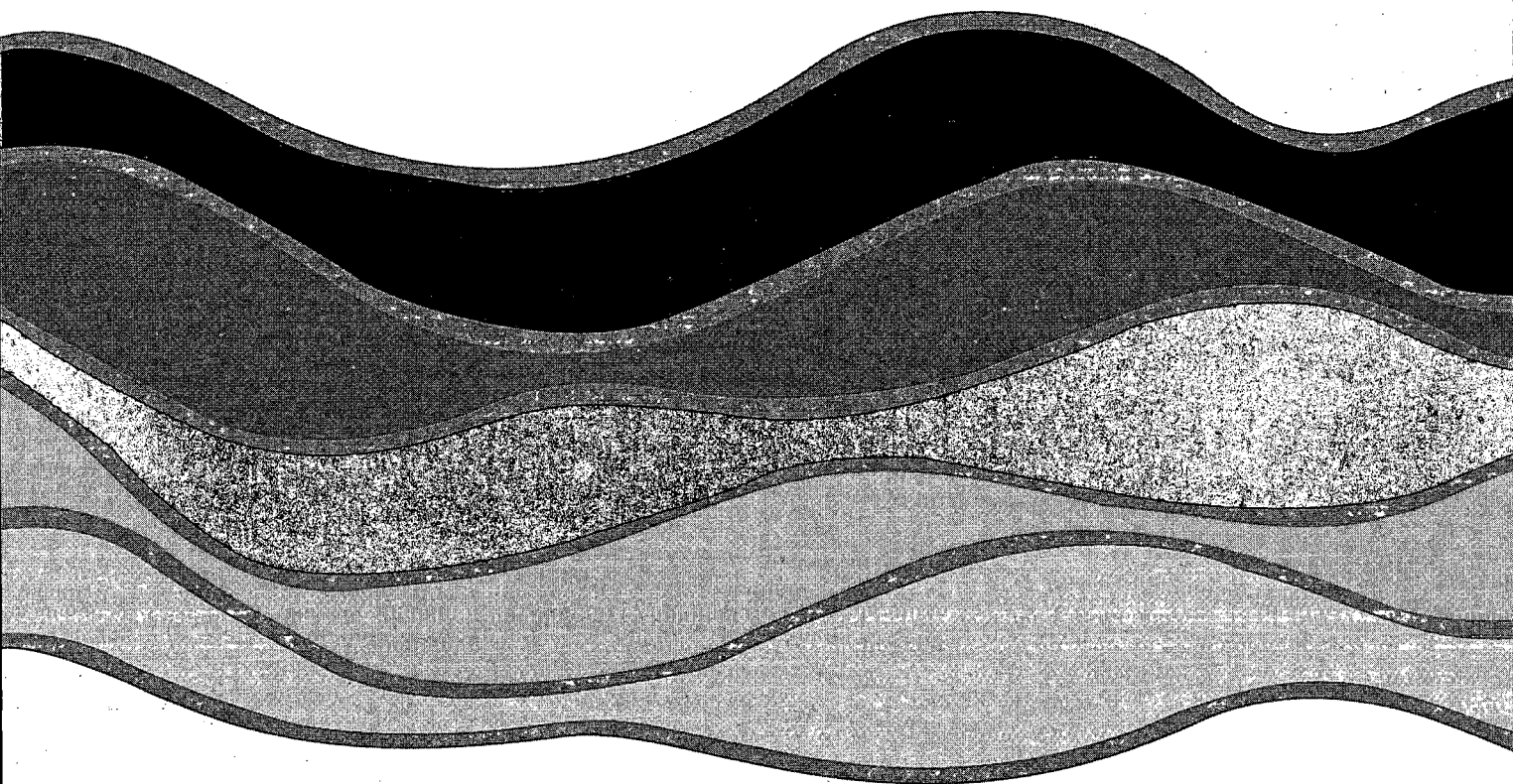Figure 5.   LEAF calibration curve (25μL injection) for direct analysis of Pb in water.
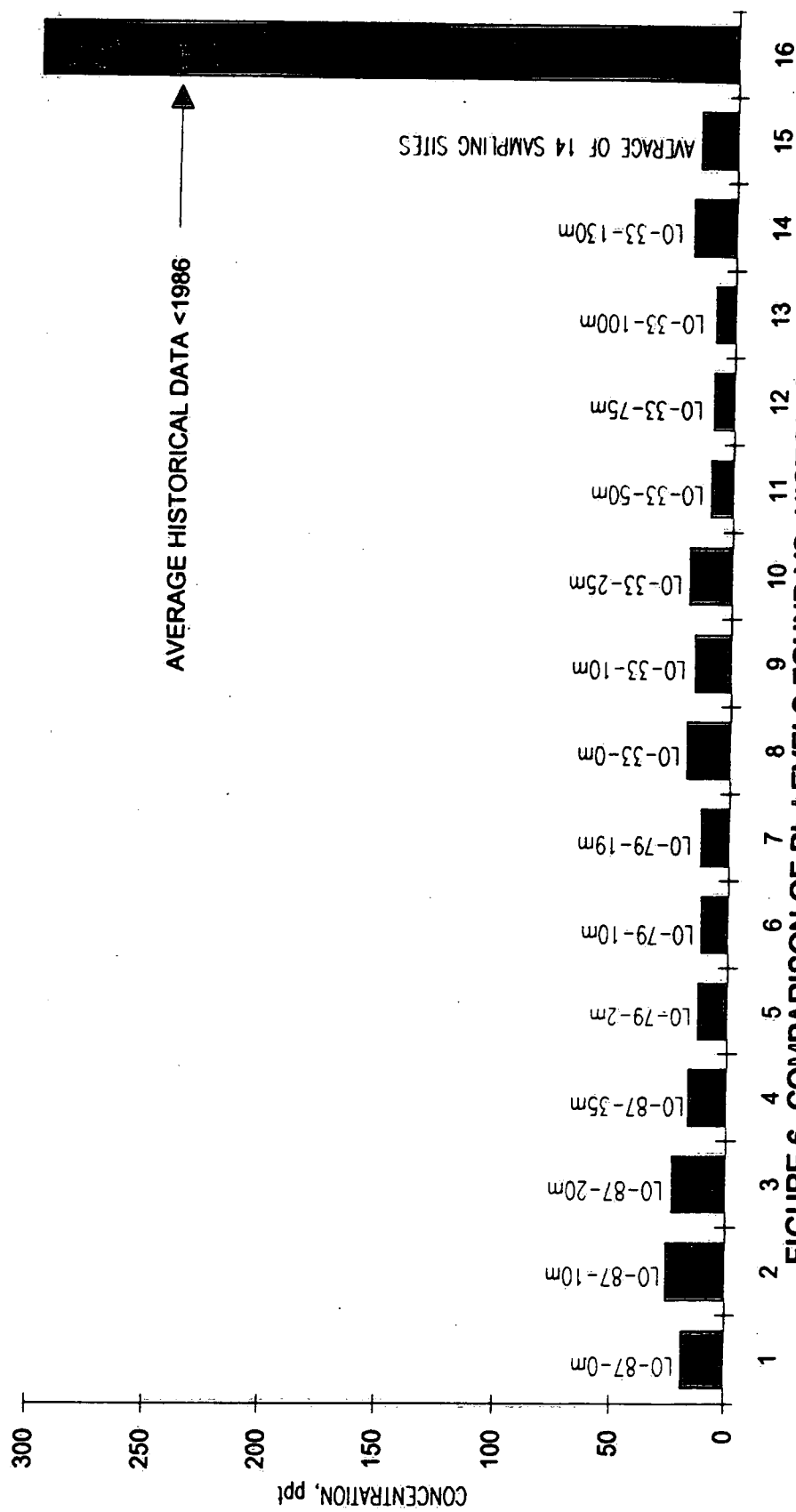
FIGURE 6. COMPARISON OF Pb LEVELS FOUND VS. HISTORICAL DATA