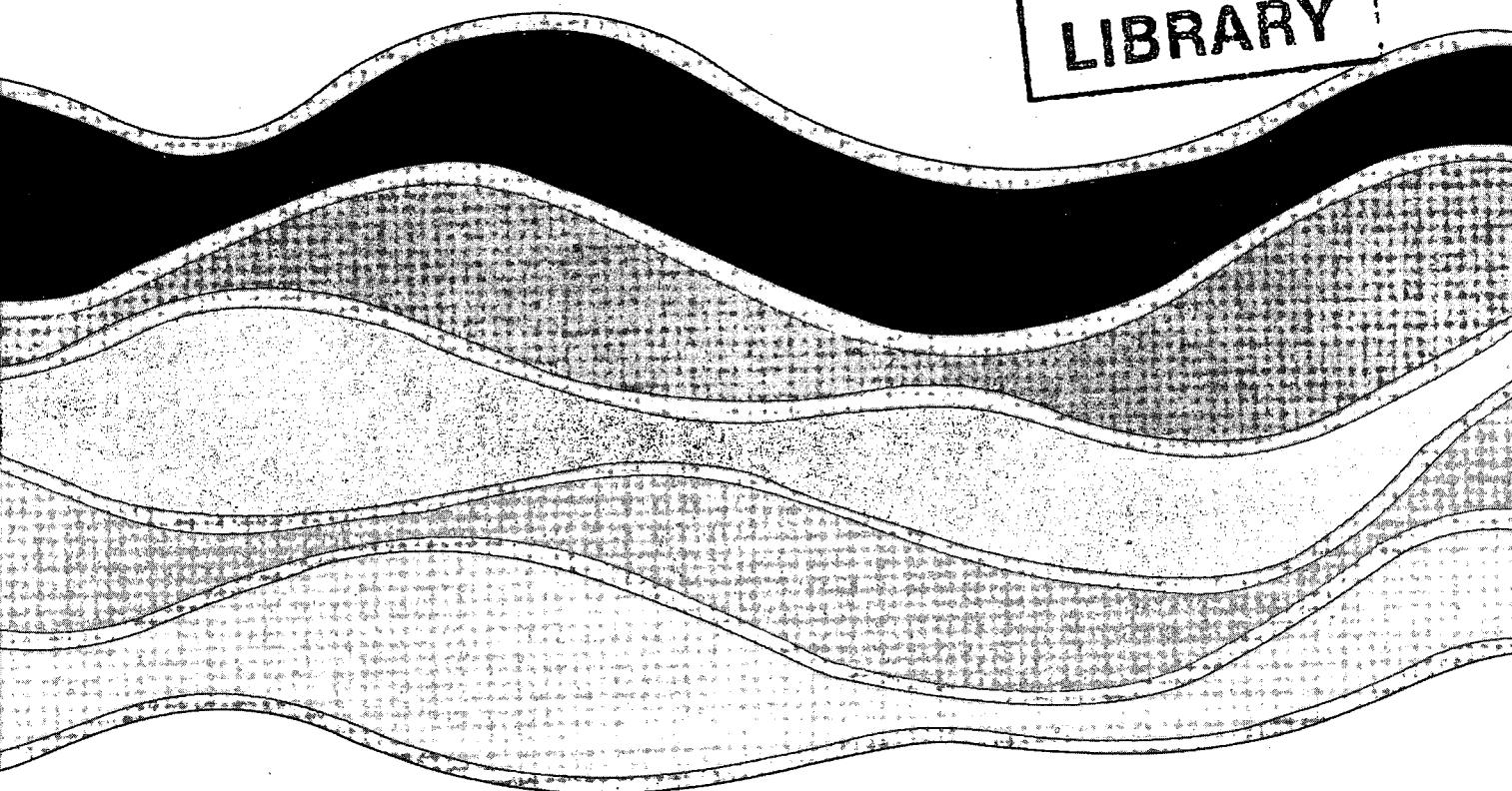
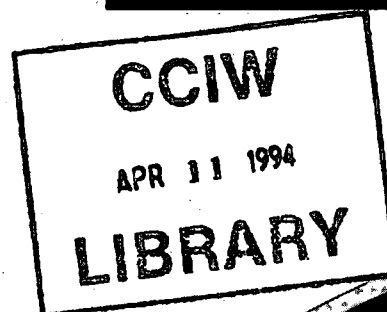
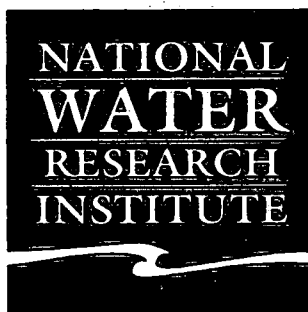


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**LASER-EXCITED ATOMIC FLUORESCENCE
SPECTROMETRY: APPLICATIONS AND
POTENTIAL IN WATER ANALYSIS**

**V. Cheam, J. Lechner, R. Desrosiers,
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NWRI Contribution No. 94-52

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**LASER-EXCITED ATOMIC FLUORESCENCE SPECTROMETRY:
APPLICATIONS AND POTENTIAL IN WATER ANALYSIS**

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MANAGEMENT PERSPECTIVE

Laser-Excited Atomic Fluorescence Spectrometry (LEAFS) has been shown to be an ultrasensitive technique for trace metals determination and has become more and more attractive to analysts in research as well as in service laboratories due to its applicability to analysis of environmental samples. This report describes LEAFS in relation to conventional instruments such as AAS and ICP, its performance in analyses of real substrates including a comprehensive review of literature, and offers the authors views vis-à-vis its potential for routine use. Lead results in accumulated snow/ice layers from the Agassiz ice cap are in general agreement with historical chemical data in the region. The report is the basis of an invited lecture presented at International Symposium on Chemistry and Biology of Municipal Water Treatment, CCIW, October 24-29, 1993.

SOMMAIRE À L'INTENTION DE LA DIRECTION

La LEAFS (spectrophotométrie à fluorescence atomique avec excitation au laser) s'est révélée une technique ultra-sensible pour l'analyse des métaux traces; elle est devenue de plus en plus attrayante pour les analystes en recherches ainsi que pour les laboratoires de services, en raison de son applicabilité à l'analyse d'échantillons environnementaux. Le présent rapport décrit la LEAFS comparativement à des techniques classiques, comme l'AAS (spectrophotométrie d'absorption atomique) et l'ICP (plasma induit par haute fréquence), ainsi que son rendement dans les analyses de substrats réels, avec une étude complète de la documentation scientifique; le rapport présente en outre le point de vue des auteurs au sujet des possibilités pour les analyses régulières. Les résultats dans le cas du plomb présent dans les couches de neige/glace accumulées du lac glaciaire Agassiz révèlent généralement une bonne corrélation avec les données chimiques historiques dans la région. Le rapport était le sujet principal présenté par un conférencier invité lors d'un colloque international sur la chimie et la biologie du traitement des eaux urbaines, organisé par le CCEI du 24 au 29 oct. 1993.

ABSTRACT

This report describes the application of LEAFS to the analysis of real substrates. The analytical results on Great Lakes waters, oceanic waters, Canadian Arctic snow and ice, and the results on dissolved versus total lead are discussed. The concentration of lead in the snow-ice layers peak in the late winter/early spring period. A substantial amount of Pb was found to be present in particulate form. Also a comprehensive literature review is presented along with a discussion on LEAFS potential for routine use. When a commercial unit is available, a rapid increase in usage is expected.

RÉSUMÉ

Le présent rapport décrit l'application de la technique LEAFS à l'analyse de substrats réels. Il examine les résultats analytiques avec les eaux des Grands Lacs, les eaux océaniques, la neige et la glace de l'Arctique canadien, ainsi que les résultats obtenus pour le rapport plomb dissous/plomb total. La concentration de plomb dans les couches de neige-glace est maximale pendant la période fin hiver - début printemps. Une quantité importante de Pb était présente sous forme particulaire. On présente également une étude complète de la documentation scientifique et une évaluation des possibilités du LEAFS pour les analyses régulières. Lorsqu'une unité commerciale est disponible, on peut prévoir une augmentation rapide de l'utilisation.

Introduction

Analytical methods for trace metals analysis are many, the most common ones being those based on Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) or - Mass Spectrometry (ICP-MS). Why then does one need more methods now that there are so many AA and ICP instruments and so many trained analysts using them ? It is because in many cases these instruments are not sensitive enough for analysis of very low level samples without relying on tedious sample pretreatments, which are time consuming and are prone to introducing and accumulating contamination. Laser-Excited Atomic Fluorescence Spectrometry (LEAFS) has attracted much attention due to its ultrasensitivity and great potential for use in service laboratories.

This report discusses three main areas-- a description of LEAFS, its applications and its potential for routine analysis. A comprehensive literature review dealing with LEAFS applications in analyses of real substrates will be given. The applications from this laboratory are highlighted by direct analysis of various aqueous matrices, including Great Lakes waters, oceanic waters and Canadian Arctic snow and ice; also, the results on dissolved and total lead will be discussed. The potential for routine use is discussed and arguments presented as to why it has only been sporadically used in spite of its outstanding performance.

Laser-Excited Atomic Fluorescence Spectrometry

Laser excited atomic fluorescence is a process whereby the analyte atoms in an atomizing cell are excited by a laser beam; atomic fluorescence results when a fraction of the excited atoms undergo radiational deactivation to a lower state. Atomic

fluorescence transitions are many-- resonance, direct-line, stepwise line, thermally assisted, Stokes, anti-Stokes, The more commonly used is the direct-line transition, in which the atoms are excited to a high excited state (usually the second or third) and deactivate to a lower excited state (usually the first or second, but not ground state). When the direct-line transition is not a favourable process, the resonance transition may be relied upon. In the latter case however, because the laser excitation wavelength is the same as the fluorescent emission wavelength, light scattering problems need to be dealt with. Figure 1 illustrates specific examples of a Pb direct-line transition and a Cd resonance transition energy diagrams.

A LEAFS mainly comprises a pumping laser, a tunable laser, a second harmonic generator, an atomizer, a detection system, and a data processor (Fig. 2). Pumping lasers can be continuous wave lasers (Argon ion, Krypton, Krypton-Argon, Helium-Neon, Nd-YAG, semiconductor diode lasers, Cadmium vapor), or pulsed lasers (Nitrogen, Excimer-- XeF, XeCl, KrF, ArF--, Ruby, Nd:YAG, Nd:YLF, Metal vapor-- Au and Cu). Tunable lasers are usually dye lasers (Hansch Cavity, Grazing Incidence Cavity), solid state Titanium:Sapphire lasers and solid state Optical Parametric Oscillators (OPO) which cover the widest spectral range of $\sim 400\text{-}2000$ nm but are the most expensive. Dye lasers use various organic dyes to provide wavelength ranges of interest. The tunable lasers are tuned via a flame atom cell, an Electroless Discharge Lamp or Hollow Cathode Lamp, or optogalvanometrically. A second harmonic generator, consisting of a crystal KDP (Potassium Dihydrogen Phosphate) or BBO (β -Barium Borate), frequency doubles a fraction of the light from the tunable laser to the analytical UV light. Although electrothermal atomizers (ETA) such as graphite tube, rod or cup are most commonly used, other atomizers have also been used, for example flame, ICP, DCP, glow discharge, and laser ablation. The detection system usually consists of a narrow bandpass filter, a monochromator, a photomultiplier, an amplifier, a boxcar (gated integrator), or a multi-channel analyser, or a lock-in amplifier for continuous systems. The data processor consists of an analog-to-digital converter, interface electronics and a computer with data acquisition/analysis software.

Applications of LEAFS in Analysis of Real Substrates

Comprehensive Review of LEAFS Applications in Analysis of Real Substrates

Liquid Samples. There are numerous aqueous solutions that have been analysed by LEAFS. Certified reference materials were analysed for many elements by several authors. Epstein et. al.¹⁻² used non-resonance flame LEAFS to satisfactorily recover the content of Ni and Fe in river waters reference materials. Spectral interferences were minimized by the use of an intracavity etalon narrowing the laser bandwidth. Horvath et al.³ analysed a Standard Reference Material for Pb also using non-resonance LEAFS with a O₂-Ar-Acetylene mini- flame. Cheam et al.⁴⁻⁵ optimized their copper vapor laser-based LEAFS to analyze several riverwater and seawater reference materials for Pb. They used a graphite furnace tube as an electrothermal atomizer (ETA). Snow and ice from Antarctic and Greenland was analysed for Cd and Pb by Bolshov et. al.⁷⁻¹⁰ using an Excimer-pumped dye laser. For Cd these authors used a resonance transition of 228.8 nm. Other samples include river waters^{1,2,4,6}, ore process solutions¹¹, blood¹², tap water¹³, organic solvents and salt solutions¹³⁻¹⁴, Great Lakes waters^{4,15}, oceanic waters⁵, and rat urine¹⁶.

Biologicals and Agriculturals. Trace metals were determined in wheat, potato and grass mixture by various techniques of atomization (ETA with Argon atmosphere^{11,20} or under vacuum, VETA^{17,20}) and of sample state (solid^{11,17,20} and acid digest²⁰). Although it's not as sensitive as Argon ETA, the vacuum technique was found to effectively minimize matrix interferences for solid sample analysis. Other substrates investigated for metals include pine needles^{3,21,22,29}, wheat flour¹⁸, spinach¹⁸, mouse brain¹⁹, bovine liver^{19,21,29}, tomato leaves^{21,29}, citrus leaves^{21,22,29}, milk powder^{21,29}, and rat urine¹⁶.

Pure, alloyed and unalloyed metals. This group of substrates has been often studied also for the determination of trace metal impurity. Pure and suprapure metals

(Copper^{24,30}, Lead¹³, Tin^{17,20}, Steel¹⁸, Germanium²⁴, Indium²⁵ and Gallium²⁵), unalloyed Copper¹⁻³, Nickel alloys^{26,27,29} and lead alloy²⁶ have been analysed by LEAFS. Solids or acid digests were atomised usually by graphite furnace techniques.

Others. Other substrates encompass silica and quartz¹⁷, glass²⁰, powder²⁸, coal fly ash^{1,2,22}, soil and sediments^{11,22}, and air samples²³. Table 1 summarizes all the analyses of the various substrates along with analytes, detection limits, atomizer type, and sample form. Table 2 lists the authors, elements, excitation/measurement wavelengths, and the laser systems used by each investigator.

LEAFS Analysis of Environmental Samples at NWRI

Our LEAFS system (Fig. 3) comprises a Copper Vapor Laser (Metalaser Technologies MLT20), which optically pumps a Rhodamine 6G dye laser (Laser Photonics). An EDL lamp is used for laser tuning³¹. The dye laser output (566 nm) is then frequency-doubled by a second harmonic generator (Autotracker II, Inrad Inc., KDP crystal) to give the 283 nm UV light. This light, directed through a pierced mirror into a graphite furnace (Perkin-Elmer HGA 2100), excites Pb atoms generated in the furnace. The fluorescent light (406 nm) emitted by the deactivated atoms is collected and measured via a monochromator- photomultiplier- boxcar system. A 6 kHz repetition rate is used. Ideally, the laser energy should be adjusted to just saturate the atomic transition. In practice however, we reduced the laser power so that peak irradiance of the 283 nm beam in the furnace was about 2 kW/cm² in order to increase the copper vapor laser lifetime. This was adequate for most of our requirements.

Great Lakes waters. Great Lakes waters have been traditionally analysed for trace metals by AA or ICP after a large volume (~ 0.1-2 l) has been preconcentrated by several orders of magnitude. With the LEAFS system which has a detection limit of 0.4 ng/l (10 fg absolute), a mere 20 µl of sample was directly analysed without any preconcentration. A linear dynamic range of 5 orders of magnitude, unheard of in AAS, can be easily obtained. Figure 4 shows typical

fluorescence peaks for blanks, standards and samples. As can be seen, the instrument sensitivity can be easily adjusted by simply changing the PMT voltage instead of using neutral density filters; specifically 1.6 kV was for low sensitivity (where the responses for 50 ng/l generated ~ 4V responses) and 1.9 kV for high sensitivity (where 20 ng/l generated almost 8V responses). The ten replicate analyses of 50 ng/l standard show good reproducibility giving an RSD of 1.8%. An exhaustive 9-step labware cleaning procedure and clean room practices³² were used throughout.

Figure 5 shows typical vertical concentration profiles for Lake Superior, the biggest and deepest of the Great Lakes. The general trend as a function of depth is almost asymptotic -- high levels at surface sites which decrease rapidly to a near constant concentration for the deeper sites. This suggests that atmospheric inputs are more significant than sediment-water releases. Across Lake Ontario, thirteen stations with a total of fifty four sampling sites were studied. For each station, the average concentration of Pb at the sampling sites was calculated and plotted in Figure 6, which shows particularly high Pb concentrations in the western part of the Lake, the Niagara River-Hamilton-Toronto region (stations 21, 104 and 9B). The overall average concentration of dissolved Pb in Lake Ontario was 25 ng/l (range 4-154 ng/l). For lakes Erie and Superior the average concentration was 9 ± 11 and 4 ± 5 ng/l respectively.

Figure 7 represents the precision function of all LEAFS analyses of the three Great Lakes waters, and indicates that the method is capable of producing precise results even at the very low concentration levels. The method accuracy was well demonstrated by excellent recoveries from Certified Reference Materials (CRMs) and spiked samples. The figure also shows that except a few highly concentrated areas (> 50 ng/l), most sites contain less than 25 ng/l of Pb.

Oceanic waters. Seawater is a very complex, interference-causing matrix containing trace levels of lead and other elements (ng/l). These characteristics form a

troublesome but challenging problem for analytical chemists, as evidenced in the literature by numerous publications. The bulk of the past works relies on techniques to minimize the salt matrix and to preconcentrate the metals before their determination can be made by various methodologies. Table 3 summarizes the conventional methodologies and preconcentration techniques.

The LEAFS ultrasensitivity makes direct analysis of seawater possible. A study on salinity effect showed that the optimal volume of sample to be used was 3 μl . Since there is no representative seawater matrix which can be used for the standards calibration technique, an "in situ" known addition technique was devised using a programmable micropipette. The pipette was programmed to perform segmented sampling of 17 μl of Milli-Q water carrier, 3 μl seawater, 2 μl air gap, and 5 μl standard (or MQW), and to dispense the ensemble into the graphite tube (Fig. 8). The sampling/dispensing sequence takes about 30 s.

The 3 μl sample volume used in our method is much smaller than that used by conventional methods, 5-2000 ml. This translates into a LEAFS absolute detection limit of 3 fg, which is far superior to others (6000 - 50,000 fg) as seen in Table 4. The good reproducibility is well illustrated by duplicate analyses of numerous samples shown in Figure 9, resulting in a range of RSD of 0.3-8 %. The accuracy is well demonstrated by the excellent recoveries of four seawater CRMs (Fig. 10) and by the agreement with ICPMS results on a vertical profile from a Russian Hydro station in the Pacific Ocean (Fig. 11).

In short, the method has the lowest detection limit reported to date. The method voids the tedious, time-consuming preconcentration steps, minimizes contamination sources, and lends itself to easy automation.

Canadian Arctic Snow and Ice. The effects of long-range transport of atmospheric pollutants, trace metals included, have been well documented; effects

which can be detrimental to the Canadian Arctic³³⁻³⁴. Data on metals accumulation in snow and ice layers in this environment is lacking. Preserving the Integrity of the Arctic is one of Green Plan goals, for which improvements in analytical capability and data quality are a key initiative³⁵. The recently developed LEAFS is an ideal analytical instrument for Arctic snow and ice samples as they are relatively difficult to acquire (more so in large quantity) and toxic metals levels are expected to be relatively low.

Protocols and facilities for collecting trace metals samples in the Arctic is an uncharted territory. Using our expertise in clean room practices for handling Great Lakes waters we were able to obtain some representative samples from the Agassiz Ice Cap (North-central Ellesmere Island, Northwest Territories, Canada). The sampling site was about 2 km NW (upwind) from the base camp (80°40'N 73°30'W) and about 1800 m above sea level. The site was chosen because the seasonal stratification is known to be minimally affected by the snow drift and snow melt³⁶⁻³⁷, making the spatial study of metal accumulation meaningful.

Sampling was done in March 1993, all equipment used being made of plastic except for the stainless steel shovel. The shovel was used to dig a pit of ~ 1 m² area and 2.5 m deep. Sampling was done down the side of the pit using a Teflon coring tube, which was pressed into a freshly scraped area. The corer sides were pressed to crumble and free the ice/snow sample, which was then transferred into a 1 litre low density linear polyethylene bottle. The samples were then brought to the clean room and acidified to pH 1.5 and analysed by LEAFS.

Figure 12 shows that the concentration of total (unfiltered) Pb and the conductivity peak during late winter /early spring of each year (preceding summer months marked by solid triangles). These peaks coincide with the Arctic haze phenomenon, which occurs in the same season and which is characterized by the presence of elevated toxic pollutants³⁸⁻³⁹. Although no definite statement can be made

concerning metal accumulation based on these limited data, the results do show marked differences between the high Pb concentration in the "Arctic winter" snow layers (corresponding to late winter/early spring period) and the low Pb concentration in the summer/fall layers. Earlier observations³⁶ showed that atmospheric trace metals and major ions in the Canadian Arctic also peak during the Arctic haze period. The historical conductivity and acidity values in ice cores from Agassiz ice cap also peak as the Arctic air pollution does during the December-April period³⁷. Thus the Pb results in accumulated snow/ice layers are in general accordance with the regional, historical atmospheric and snow/ice chemistry. A study on more detailed samples / deeper profiles is desirable to elucidate historical metal accumulation.

Dissolved and Total Pb. An unfiltered, unacidified seawater sample was collected from the nearshore of Pacific Ocean near Vancouver, B. C. Upon arrival to the clean laboratory, a part of the sample was filtered and acidified, another part was acidified unfiltered (the precipitate on the original bottle not included). Both parts were spiked at three different levels and acceptable recoveries of $100 \pm 10 \%$ were obtained ($n = 24$). The ratio of dissolved (filtered) / total (unfiltered) was 53%, indicating a significant amount of Pb in particulate form. For Arctic snow and ice water, on-site filtration was carried out on three subsurface samples collected ~ 200 m away from the campsite, and analyses made on both filtered and unfiltered samples. The results indicate the fraction of filtered / unfiltered fluctuate around 60%, again indicating a significant amount of particulate form (Table 5).

The analytical methods for filtered Great Lakes waters⁴ and seawaters⁵ were used. Further method validation and analyses of unfiltered samples including Great Lakes waters are needed to firm up this observation. It seems that total Pb content can be directly determined with just a few microliters of sample without any preconcentration/digestion procedure, which requires filtering large volume of water (minimum 600 litres) followed by lengthy acid digestion prior analysis.

Potential of LEAFS

ETA-LEAFS is superior to ETA-AAS for many reasons. Due to the utmost selectivity inherent from single-line laser excitation and from emission selectivity, LEAFS has the highest spectral selectivity, thus the least spectral interferences among all atomic methods. Lasers have higher spectral power density than classical light sources which makes optical saturation attainable and improves the detection limit. LEAFS has smaller background signals than ETA-AAS; much larger linear dynamic range, 4-7 orders of magnitude vs. 1-3; and permits direct analysis of diverse matrices without tedious sample pretreatment.

Why then has LEAFS not been as much used as AAS ? The first obvious reason is that it's not commercially available. To use one means to build one, and there are not enough experts around. There are not enough trained analysts to use them. Lasers are still relatively large and expensive.

The ultrasensitivity and practicality of LEAFS as shown in the achievements section are too appealing to not expect availability of commercial units soon. At that time, routine use will rapidly expand, and more analysts will strive to achieve its ultimate potential. Multi-element analysis will be achieved by the use of very small, efficient diode lasers in series focused through a graphite furnace and with fluorescence detected by photodiodes (PMT unnecessary).

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Table 1. Summary of Analyses of Various Substrates by LEAFS

Substrate	^c Element	Detection Limit, * ng/ml (pg)	^a Atomizer Type	^m Medium	Reference
Aqueous Reference Materials	Ni	0.5	Flame (Air-Ac)	Acidified	(1980) ¹
	Fe	0.06	Flame (Air-Ac)	"	(1980) ²
	Pb	0.2 (0.9)	Flame(O-Ar-Ac)	"	(1981) ³
	Pb	0.4 ng/l (0.01)	GF-ETA (Tube)	"	(1992) ⁴
	Pb	1 ng/l (0.003)	GF-ETA (Tube)	"	(In press) ⁵
River Waters	Ni, Sn	0.5, 3	Flame (Air-Ac)	Acidified	(1980) ¹
	Fe	0.06	Flame (Air-Ac)	"	(1980) ²
	Co, Au	4 fg, 10 fg	GF-ETA (Tube)	"	(1990) ⁶
	Pb	0.4 ng/l (0.01)	GF-ETA (Tube)	"	(1992) ⁴
Snow & Ice	Pb	0.18 pg/g	GF-ETA (cup)	Acidified	(1989) ⁷
	Pb	0.18 pg/g	GF-ETA (cup)	"	(1990) ⁸
	Cd	0.01pg/g(.0005)	GF-ETA (cup)	"	(1991) ⁹
	Pb, Cd	0.18, 0.07 pg/ml	GF-ETA (cup)	"	(1992) ¹⁰
Ore Process Solutions	Ir	0.2 µg/l (6)	GF-ETA (cup)	Extr. Soln.	(1981) ¹¹
Blood	Pb	4	Flame (Air-Ac)	TritonX dln	(1984) ¹²
Tap Water	Pb	(0.006)	GF-ETA (cup)	Acidified	(1988) ¹³
Organic Solvents	Pd, Rh, Ir	(1.0 - 45)	GF-ETA (cup)	Acid. & Sol	(1987) ¹⁴
	Pb	(0.006)	"	"	(1988) ¹³
4% NaCl	Pb, Tl,Pd,Rh,Ir	(.05,.6,.7,2,140)	GF-ETA (cup)	Acidified	(1987) ¹⁴
	Tl, Pb, Co, Sn	(.6,.06,12,510 ⁴)	GF-ETA (cup)	"	(1988) ¹³
4% PbCl ₂	Tl, Bi	(24, 36)	GF-ETA (cup)	Acidified	(1988) ¹³
Great Lakes Waters	Pb	0.4 ng/l (0.01)	GF-ETA (tube)	Acidified	(1992) ⁴
		0.4 ng/l (0.01)	GF-ETA (tube)	"	(1993) ¹⁵
Oceanic waters	Pb	1 ng/l (0.003)	GF-ETA (tube)	Acidified	(In Press) ⁵
Rat urine	Mn, Sn (o-m)	(8-22), 12 ng/ml	Flame (Air-Ac)	HPLC extr.	(1991) ¹⁶
Biologicals & Agriculturals	Co	2 ng/l (0.06)	GF-ETA (cup)	Dry Solid	(1981) ¹¹
	Pb	4	Flame (Air-Ac)	TritonX dln	(1984) ¹²
	Sr, Fe	---	Flame	Acid digest	(1981) ³
	Co	0.5 ng/g	GF-VETA (cup)	Solid	(1986) ¹⁷
	Mn, Cu	1, 2 pg	GF-ETA (cup)	Acid digest	(1986) ¹⁸
	Tl	---	GF-ETA (tube)	Acid digest	(1988) ¹⁹
	Co	---	GF-ETA (cup)	Dil extract	(1988) ²⁰
	Co	---	GF-VETA (cup)	Solid	(1988) ²⁰
	Tl, Mn, Pb	0.5-15 fg	GF-ETA (tube)	Ad & slurry	(1990) ²¹
	Pb, Co	0.4, 50 pg/g	GF-ETA (tube)	Acid digest	(1992) ²²

Table 1. Summary of Analyses of Various Substrates by LEAFS (continued)

Substrate	Element	Detection Limit, *ng/ml (pg)	^a Atomizer Type	^m Medium	Reference
Biologicals & Agriculturals	Mn P	(8-22) (8)	Flame (Air-Ac) GF-ETA (tube)	HPLC extr. Acid digest	(1991) ¹⁶ (1992) ²⁹
Air Samples	Pb, Tl	0.1, 0.01 pg/m ³	GF-ETA (tube)	Solid	(1990) ²³
Soil & Sediments	Fe, Cu, Co Pb, Co	(0.1, 0.15, 0.06) 0.4 - 50 pg/g	GF-ETA (cup) GF-ETA (tube)	Acid extract Acid digest	(1981) ¹¹ (1992) ²²
Coal Fly Ash	Ni Fe Pb, Co	0.5 ng/ml 0.06 ng/ml 0.4 - 50 pg/g	Flame (Air-Ac) Flame (Air-Ac) GF-ETA (tube)	Acid digest Acid digest Acid digest	(1980) ¹ (1980) ² (1992) ²²
Pure Metals	Pb Tl, Bi Co Mn, Cu Co Pb, Si Si	0.1 µg/g 0.04, 0.1 ng/g 0.5 ng/g (1, 2) 0.2 µg/l 40, 3 ng/g 0.8 (in In), 2 (in Ga) ng/g	Glow Discharge GF-ETA (cup) GF-VETA (cup) GF-ETA (cup) GF-VETA (cup) ISHCD, ISPMMD ISPMMD	Solid Solid & Ad Solid Acid digest Solid Solid Solid	(1984) ³⁰ (1988) ¹³ (1986) ¹⁷ (1986) ¹⁸ (1988) ²⁰ (1991) ²⁴ (1993) ²⁵
Alloyed & Unalloyed Metals	Ni, Sn Fe Pb Ru Tl, Pb Te, Sb P	0.5, 3 ng/ml 0.06 0.2 (0.9) 1 ng/g 20, 5 fg 0.01 ng/g (8)	Flame (Air-Ac) Flame (Air-Ac) Flame GF-VETA (cup) GF-ETA (tube) GF-ETA (tube) GF-ETA (tube)	Acid digest Acid digest Acid digest Solid Acid digest Acid digest Acid digest	(1980) ¹ (1980) ² (1981) ³ (1988) ²⁰ (1990) ²⁶ (1993) ²⁷ (1992) ²⁹
SiO ₂ & Quartz Glass	Co Co Co	0.5 ng/g 0.02 ng/g ---	GF-VETA (cup) GF-ETA (cup) GF-VETA (cup)	Solid HF treated Solid	(1986) ¹⁷ (1988) ²⁰ (1988) ²⁰
Powder	Co	5 (Al ₂ O ₃), 1 (SiO ₂) ng/g	Hot HCA (cup)	Solid	(1992) ²⁸

* The detection limits shown are not necessarily the method's detection limits

^c Mn, Sn (o-m) = organomanganese and organotin

^a Flame(O-Ar-Ac) = O₂-Ar-C₂H₂ mini-flame with ultrasonic nebulizer

^a GF-ETA = Graphite Furnace - Electrothermal Atomizer

^a GF-VETA = Graphite Furnace - Vacuum Electrothermal Atomizer

^a ISHCD, ISPMMD = Ion Sputtering in a Hollow Cathode Discharge and in a Planar Magnetron Discharge

^a Hot HCA (cup) = Hot Hollow Cathode Atomizer (cup)

- ^m Acidified = Acidified in aqueous solution
- ^m Extr. Soln. = Extracted Solution.
- ^m Acid. & Sol = Acidified in aqueous solutions and solvent
- ^m HPLC extr. = HPLC extracts
- ^m Solid & Ad = Solid & Acid digest
- ^m TritonX dln = Dilution with TritonX (1+10)
- ^m Dil extract = Diluted acid extract

Table 2. Summary of Authors Using LEAFS to Analyse Real Substrates

Reference	Substrate	Element	Wavelength, nm excitation/measurement	Laser
(Epstein et al., 1980) ¹	Aqueous CRM	Ni	300.249/342 (center of lines)	CMX-4 (Chromatrix), Flash-lamp pulsed dye laser
	River Waters	Ni, Sn	300.249/342, 300.914/317.505	
	Coal Fly Ash	Ni	300.249/342	
	Unalloyed Copper	Ni, Sn	300.249/342, 300.914/317.505	
(Epstein et al., 1980) ²	River Water CRM	Fe	296.7/373.5	CMX-4 (Chromatrix), Flash-lamp pulsed dye laser
	Coal Fly Ash	Fe	"	
	Unalloyed Copper	Fe	"	
(Horvath et al., 1981) ³	Aqueous CRM	Pb	283.3/405.8	Molelectron UV-14 N ₂ with DL300 dye laser (for Fe, CMX-4 (Chromatrix)
	Unalloyed Copper	Pb	"	
	Pine needles	Sr, Fe	460.7/460.7, 296.7/373.5	
(Cheam et al., 1992) ⁴	Aqueous CRM: SRM1643c	Pb	283.3/405.8	Copper Vapor Laser (Metalaser), DL-16 dye laser (Laser Photonics)
	River Water CRM: SLRS-2	Pb	283.3/405.8	
	Great Lakes waters: Ontario, Erie, Superior	Pb	283.3/405.8	
	Seawater CRMs: NASS-3,-4, CASS-2, SLEW-1 Oceanic waters	Pb	283.3/405.8	
(Cheam et al., in press) ⁵		Pb	283.3/405.8	Copper Vapor Laser, DL-16 dye laser
(Remy et al., 1990) ⁶	River Waters	Co, Au	308.26/345.35, 242.80/312.28	Nd-YAG pumped d. laser
(Bolshov et al., 1989) ⁷	Ancient Antarctic Ice	Pb	283.3/405.8	XeCl-pumped dye laser " " "
(Boutron et al., 1990) ⁸	Vostok Antarctic Ancient Ice	Pb	283.3/405.8	
(Bolshov et al., 1991) ⁹	Antarctic and Greenland Ancient Ice & recent snow	Cd	228.8/228.8	
(Bolshov et al., 1992) ¹⁰	Antarctic and Greenland Ancient Ice & recent snow	Pb, Cd	283.3/405.8, 228.8/228.8	
(Bolshov et al., 1981) ¹¹	Ore Process Solutions	Ir	295.1/322.1	Nd-YAG pumped dye laser
	Wheat, potato and grass mixture Soil & Sediments	Co	304.4/340.5	
		Fe, Cu, Co	297/373; 325/510; 304.4/340.5	
	Blood	Pb	283.3/405.8	
(Omenetto et al., 1984) ¹² (Falk et al., 1988) ¹³	4% PbCl ₂	Tl, Bi	276.79/352.94; 306.77/472.22	XeCl-pumped dye laser N ₂ -pumped dye laser (20 Hz)
	Tap water	Pb	283.3/405.8	
	Ethanol	Pb	283.3/405.8	
	4% NaCl	Tl, Pb, Co, Sn	277.79/352.94; 283.3/405.8; 308.26/345.35; 286.33/317.51	
	Suprapure lead	Tl, Bi	276.79/352.94; 306.77/472.22	

(Falk & Tilch, 1987) ¹⁴	4% NaCl Ethanol, Acetone, Methanol (purified versus commercials)	Pb, Ti, Pd, Rh, Ir Pd, Rh, Ir	not given	N ₂ -pumped dye laser (20 Hz)
(Cheam et al., 1993) ¹⁵	Great Lakes Waters: Ontario, Erie, Superior	Pb	283.3/405.8	CVL, DL-16 dye laser
(Walton et al., 1991) ¹⁶	Organo-metallics Rat urine	Mn, Sn Mn	280/403; 300/300 & 300/317 280/403	XeCl-pumped dye laser
(Bolshov et al., 1986) ¹⁷	Wheat, potato and grass mixture Tin SiO ₂ & Quartz Glass	Co Co Co	304.4/340.5 " "	Nd-YAG pumped dye laser
(Goforth et al., 1986) ¹⁸	Wheat flour and spinach Steel	Mn, Cu Mn, Cu	not given "	N ₂ -pumped dye laser
(Dougherty et al., 1988) ¹⁹	Mouse brain and bovine liver	Ti	276.8/352	XeCl-pumped dye laser
(Bolshov et al., 1988) ²⁰	Wheat, potato and grass mixture Tin Lead and Copper alloys SiO ₂ & Quartz Glass	Co Co Ru Co	304.4/340.5 304.4/340.5 287.5/366.3 304.4/340.5	Nd-YAG pumped dye laser
(Butcher et al., 1990) ²¹	Bovine liver, pine needles, tomatoe leaves, citrus leaves, milk powder	Ti, Mn, Pb	277/353; 279/403; 283/405	XeCl-pumped dye laser
(Irvin et al., 1992) ²²	Citrus leaves, pine needles Soil & Sediments Coal Fly Ash	Pb, Co Pb, Co Pb, Co	283.3/405.8; 304.4/340.5 283.3/405.8; 304.4/340.5 283.3/405.8; 304.4/340.5	
(Liang et al., 1990) ²³	Air Samples	Pb, Ti	283.3/405.8; 276.79/352.94	XeCl-pumped dye laser
(Dashin et al., 1991) ²⁴	Pure Copper and Germanium	Pb	283.3/405.8;	XeCl-pumped dye laser
(Dashin et al., 1993) ²⁵	High purity Indium and Gallium	Si	251.432/~ 252 center of 3 lines	XeCl-pumped dye laser
(Irvin et al., 1990) ²⁶	Nickel alloy	Ti, Pb	276.79/352.94; 283.3/405.8	XeCl-pumped dye laser
(Liang et al., 1993) ²⁷	Nickel alloy	Te, Sb	214/238.3 & 238.6; 212.7/259.8	XeCl-pumped dye laser
(Lunyov et al., 1992) ²⁸	Powder	Co, Ni	304.4/340.5; 301.914/310.155	Nd-YAG pumped dye laser
(Liang et al., 1992) ²⁹	Nickel alloy Bovine liver, non fat milk powder, pine needles, citrus leaves, tomatoe leaves.	P, PO P	213.62/253.5; 246.3/324.5 213.618/253.5	XeCl-pumped dye laser
(Smith et al., 1984) ³⁰	Pure copper rod	Pb	283.3/405.8	N ₂ -pumped dye laser

Table 3. Preconcentration Techniques and Associated Blank Concentrations

Technique	Methodology	Pb blank concentration
Chelation-Extraction - Carbamate extraction - Dithizone-chloroform	GFAAS IDMS	24-36 ng/l total blank 0.1 ng per extraction
Resin - Chelamine - Chelex 100 resin	GFAAS ICPMS	1.2 ng absolute 0.08 ng column blank
Reductive precipitation - Tetrahydroborate	GFAAS	1.7 ng absolute
Immobilized chelate - 8-Hydroxyquinoline - 8-Hydroxyquinoline	GFAAS IDICP-MS	< 0.8 ng absolute 2.99 ng/l final col blank ^a
Electrochemical deposition - Hg film electrode	DPASV	~ 5 ng/l
Insitu/online concentration - I-8-HOQ	FI-GFAAS	3.7 pg Pb absolute

^a Various blanks range from 0.2 to 140 ng/l

Table 4. Comparison of detection limits

Methodology	Preconcentration procedure	Relative detection limit, ng/l	Absolute detection limit, fg
DPASV	Rotating, glassy carbon, Hg film electrode	1	50,000
GFAAS/ Extraction	APDC / DDDC	5	20,000
GFAAS/ Chelex	Chelex-100	1.2	24,000
ICP-MS	I-8-HOQ	0.4	20,000
ICP-MS	Chelex-100	0.4	50,000
FI-GFAAS	I-8-HOQ	1.14	5,700
LEAFS	None	1	3

Table 5. Dissolved vs. Total Pb

Arctic snow/ice	Dissolved / Total
Sample # 1	58%
Sample # 2	55%
Sample # 3	62%
Seawater	Dissolved / Total
PC-2	53%

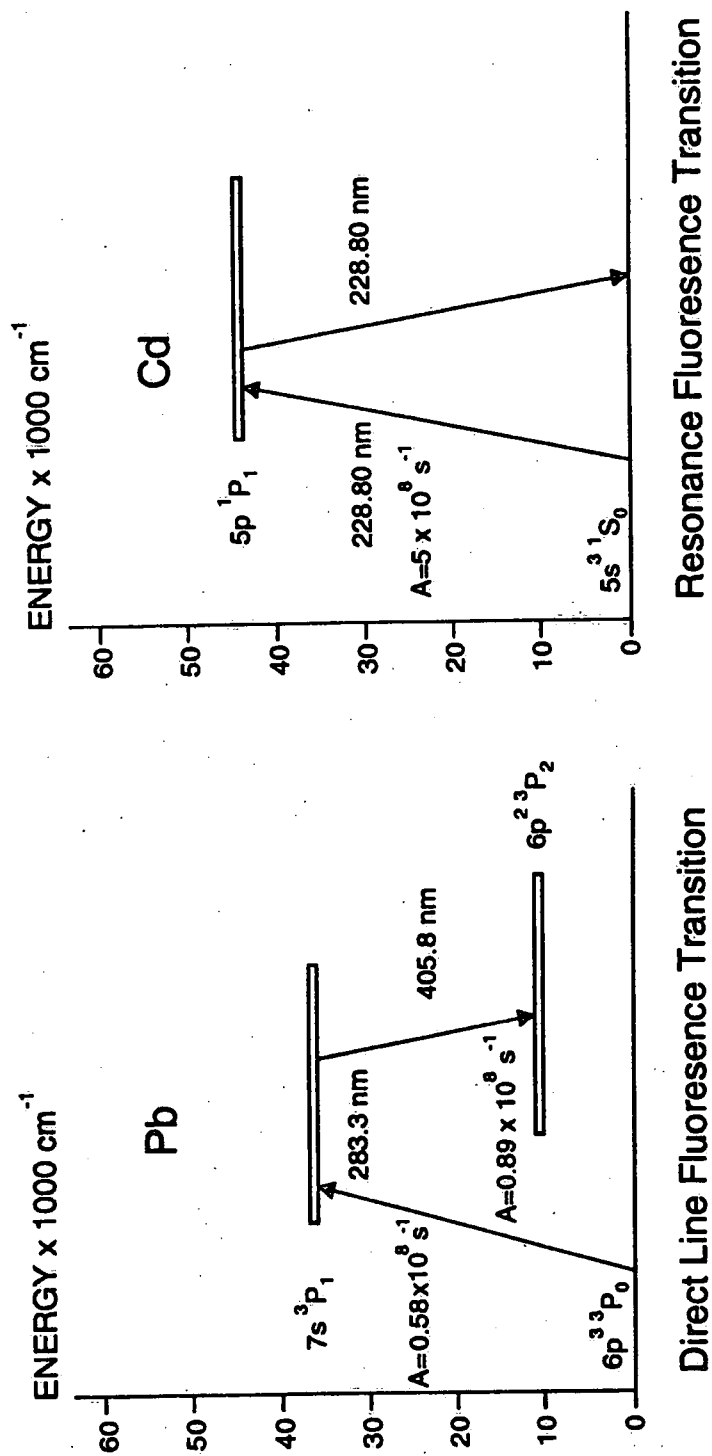
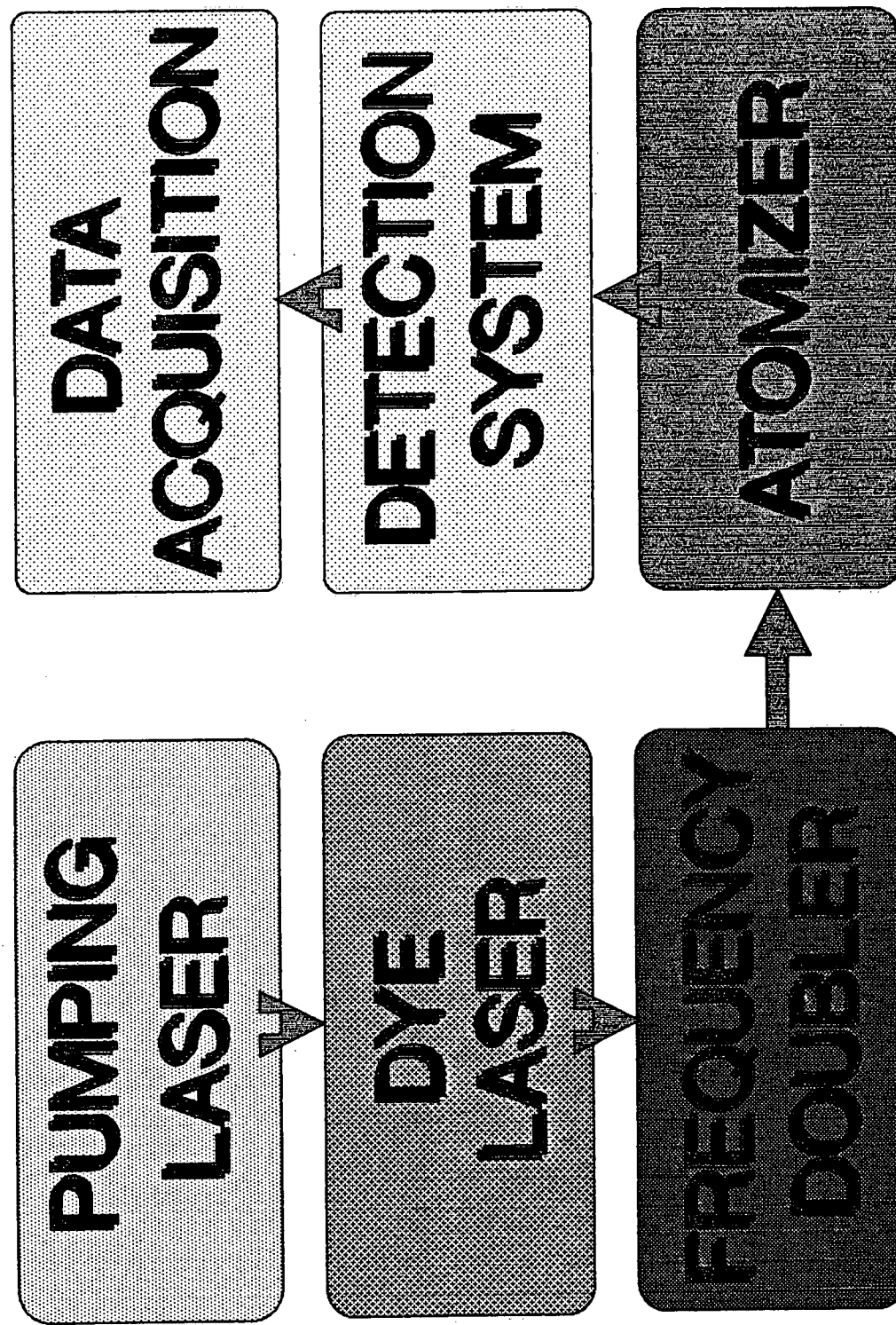


Figure 1. Energy level diagrams for Pb and Cd measurement

FIGURE 2
LEAFS SCHEMATICS



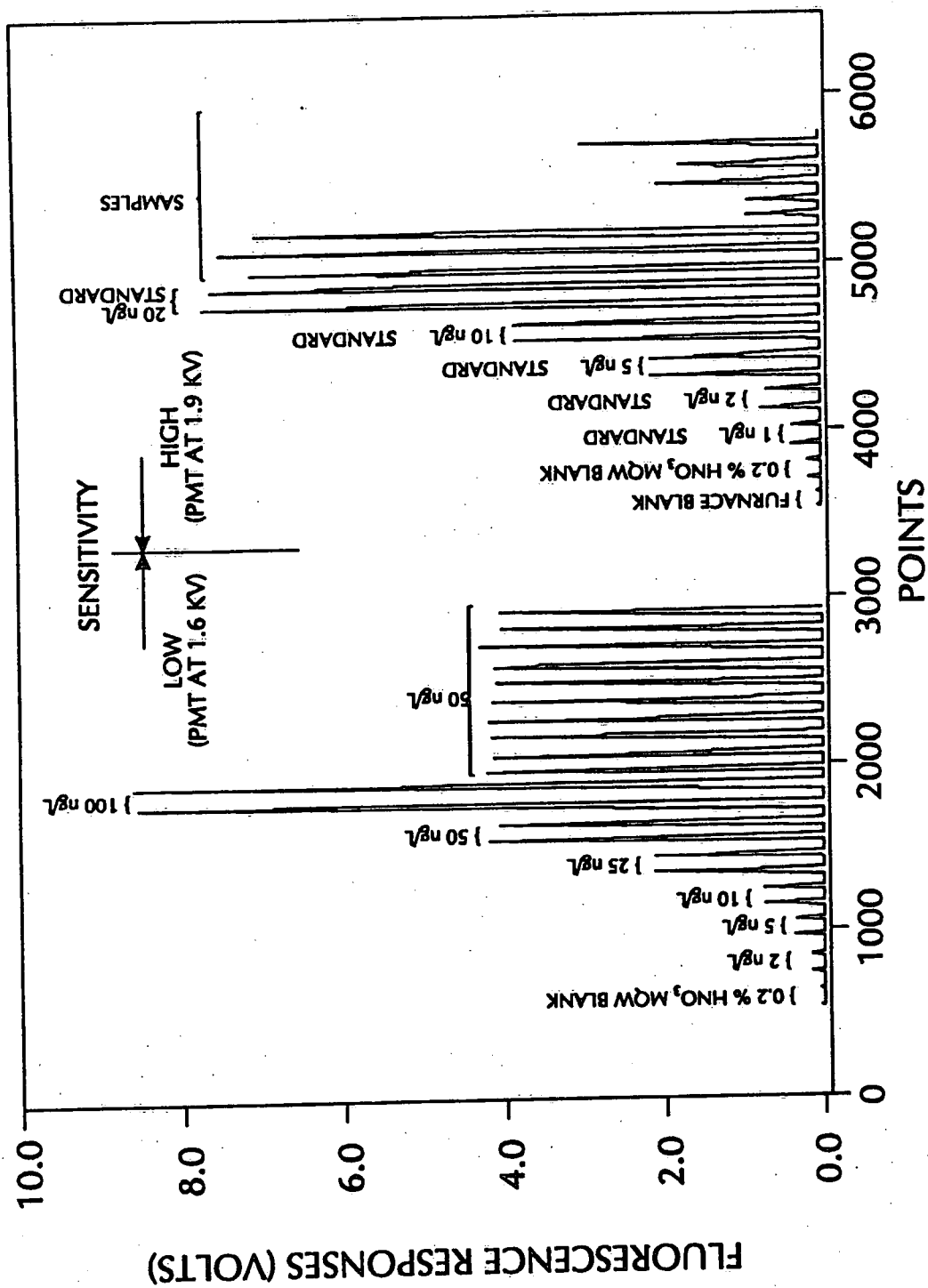


Figure 4: Typical fluorescence responses for standards and samples containing Pb (20 μ L injection)

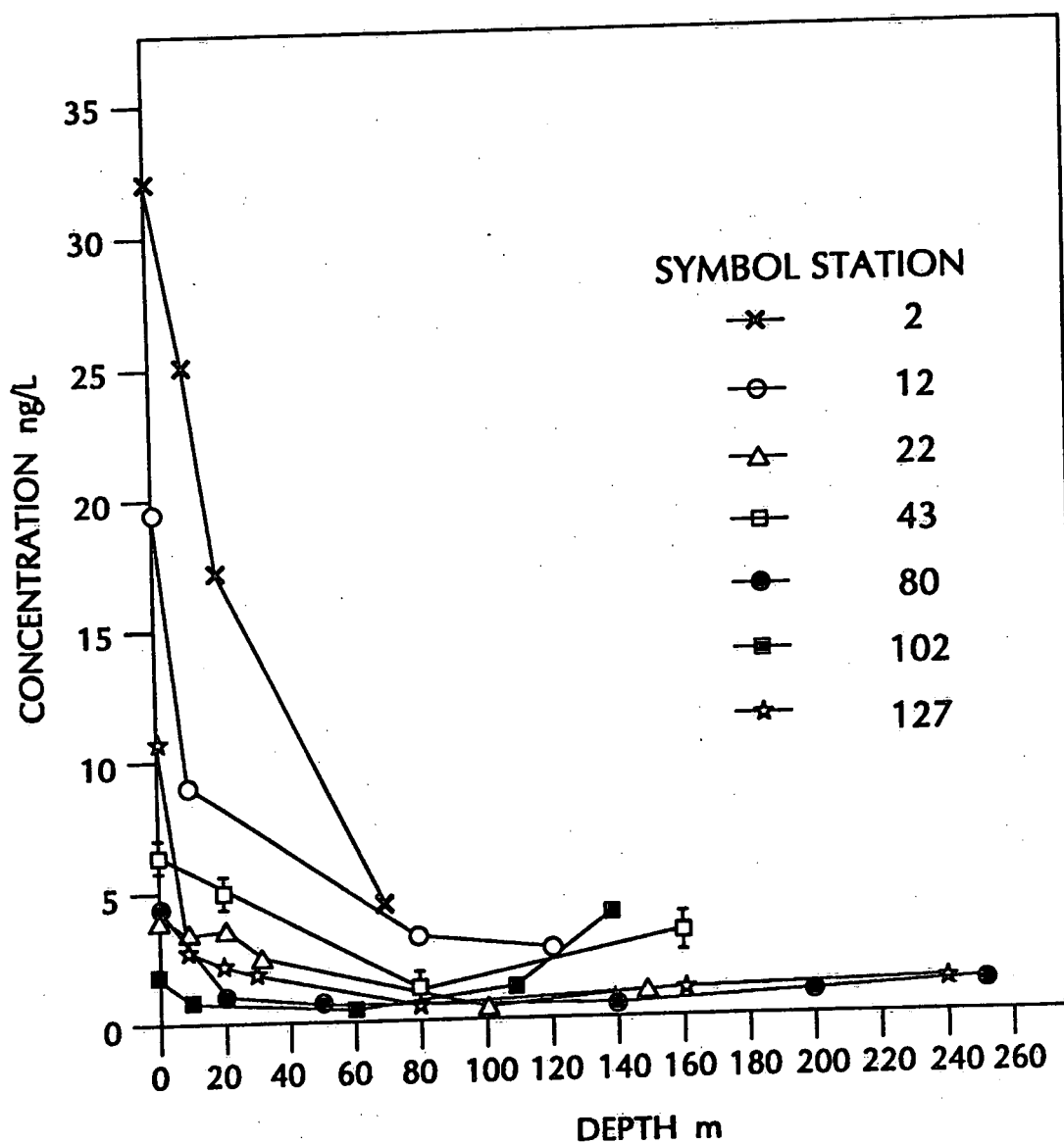


Figure 5: Typical vertical profiles of Pb in Lake Superior

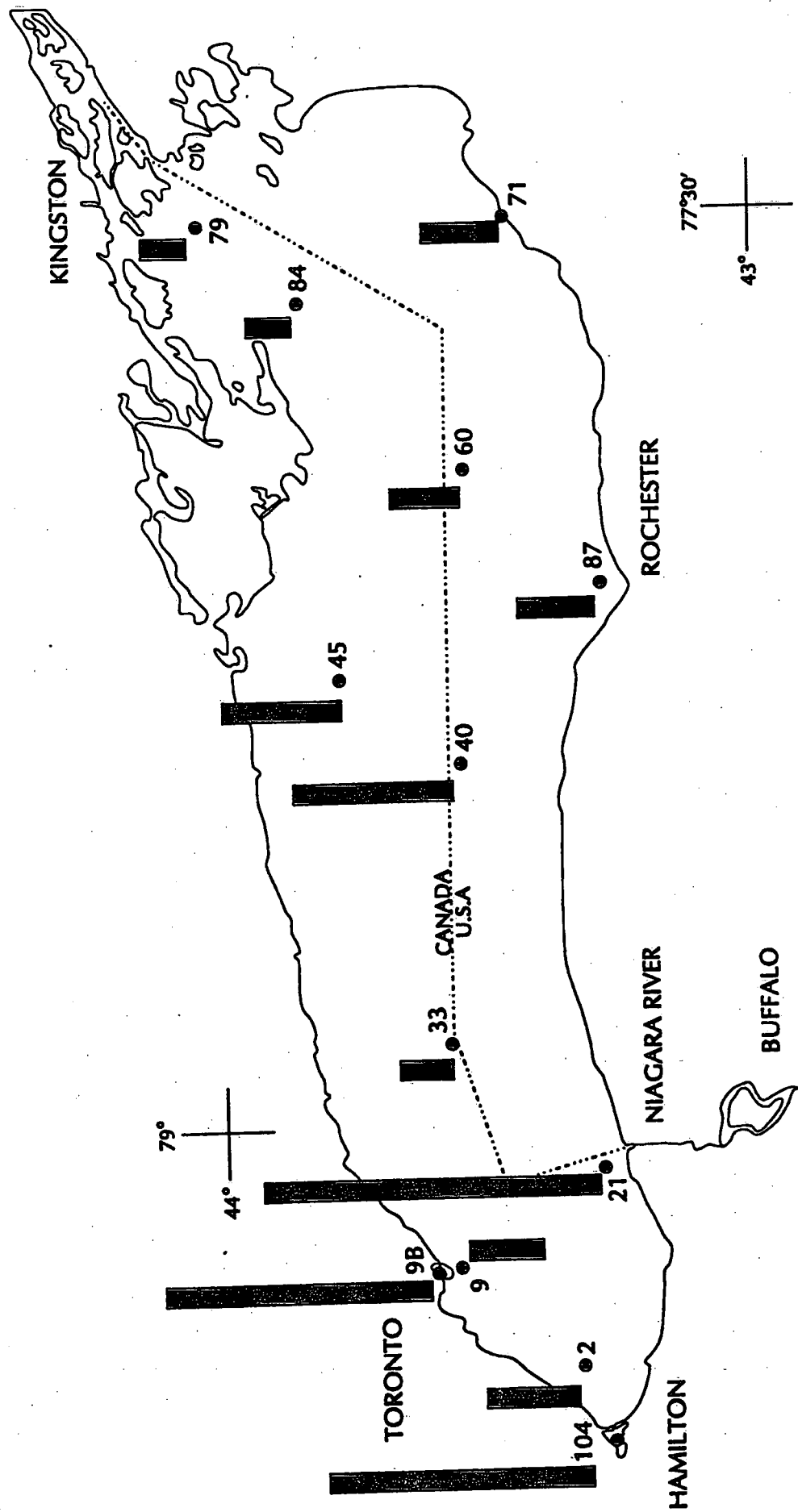
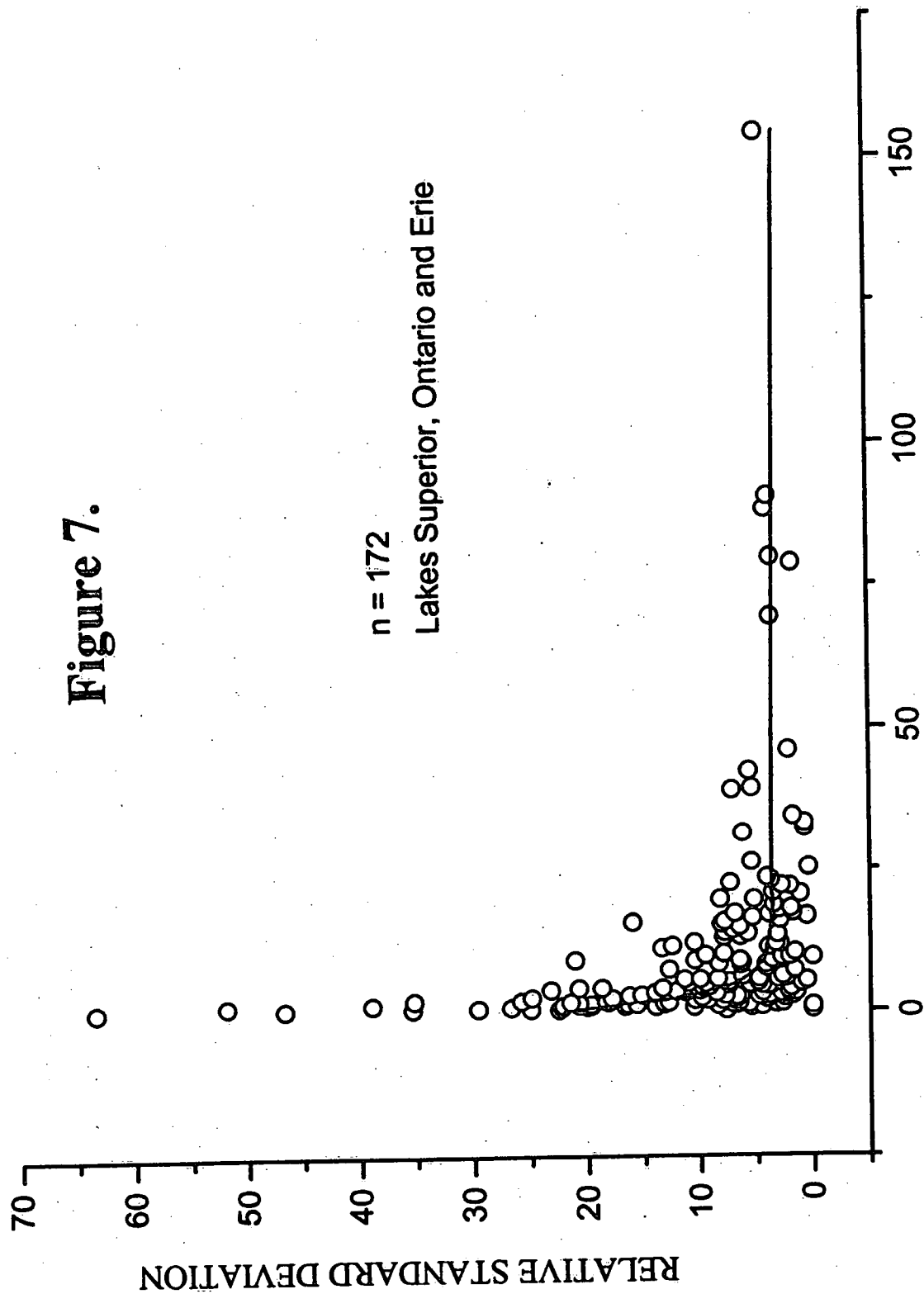


Figure 6: Average Pb concentration (\blacksquare = 10 ng/L) of each vertical profile for the studied stations in Lake Ontario

Figure 7.



MEANS OF REPLICATE ANALYSES OF G. L. WATERS

PRECISION FUNCTION OF G. L. WATERS ANALYSIS BY LEAFS

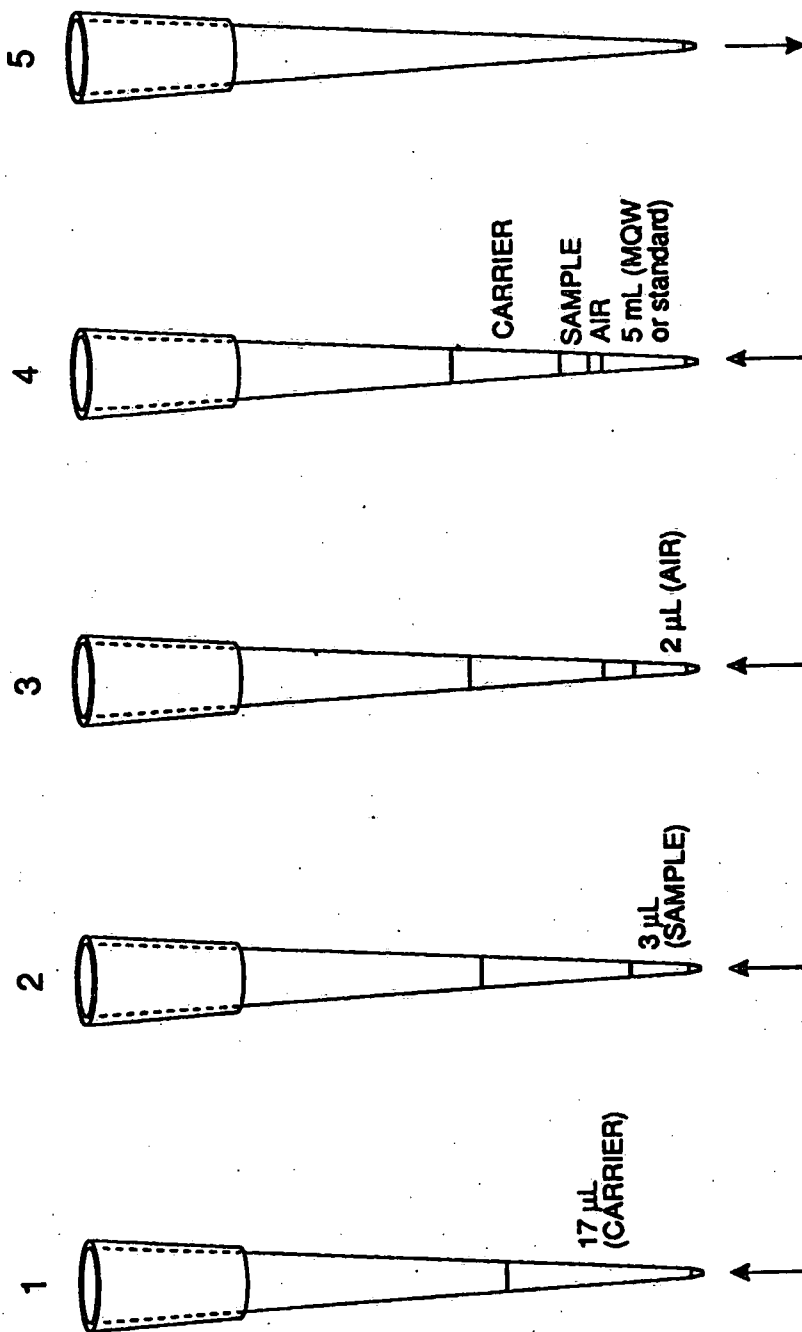


FIGURE 8. A PICKUP AND DISPENSE SEQUENCE, 17-3-2-5

1. PICKUP CARRIER (17 µL MQW)
2. PICKUP SEAWATER (3 µL)
3. PICKUP AIR SPACER (2 µL)
4. PICKUP STANDARD OR MQW (5 µL)
5. DISPENSE TOTAL CONTENT OF TIP

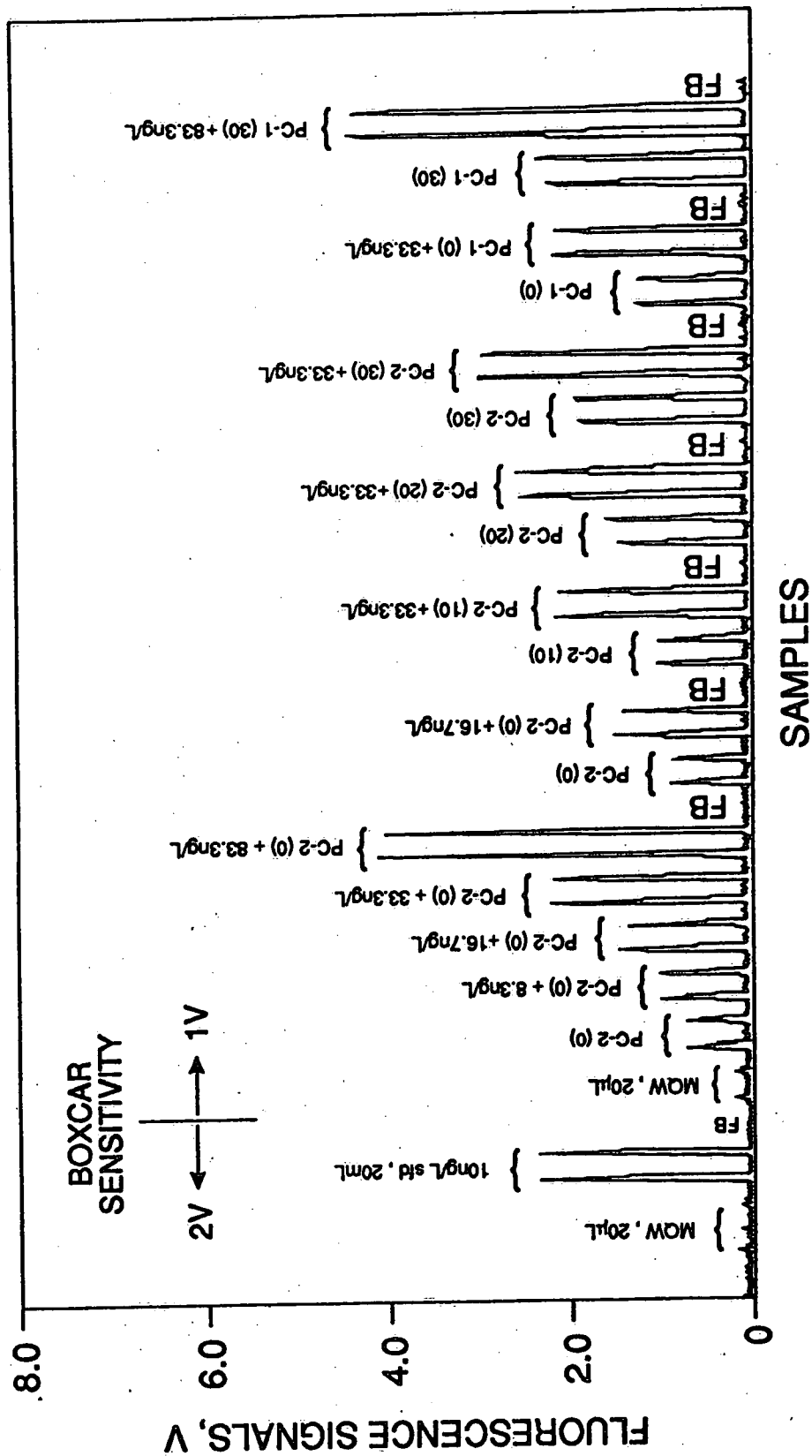


Figure 9. TYPICAL FLUORESCENCE SIGNALS FOR SPIKED AND UNSPIKED SEAWATER SAMPLES USING THE 17-3-2-5 SEQUENCE.

FB = Furnace Blank, PC-2 (0) = an unspiked seawater sample from Pacific Ocean

ANALYSIS OF CERT. REF. MATERIALS

Pb Concentrations in ng/L

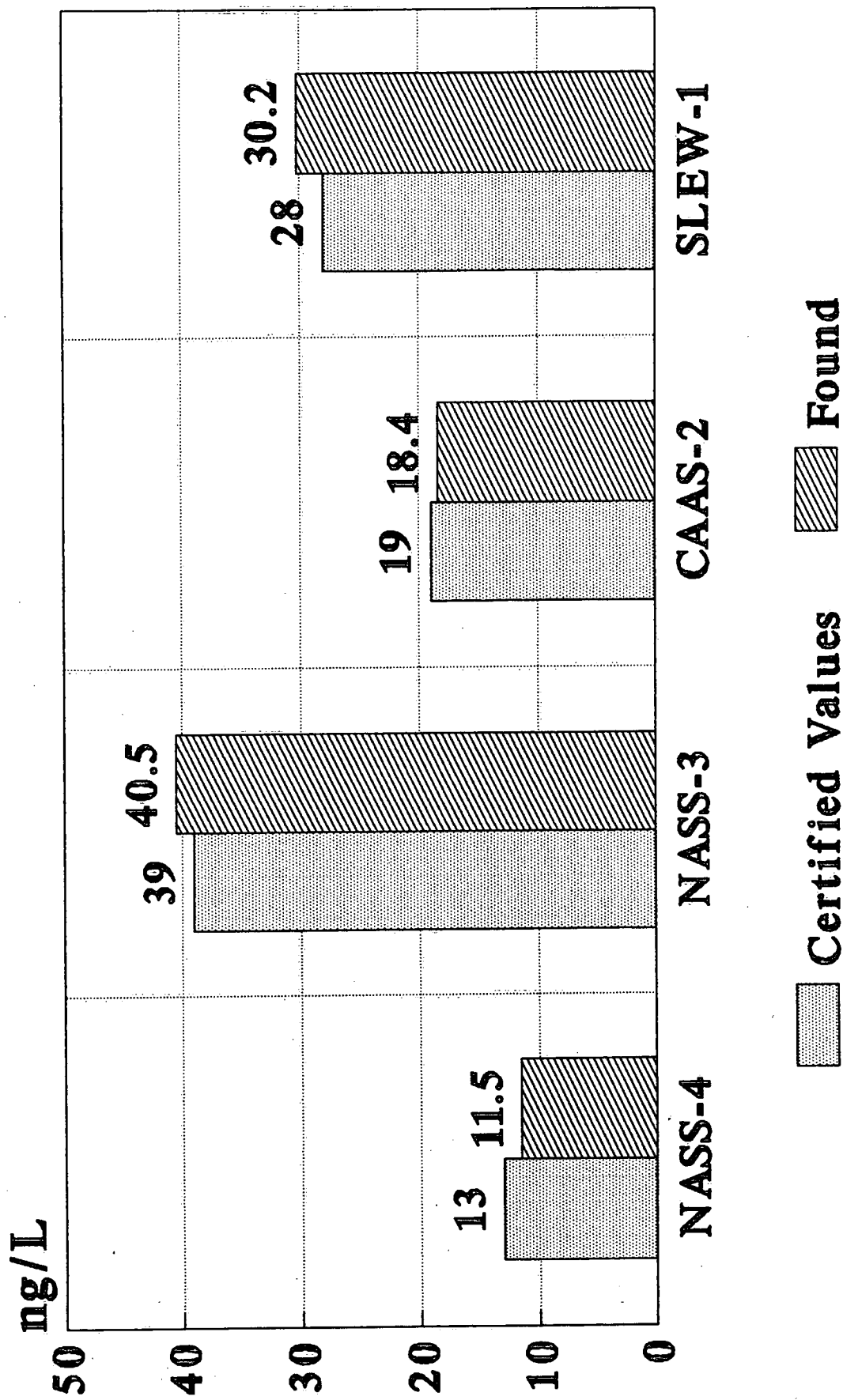


FIGURE 10

VERTICAL PROFILE OF PACIFIC OCEAN Pb concentration in ng/L

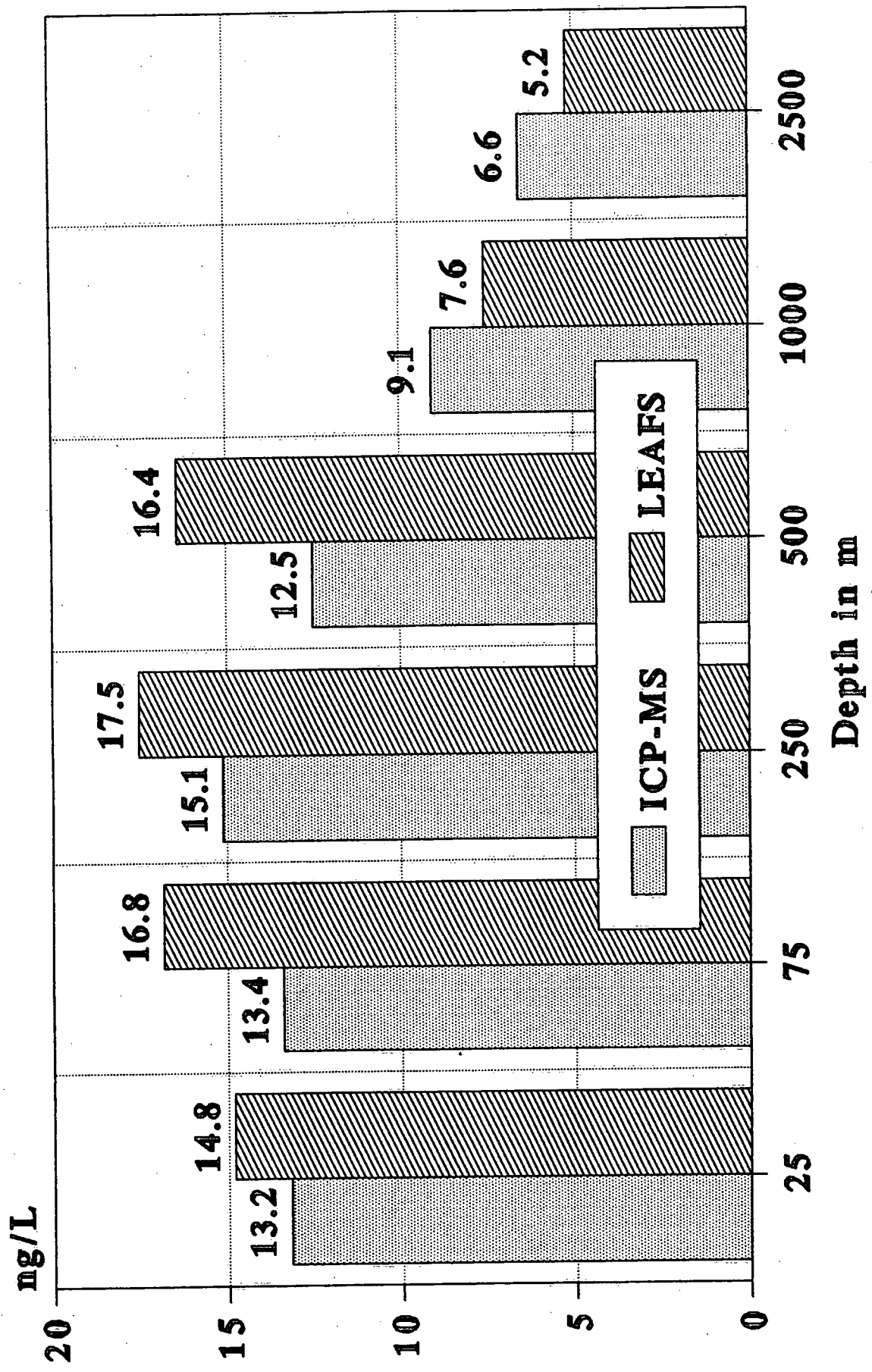
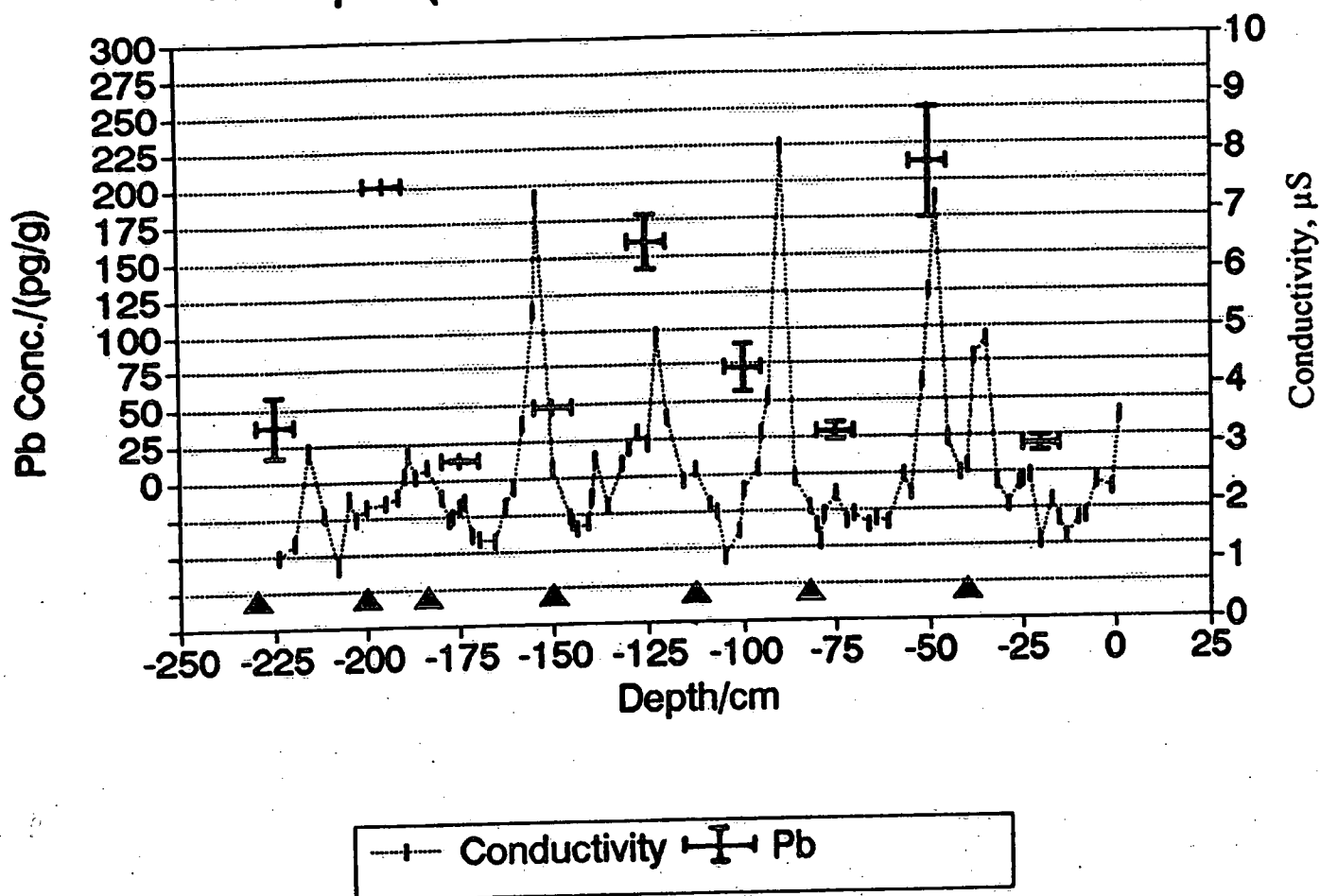


FIGURE 11

Figure 12.

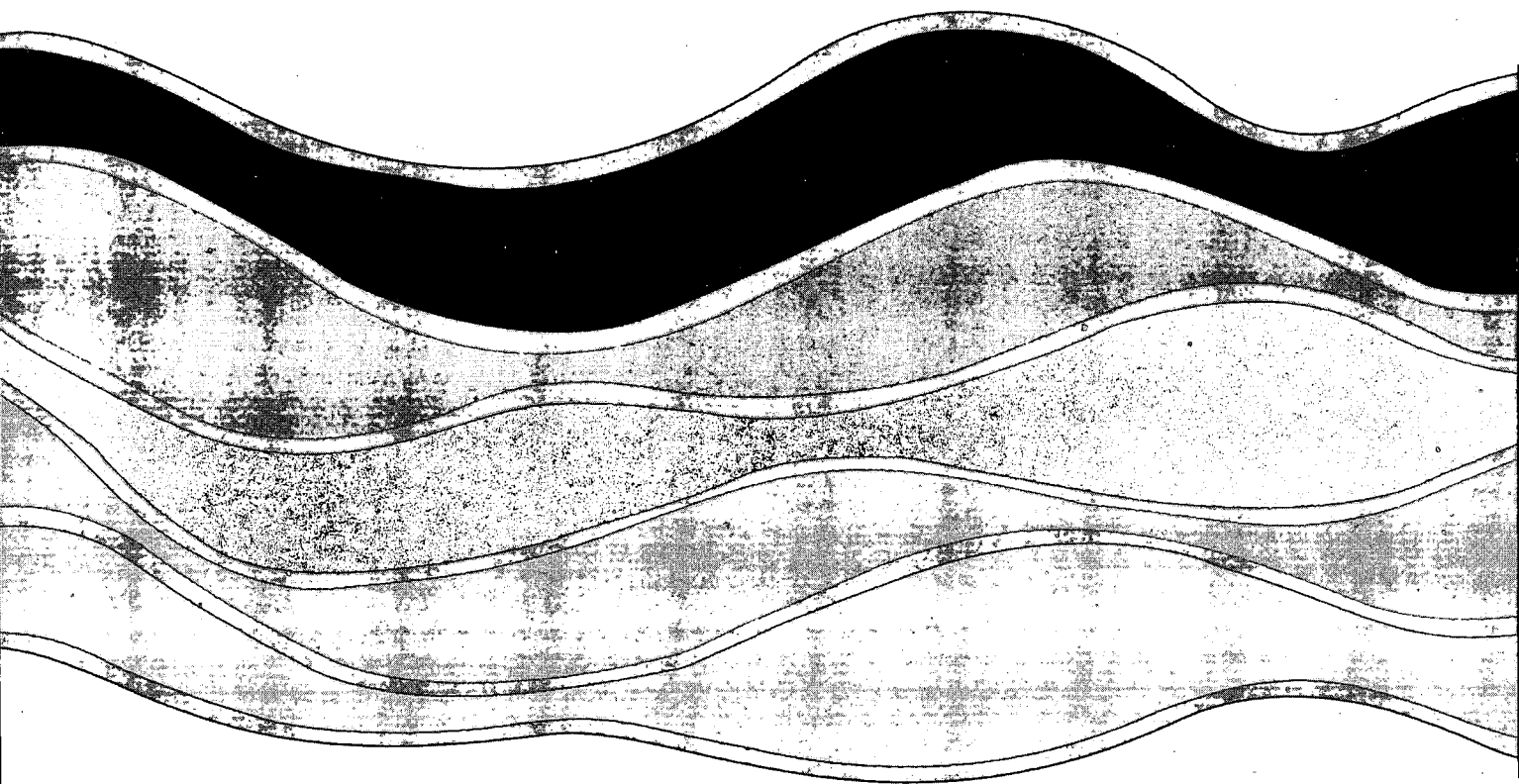
Arctic Snow and Ice: Pb and Conductivity
vs Depth (Summer Ice Layers Marked ▲)



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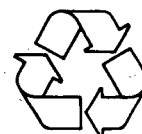
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