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SPECTROMETRY**

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**DIRECT DETERMINATION OF LEAD AND CADMIUM DOWN TO SUB pg/g LEVEL IN ANTARCTIC AND GREENLAND SNOW AND ICE BY LASER ATOMIC FLUORESCENCE SPECTROMETRY**

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**Abstract.** We present here the results of the first direct measurements of Pb and Cd in Antarctic and Greenland ancient ice and recent snow at ultralow concentration levels by Laser Excited Atomic Fluorescence Spectrometry with Electrothermal Atomization (LEAF-ETA) in clean room conditions. The limit of detection was found to be about 5 fg for Pb and 0.5 fg for Cd. Various snow and ice samples were analysed, allowing to reconstruct the past variations of the natural global atmospheric cycles of these two toxic metals during the last climatic cycle and to assess their recent alteration by man in both hemispheres.

## 1. Introduction

The current interest in environmental problems has created the need for ever more sensitive analytical techniques, capable of detecting and measuring concentrations of ultratrace species in a variety of samples. Of particular importance is the determination of heavy metals in deep ocean water /1, 2/, in atmospheric aerosols from remote oceanic or continental regions /3/, and in snow and ice from the large Greenland and Antarctic ice caps /4, 5/. Such data are of great importance to assess the past natural major reservoirs, principal pathways and fluxes of these toxic metals in the environment and to determine to what extent they have been altered by increasing man's activities.

The present work deals with the determination of Pb and Cd in Antarctic and Greenland ancient ice and recent snow. Concentrations to be measured are so low (they range from about 0.3 to 200 pg/g for Pb and 0.05 to 5 pg/g for Cd) that until recently, the few available analytical techniques (such as Isotope Dilution Mass Spectrometry (IDMS) and Graphite Furnace Atomic Absorption Spectrometry (GFAAS)) were not sensitive enough to allow direct determination of these two metals using small size samples : a preconcentration /6/ or extraction /5/ step was necessary, resulting in the need of large size samples. Such step was moreover time consuming and could lead to serious errors at the very low concentrations involved.

Laser induced fluorescence techniques, on the other hand, have long been known for their very high sensitivity /7/. In this study, we used Laser Excited Atomic Fluorescence Spectrometry with Electrothermal Atomization (LEAF-ETA)/8/ which allowed us to measure Pb and Cd directly down to sub pg/g level using very small sample volumes. Let us mention that another ultrasensitive laser technique, Resonance Ionization Spectroscopy (RIS)/9, 10/ has been applied to the determination of Pt ore metals in sediments and seawater using sorbent extraction /2/. The ultimate sensitivity of both techniques, whose emergence in the analytical field resulted from close collaboration between laser spectroscopists and geochemists, has been evaluated from a fundamental point of view /11/.

## 2. The LEAF-ETA spectrometer

The LAFAS-1 automated spectrometer used in this work has been described in details elsewhere /8/. Only a brief outline will be given here. The principle of the measurement is to observe the fluorescence of the sample atoms following excitation by a dye laser beam tuned to a suitable absorption line. The sample (20-50  $\mu\text{l}$ ) is introduced into a pyrolytically coated graphite cup inside the atomizer chamber and vaporized during a well controlled thermal cycle. The laser beam is about 3 mm above the brim of the cup. For Pb, the excitation takes place at 283.3 nm and the fluorescence at 405.8 nm is observed ; for Cd, both excitation and observation take place at 228.8 nm. These excitation wavelengths are generated by frequency doubling of an excimer pumped dye laser beam in a non linear crystal (KDP and KPB, respectively). The radiation power, spectral width and repetition rate of the UV pulses are 3 (0.16) kW, 1.6  $\text{cm}^{-1}$  and 25 Hz for Pb (Cd), respectively. The fluorescence light, collected at right angle, is sent through a monochromator onto a photomultiplier followed by an A/D converter and a micro computer controlling the whole data acquisition and treatment sequence.

To minimize metal contamination problems during samples handling, the whole spectrometer is located inside a specially designed room flushed with filtered air. Moreover, the atomizer chamber and a small plain bench, covered with polyethylene film, onto which the conventional polyethylene bottles containing the standards and samples are handled by operators wearing full clean room clothing and shoulder length polyethylene gloves, is flushed with a vertical laminar flow of air filtered through high efficiency particulate (HEPA) filters /8/.

## 3. Calibration procedure

Detailed calibration of the spectrometer for Pb and Cd was performed down to sub pg/g level using ultralow concentration slightly acidified (0.1 % ultrapure  $\text{HNO}_3$  from NIST/12/) standards whose concentrations overlapped those in the ice and snow samples. They were prepared inside the clean laboratory /13/ of the Laboratoire de Glaciologie et Géophysique de l'Environnement according to ultraclean procedures which have been described in details elsewhere/8, 13, 14/. The calibration curves so obtained are shown in Fig. 1. The limit of detection was found to be typically 5 fg for Pb and 0.5 fg for Cd.

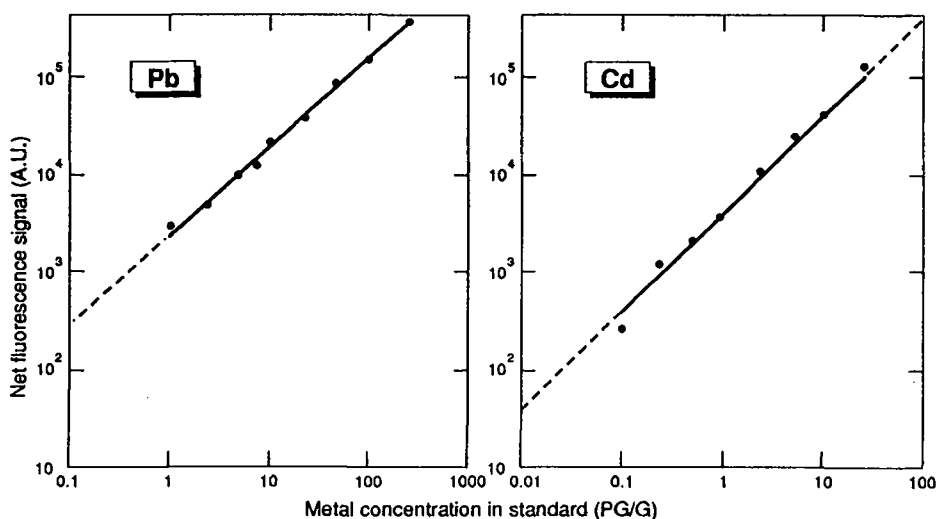


Figure 1. Calibration of the LEAF-ETA spectrometer for Pb and Cd using ultralow concentration 0.1 %  $\text{HNO}_3$  standards (20  $\mu\text{l}$  injections for Pb, 50  $\mu\text{l}$  for Cd).

#### 4. Antarctic and Greenland ice and snow samples

We have analysed by LEAF-ETA various Antarctic and Greenland samples. They include ancient Antarctic ice from the 905 m Dome C core (which covers the past 40000 years) /14, 15/ and from the 2083 m Vostok core (which covers the past 160000 years back to the end of the next to last ice age) /15, 16/. Part of these samples had previously been analysed by IDMS (Pb) or GFAAS (Cd), giving results which are in excellent agreement with the LEAF-ETA ones, as illustrated in Tables 1, 2 (but much larger

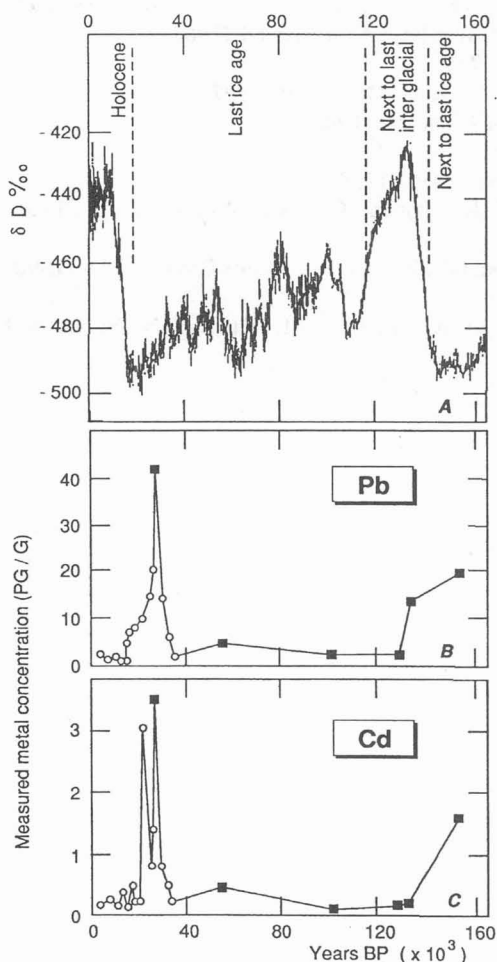
**Table 1.** Comparative determination of Pb by direct LEAF-ETA and IDMS after extraction in ancient Dome C Antarctic ice (from /14/). Precision of both sets of data is about 20 %.

Depth (m)	Measured Pb concentrations (pg/g)	
	LEAF-ETA	IDMS
300.6	0.69	0.47
451.9	0.32	0.43
658.2	13.8	14.0

**Table 2.** Comparative determination of Cd by direct LEAF-ETA and GFAAS after preconcentration in recent Greenland snow. Precision of both sets of data is about 20 %.

Depth (m)	Measured Cd concentrations (pg/g)	
	LEAF-ETA	GFAAS
1.97	1.4	1.3
6.60	1.9	1.6
7.25	3.6	4.5

sample volumes in the 50-200 ml ranges were required for these previous IDMS or GFAAS measurements because of the need of an extraction or preconcentration step).



As an example, Figure 2 shows the changes in Pb and Cd concentrations in Antarctic ice during the past 155000 years /15, 16/. Concentrations of these two metals are found to have strongly varied in the pristine past unpolluted global atmosphere during the last climatic cycle : they were rather high during the coldest glacial stages (especially during the Last Glacial Maximum around 20000 years BP, Figure 2). They were on the other hand much lower during the Holocene and the next to last interglacial. These variation profiles have allowed to clearly understand for the first time the past natural atmospheric cycles of these two metals : these cycles were dominated by wind blown rock and soil dust during the full glacial periods while during interglacial periods other contributions from volcanoes or biogenic activities became significant.

**Figure 2.** (A) Variations of climate during the past 160000 years as shown by variations of deuterium/hydrogen ratio in Antarctic ice (from /17/ ; ratio expressed in ‰ with respect to mean ocean water). Also shown are the approximate limits of the successive climatic stages. (B) and (C) Variations in Pb and Cd concentrations in Antarctic ice during the same time period (LEAF-ETA measurements after mechanical decontamination of the ice core sections). Open dots are for data obtained from the analysis of the Dome C core ; squares are for the Vostok core.

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