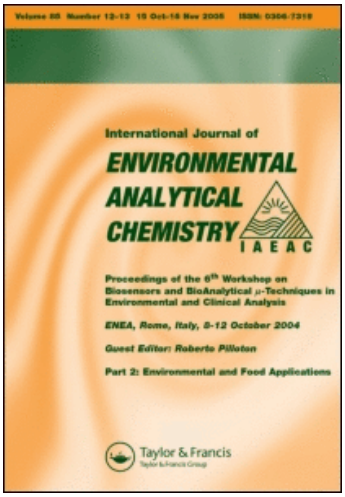

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Determination of Thallium in Antarctic Snow by Means of Laser Induced Atomic Fluorescence and High Resolution Inductively Coupled Plasma Mass Spectrometry

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DETERMINATION OF THALLIUM IN ANTARCTIC SNOW BY MEANS OF LASER INDUCED ATOMIC FLUORESCENCE AND HIGH RESOLUTION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Measurements of thallium levels in Antarctic snow samples collected in an area surrounding the Italian Station at Terra Nova Bay in different campaigns have been performed without preconcentration by means of Laser Induced Atomic Fluorescence Spectroscopy (LIAF) as well as by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICP-MS).

The data obtained by both methods compare favourably and are of the order of tenths of pg/g. The data is discussed taking into account the effect of the marine aerosol and the crustal contribution to the thallium content in samples.

KEY WORDS: Antarctica, snow, thallium, fluorescence.

INTRODUCTION

The literature on the content of heavy metals in Antarctic snow shows that the concentrations reported in recent papers on the subject are much lower than the previous findings[1-4]. This is the result of the procedures developed with the aim of avoiding contamination during sampling as well as during analytical manipulations. In fact, when analyzing metals at levels of pg/g or below, it is necessary to remove all possible sources of contamination by working in clean laboratories[5,6] and by using carefully cleaned containers[7,8] as well as ultrapure reagents and water.

Usually the instrumental technique for trace or ultratrace analysis is Graphite Furnace Atomic Absorption Spectrometry (GFAAS) or Differential Pulse Stripping Anodic Voltammetry (DPSAV), and the less common Isotopic Dilution Mass Spectrometry (IDMS).

The first and the third techniques in ultratrace analysis involve a preconcentration step, e.g. extraction with solvents and complexing agents[9], precipitation with carriers[10,11], electrolysis[12], fixation on suitable supports, for example polymeric materials[13] (and subsequent elution with the smallest volume of a reagent) or nonboiling evaporation[14]. Some of us have attempted to preconcentrate snow samples by lyophilization, which appears to be a promising method, if one takes into account that it is performed at low temperature and pressure, but high results were found[15].

A more radical procedure would be the choice of an instrumental method that does not require preconcentration; therefore determinations of lead and cadmium levels in Antarctic snow were made by using Laser Induced Atomic Fluorescence Spectroscopy (LIAF), the extremely high sensitivity of which allows the instrumental measurement to be taken directly in the acidified snowmelt without preconcentration[16–20].

The determination of metals by means of LIAF requires proper assembly of the apparatus for each element to be investigated, thus precluding, to date, the rapid, sequential determination of two or more metals. In light of this the recently developed High Resolution Inductively Coupled Mass Spectrometry (HR ICP-MS)[21,22], which is also capable of attaining detection limits at the ppt level, appears to be a proper instrumental technique for trace or ultratrace analysis..

In order to assess the capabilities of both techniques at such extremely low concentration levels, and to therefore be able to evaluate the accuracy of the determination by a direct comparison of the results, it seemed logical to apply both of them to the analysis of environmental samples like Antarctic snow.

The concentration level of thallium was investigated. Its determination by LIAF has been thoroughly investigated and optimized previously by some of us[23,24] and an absolute detection limit of 0.1 femtograms was reported.

Thallium can easily be determined by means of HR ICP-MS at mass 205 by working at low resolution due to the absence of overlap around this mass, thus ensuring high sensitivity to this determination.

The present paper describes the results found in snow samples collected in an area surrounding the Italian Station at Terra Nova Bay.

EXPERIMENTAL

Sampling

Table 1 reports the relevant data concerning the sampling sites (geographical coordinates, height and sampling campaign).

The sampling was performed by discarding the top layer (2–3 cm) of fresh snow by means of an acid cleaned polyethylene scoop. The operator wore a particle mask and PVC gloves and faced the wind. The samples were collected in 5 L polyethylene bottles, cleaned with

Table 1 Sampling Stations

Code	*Lat. S*	*Long. E*	*Height on Sea (m)*
Tourmaline Plateau	74°11′	163°30′	1650
Edmonson Point	74°20′	165°07′	190
Priestley Plateau	73°38′	160°38/32″	2000
Mount Melbourne	74°26′	164°45′	1130
Mount Crummer	76°05′	162°40′	700

the following procedure: after washing with analytical grade chloroform the bottles were filled in turn with analytical grade 1 M HCl diluted with Millipore Milli Q water and stored 3 days at room temperature, and then, after empting, the same operations were repeated with analytical grade nitric acid, Suprapur grade Merck HCl and Suprapur grade nitric acid, all diluted to 1 M concentration. Lastly the bottles, after rinsing with Milli Q water and draining, were closed and wrapped in double polyethylene bags.

The containers, after filling with samples, were closed, wrapped again in double polyethylene bags and immediately stored at −30 °C. During shipping and storage in our laboratory they were maintained frozen at the same temperature. Before measurement, the samples were extracted from the freezer, brought to room temperature in a hood with air filtered through an EPA filter, class 100, blowing horizontally outside. The snow samples contained about 0.1 % sand particles that sedimented in the course of melting. In order to avoid contamination during this operation, no filtration of the snowmelt was performed,. Portions of the snowmelt were transferred by means of a Gilson pipette to 30 mL polyethylene bottles cleaned by immersion for 20 hours in Suprapur Merck nitric acid at 50° C, then washed with Milli Q water, further distilled by subboiling. The tips of the pipettes were cleaned in the same way. The snowmelt was acidified by addition of some drops of Ultrapur Merck nitric acid to a final concentration about 1 % and the same procedure was adopted for preparation of standard solutions.

Apparatus

The laser fluorescence spectrometer was assembled as described elsewhere[23,24].

The excitation and fluorescence transitions are reported in Figure 1.

To illustrate the sensitivity of the technique, Figure 2 shows fluorescence peaks obtained in three consecutive atomization cycles, following manual introduction of 10 uL of a solution whose nominal concentration was 1 pg/mL of thallium, thus corresponding to an absolute amount, deposited in the furnace, of 10 fg.

The relevant data for the analytical procedure followed are the following: excitation laser (pulsed excimer laser plus a frequency doubled laser), wavelength 276.787 nm; fluorescence wavelength 351.924 nm. Atomisation system: Perkin-Elmer graphite furnace HGA 500. The procedure consisted in the introduction of 5 to 20 uL of sample into the furnace by means of a pipette and in the determination by standard addition method.

The HR ICP-MS apparatus used was a Plasmatrace, Fisons Instrument. It includes an ICP torch box, a sampling interface, an electrostatic analyzer (ESA), a magnetic sector and

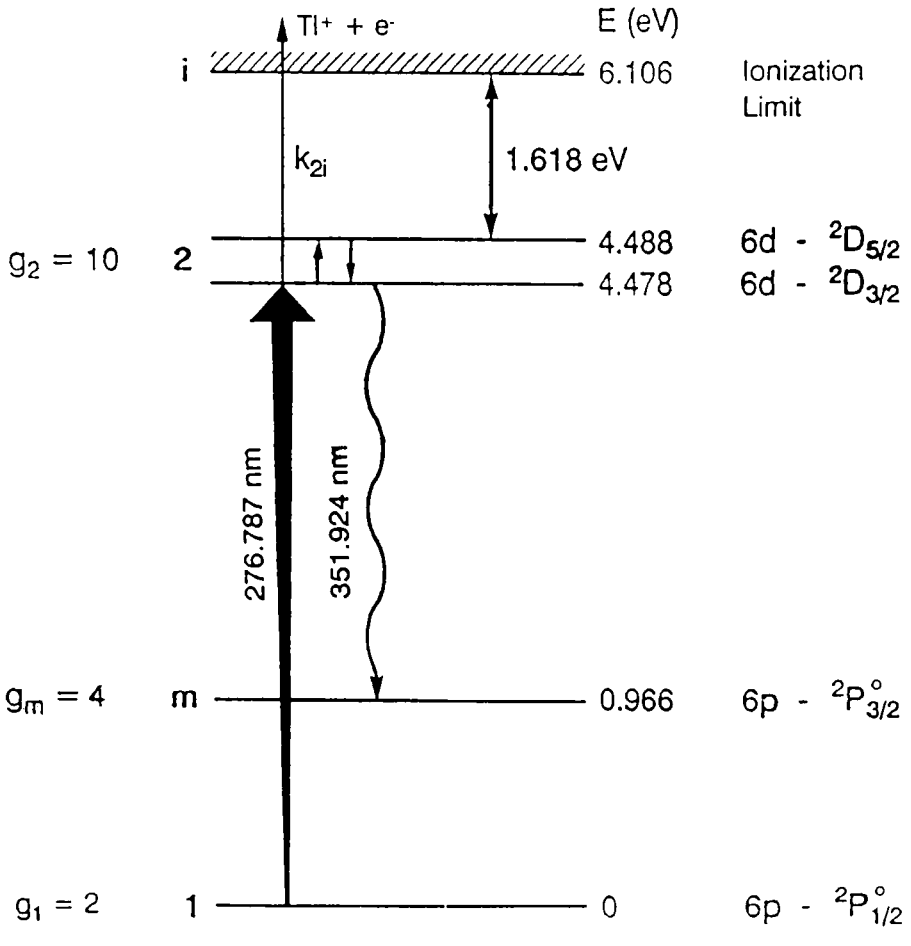

Figure 1 Fluorescence transition of thallium

detectors. The ion beam is accelerated into the field of the ESA, which acts as an energy focusing device. The ESA and the magnetic sector focus ions of different energies onto the collector. The resolution is adjusted by changing the width of the source and collector slits.

An external calibration curve was obtained with standard solutions prepared by dilution of a mother standard with doubly subboiled Millipore Milli Q water and acidified with NIST nitric acid to about 2%. The standard operating conditions were the following:
coolant gas flow rate 13 L/min: carrier gas flow rate 0.96 L/min solution uptake rate 1.3 mL/min. The accelerating voltage of the mass spectrometer was 4.7 kV. The acquisition parameters were: Tl nuclide 205: resolution 400, MCA channels 50, number of sweeps 2.

Figure 3 reports the spectral profile of Tl 205 obtained with a standard of 0.45 pg/g, compared with a blank. The calibration curve is given in Figure 4.

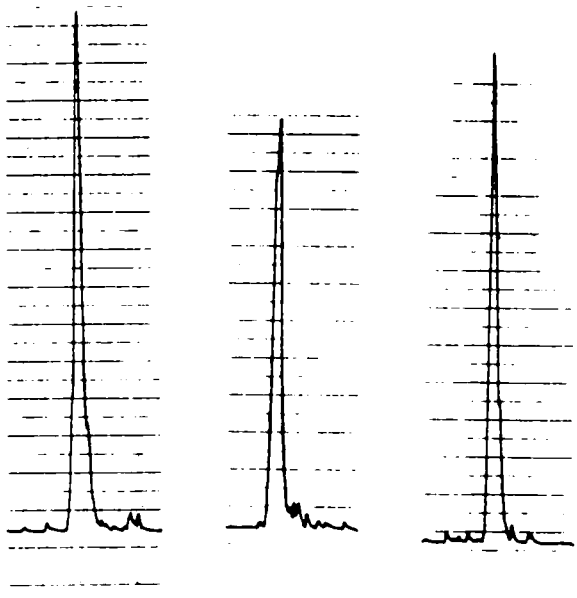

Figure 2 Typical fluorescence peaks of three consecutive atomizations of 10 uL of standards containing 1 pg/mL (10 fg in the furnace) (reproduced with permission of *Spectrochimica Acta*)

In some cases two portions of the same sample were transferred to different bottles to ascertain the reproducibility of LIAF and HR ICP-MS measurements.

RESULTS AND DISCUSSION

The results are collected in Table 2 together with blanks and standard deviations.

As can be seen, the blanks obtained with both methods are very low and very low levels of thallium are also found for samples collected far inland from Italian Station. Other samples, like the one collected at Edmonson Point, give high concentration, probably due to contamination.

In general, the data collected using the different methods are in satisfactory agreement: the somewhat higher results found by mass spectrometry could be due to the fact that the measurements with this technique were made several days after LIAF measurements, and contamination could have occurred in the meantime by opening the bottles and dipping the pipettes.

The levels of thallium in the same sites during different campaigns do not indicate an increase of thallium content with the duration of storage.

Thus, these results indicate that both instrumental techniques are well suited for the direct determination of ultratrace levels of thallium without preconcentration.

Turning now to the levels of thallium in Antarctic snow samples, it is worth mentioning that the sampling sites were near the coast, with the exception of the site in Priestley Plateau.

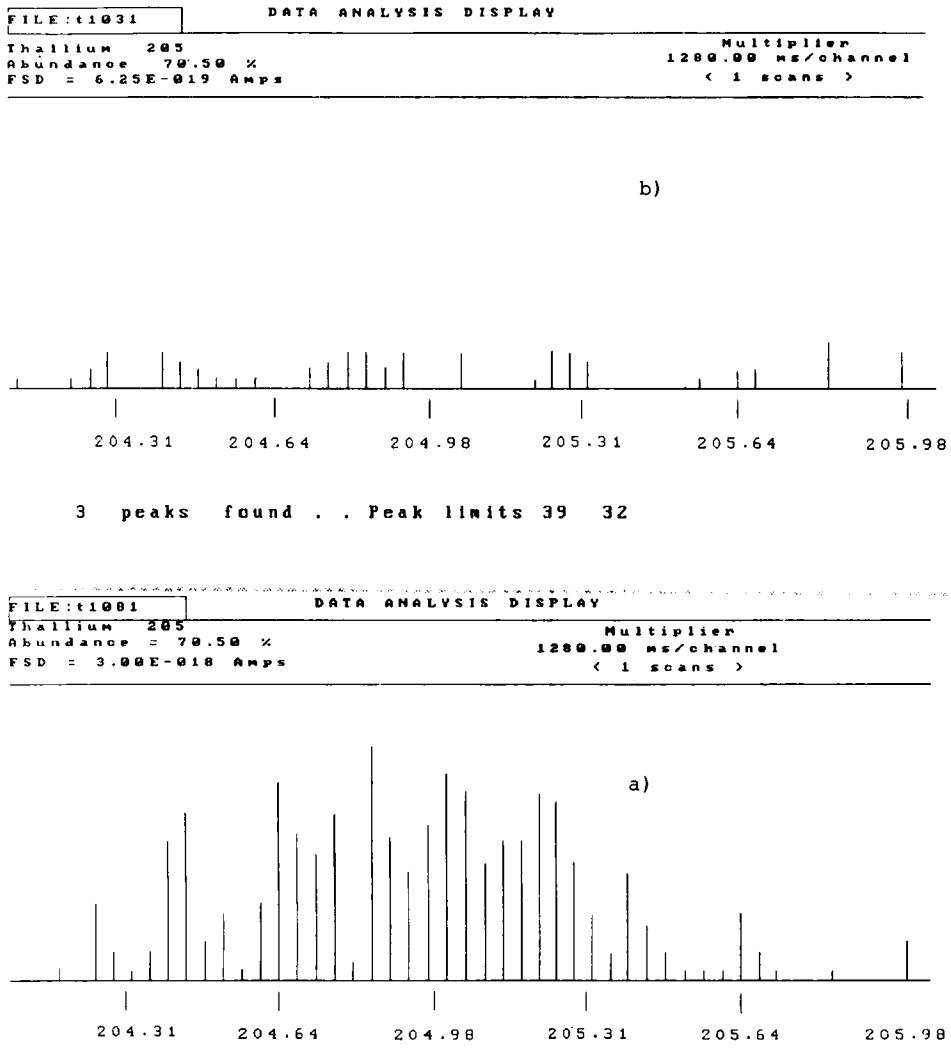

Figure 3 a) The spectral HR ICP-MS profile of Tl 205 obtained with a standard of 0.45 pg/g, as compared with blank (b)

Therefore these samples were generally affected by marine spray and aerosol, as indicated by their high content of Na and Cl[25]. A crustal contribution to the metal content of snow is probable, taking into account that in the sampling area there are exposed rocks, some of which are volcanic in origin. As said above, the snowmelt contained particulate matter. The unfiltered snowmelt probably contained some still suspended material, a small part of which may have been dissolved after acidification prior to LIAF measurements. The presence of thallium in snow samples collected in Antarctica at Ekstrom Ice shelf was found to be below

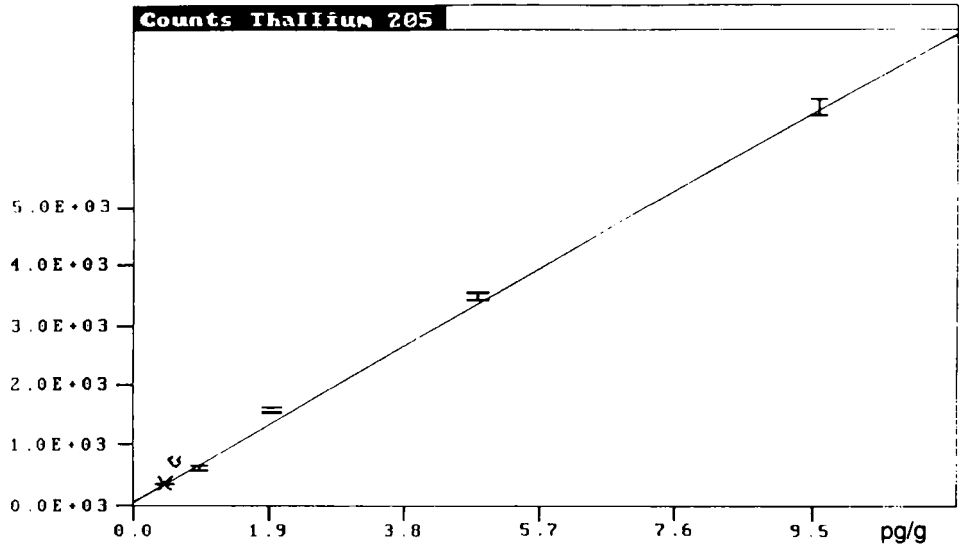

Figure 4 Calibration curve of thallium by HR ICP-MS

the detection limits of IDMS, that is about 0.2 pg/g[12]. Thallium, according to Bruland[26], is a conservative element in sea water and its concentration is about 10 pg/g, about a third of the surface cadmium concentration in open sea[27] and in Terra Nova Bay[28–30].

As regards crustal contribution, the presence of thallium in volcanic rocks has been found, although in very low concentrations.

Sophisticated methods have been developed recently for the preparation of snow samples free from contamination during sampling, including field collection and further laboratory decontamination[31]. Our fresh snow samples were collected using a simpler procedure, liable to contamination that we cannot exclude. However, taking into account the said content of

Table 2 Data on Thallium Determinations (pg/g)

Station	*Campaign*	*LIAF*	*HR ICP-MS*
Priestley Plateau	II	0.23	0.43
	III	Bk	0.44
	IV	0.23	—
		0.33	0.33
Mt Crummer	II	0.23	—
		0.33	0.33
Mt Melbourne	III	0.45	0.34
Tourmaline Plateau	III	0.23	0.43
		0.26	0.18
Edmonson Point	III	1.1	2.8
Blank		0.3	0.07
SD %		20	upto 20 (3 determ)

II: 1988/89; III: 1989/90; IV 1990/91

thallium in sea water and the probably volcanic nature of crustal contribution, it would appear that the average of data in Table 5 can be considered as an upper limit of the content of thallium in snow samples collected in that area of Antarctica.

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