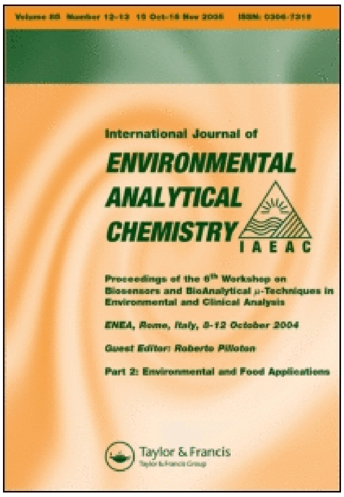

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Direct Determination of Dissolved and Total Thallium in Lake Waters by Laser-Excited Atomic Fluorescence Spectrometry

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DIRECT DETERMINATION OF DISSOLVED AND TOTAL THALLIUM IN LAKE WATERS BY LASER-EXCITED ATOMIC FLUORESCENCE SPECTROMETRY

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Thallium is a highly toxic, under-studied priority element. However, it has recently created much interest due to afresh and rapid improvements in detection limit. It appears that there are no published Tl data for Great Lakes waters, likely due to the poor sensitivity of classical methods. An electrothermal Laser-Excited Atomic Fluorescence Spectrometer has been optimized to detect sub-femtogram of thallium and used to develop a method for direct determination of dissolved and total thallium in lake waters. The method voids the labor-intensive, contamination-prone tasks of filtration, centrifugation and acid digestion of collected particulates. Adequate precision and recoveries were achieved using several lake waters (undigested and digested) and a certified reference material. The concentration of thallium in the acidified (0.2% HNO_3) Milli-Q-Water was monitored over a period of four months and averaged 0.02 ± 0.01 ng/l. The concentration in Hamilton Harbor ranged from 3 to 48 ng/l. The mean of dissolved/total fraction of Tl in the Harbor water was 80%.

KEY WORDS: Laser-excited atomic fluorescence spectrometry, thallium, *in situ* known addition, Great Lakes, Hamilton Harbor, direct determination, clean room.

INTRODUCTION

Thallium metal and compounds is one of the thirteen priority pollutant metals listed along with lead, cadmium, and mercury by the United States Environmental Protection Agency[1]. Chemically, it is an interesting element as it exhibits both the properties of alkali metals and those of heavy metals. This dual character has earned it a nickname of paradoxical, enigmatic metal. Although the average Tl content in the earth's crust is only 6×10^{-5} weight %, it is higher than some of the more commonly studied elements such as Pb, Cd or Bi[2].

The element and its compounds are very toxic, its toxicity being reported soon after its discovery in 1861[2-8]. Tl-based rodenticides were extensively used but had to be discontinued due to its high toxicity. An annual average of 13 thallium poisoning cases were reported between 1958 and 1964 in Canada[3]. Twenty four percent of bald eagles found sick or dead in 18 states during 1971–1972 were poisoned by Tl[9]. "Thallium is neither essential nor stimulatory in either man or animals. It is the most highly toxic cumulative cation"[6]. Thus it is important to determine thallium accurately.

Thallium is used to manufacture alloys, electrical devices, dyes, fireworks, special optical glass, as a dopant for nuclear spectrometer crystals, depilatory agents, fungicide, ant bait or rodenticide. One of the most important alloys is Pb alloy (20–65% Tl) which is harder and more corrosion-resistant than pure lead[2]. However, when compared to Pb, Hg, Cr, Cu, Ni or Zn for example, thallium has limited industrial uses. So economically, thallium is hardly important thus scarcely recovered from metal-based mining, ore-processings or smelting operations. It is readily disposed into the environment. High levels of Tl relative to the two commonly studied toxic elements Pb and Cd were recently found in several water samples from a region of abandoned mine tailings at Wells, B. C.[10]. In the mining industry, the usual wastewater treatment to remove heavy metals cannot remove Thallium (I). Thus, Tl usually ends up in the tailings and abounds in the disposal sites. Beside these point sources, the air emissions from coal-burning power plants form the largest collective source of thallium discharge into the environment[11]. Thus, since Tl is a very toxic element and has received minimal attention relative to other trace metals, it is obvious that thallium has been badly neglected in environmental studies.

An explanation for fewer Tl studies is that Tl is often undetected by classical analytical methods, which normally have poorer sensitivity towards Tl than other trace elements. Being a hard-to-detect, "unwanted", paradoxical and very toxic element, thallium is an interesting and important element to study. In fact, there is an increasing number of publications dealing with Tl determination in environmental samples going hand in hand with improved instrument sensitivities in for example Potentiometric Stripping Analysis[12], Inductively Coupled Plasma Mass Spectrometry (ICPMS)[13–15], or Laser-Excited Atomic Fluorescence Spectrometry (LEAFS)[15–17]. Axner *et al.*[17] used an excimer laser – based LEAFS for water analysis achieving a detection limit of 1 ng Tl/l. There are other LEAFS papers dealing with Tl determination in substrates beside natural water samples[18–22].

The lack of any historical Tl data in the Great Lakes waters compared to the large amount of data for other trace metals is a prime example of very few Tl studies. Up to now, we have no method for Tl determination in Great Lakes waters. No method means no data, no interests. In this paper we adapt a recently developed *in situ* known addition technique[23] to develop a simple method for direct determination of dissolved and total Tl in Great Lakes waters using a copper vapor laser – based LEAFS. Thallium concentration lower than 0.03 ng/l (0.6 fg absolute) can be detected. The direct determination of total Tl in unfiltered samples is especially beneficial to analysts as it voids the conventional painstaking tasks of filtration/centrifugation followed by acid digestion of collected particulates. Also, a discussion on the dissolved Tl/total Tl ratio and the distribution of Tl found in Hamilton Harbor water are presented.

EXPERIMENTAL

Laser-Excited Atomic Fluorescence Spectrometry

The details of the spectrometer have been described elsewhere[24–25]. Some essential features are given here. The 511 nm line of a copper vapor laser (Metalaser Technologies MLT20) was used to optically pump a Rhodamine 575 dye laser (Laser Photonics). The dye laser output (554 nm) was then frequency-doubled by a second harmonic generator (Autotracker II, Inrad Inc.) to give the 276.79 nm UV light. This light, directed through a pierced mirror into a graphite furnace (Perkin-Elmer HGA 2100), was used to excite Tl atoms generated in the furnace. The Stokes direct-line fluorescence light (352.94 nm) emitted by the excited atoms was collected and measured via a narrow bandpass filter (1 nm) – monochromator- photomutiplier- boxcar system. A 6 kHz laser repetition rate was used. Dye laser tuning was achieved using a thallium EDL lamp as was detailed earlier[26]. The spectrometer schematic is depicted in Figure 1.

Normal operating power outputs of the lasers are 5–6 W for the CVL and 0.3–0.4 W for the dye laser. The approximate bandwidth of the laser light is 0.003 nm. In the furnace, the area of the laser beam is about 2.1 mm^2, the pulse duration about 7 ns, and the peak power about 23 kW/cm^2.

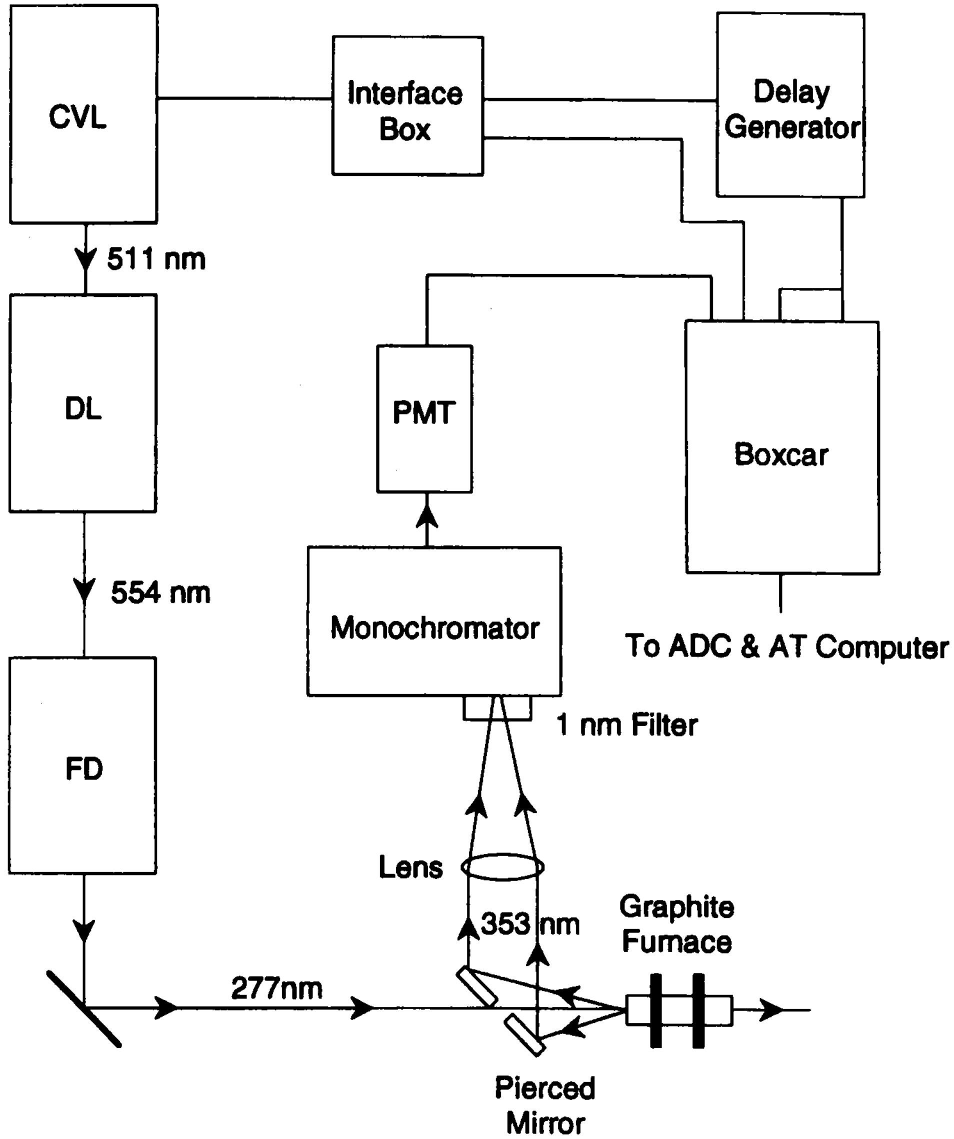

Figure 1 LEAFS schematic: CVL = Copper Vapor Laser; DL = Dye Laser; FD = Frequency Doubler; PMT = Photomultiplier.

Chemicals and sample handling

Ultrapure chemicals were used. Milli-Q Water acidified to 0.2% with ultrapure (Seastar) nitric acid, simply referred to as MQW, was used as standards matrix and carrier. Sample handling was carried out in a class 100 clean room and in a class 100 laminar flowhood (Microzone Corporation). Filtration was done using membrane filter with 0.45 μm pore size. Details of labware, cleaning procedure and sample collection have been described earlier[27]. 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. However, this contamination effect was found to be minimal.

In situ known addition analysis

A programmable micropipette (Rainin Instrument Co.) was used to carry out *in situ* known addition pick-ups and injections into the graphite furnace[23]. The sequence 10/5/2/5 (10 μl of MQW carrier followed by 5 μl of sample, 2 μl of air spacer, and 5 μl of MQW or standard) as well as 15/5/2/5 and 20/5/2/5 were found optimal, but the sequence 20/10/2/10 was sometimes used for extremely low concentration samples (low and sub-ng/l). Standard concentrations used varied from 1 to 50 ng/l and all computations utilized peak height readings.

Digestion for total metals

A digestion procedure for determination of total metals, routinely used by The National Laboratory for Environmental Testing[28], was applied and is briefly summarized here. Evaporate 100 ml of unfiltered water sample in a quartz volumetric flask to near dryness. Add 2 ml of concentrated HNO_3 and evaporate to near dryness. Add 1 ml of 50% of concentrated HCl and evaporate to almost dryness. Fill the flask back to 100 ml with ultrapure water. For LEAFS work, 20 ml (not 100 ml) of sample was used and all reagents were proportionally adjusted.

RESULTS AND DISCUSSION

LEAFS and furnace optimization

LEAFS optimization has been described elsewhere[24–25]. With the peak power of 23 kW/cm^2, optical saturation should have been reached although an actual saturation curve (fluorescence intensity-laser intensity plot) was not produced to confirm it as it wasn't necessary to do so. However, we shouldn't have been working in the plateau-region of the curve where the slope is equal to zero, since we often observe (during 3–4 hrs of continuous sample analysis) some decrease in laser intensity accompanied by some decrease in fluorescence signal. It is understood that the region of the curve most preferable for LEAFS is where the slope just starts to become zero, since 1) it would avoid the added noise (increased scatter and stray signals) should laser intensity increases; and 2) it would minimize the change in fluorescence signal due to drifts/fluctuations of the laser system. Even if we were working in the 1-1 region of the curve (where the slope is equal to one), the net effect of drifts/fluctuations would be small for each sample due to the nature of *in situ* known addition analysis.

Uncoated graphite tubes were preferred and used as they provided adequate rise time for our need; with the coated tubes, it took longer for the LEAFS signals to appear (the signals shifted to the right), thus fewer signals can be recorded in one frame. A platform was also tested and found to give too slow a rise time, i.e. no signals at all were observed for the Perkin-Elmer 2100 furnace. The atomization temperature was set at 2400°C for 3 s unramped and was found suitable, instead of the manufacturer's recommended temperature of 2100°C. Apparently the atomization temperature for Tl can vary widely from one setup to another, for example a range of 1400–2400°C has been used[29-30]. The drying and ashing temperatures were set at 120°C for 40 s ramped and 400°C for 40 s ramped, respectively. Argon was found to be a better purge gas than Ar-H_2 mixture giving a superior fluorescence intensity by a factor of about 3. The gas flow was interrupted during atomization. It might be possible that we did not run the furnace under optimized, most favorable conditions, but the used conditions abundantly satisfy our requirements.

A typical duration of the LEAFS signal is 2.5 s with a FWHM of 0.4 s. A standard calibration curve starting with 0.1 ng/l is shown in Figure 2. The linearity extends to 100 μg/l, which is a linear range of six orders of magnitude. The curvature starts at about 200 μg/l. It is an integrated curve covering three concentration ranges: 0.1–50 ng/l, 50 ng/l–50 μg/l, and 50–1000 μg/l ranges. The sensitivity setting for each range was done by adjusting PMT voltage (1–2.4 kV) and/or boxcar sensitivity setting (an 0.5–2V) so the signals (peak heights in V) were on a measurable scale. The signals for the low- and high-ranges were then multiplied by a factor so they would be in the scale of the mid-range.

Effect of sample matrix

Thallium signals are suppressed by the matrices of natural samples so that analysis by means of a standard calibration curve is likely to be unreliable. We suspected chloride to be a major interferent in these samples (Lake Ontario water contains 26 mg/l of Cl^-) and briefly attempted to use H_2SO_4 and Ni as matrix modifiers to minimize the suppression, but with little success. Since the use of a matrix modifier or other mean of sample pretreatment was deemed undesirable as it could increase background signals, we did not further attempt to solve the suppression issues, but instead we relied upon a recently developed *in situ* known addition technique[23] to handle the matrix interferences. Efforts to find an optimum sample volume to be used for all lake waters failed to show any common denominator, like for example a maximum fluorescence response at a particular volume as observed in the case of seawaters[23]. Instead, a steady increase (with slight suppression) in fluorescence signals was observed as the injected sample volume increased; each water was characterized by its own signal- volume curve. A typical curvature for lake waters is illustrated in Figure 3 along with that for seawaters (showing a common maximum response[23]) and the standard curve. It can be seen that any volume of lake water may be used in this known addition technique. A 5 μl of sample was found convenient and was used for most waters.

The acid content also affects Tl responses as seen in Figure 4, showing the signal dependence of 10 ng/l of thallium on % HNO_3. As the acid content increases, the signal decreases and this may be due to matrix interference and/or more enlarged spreading

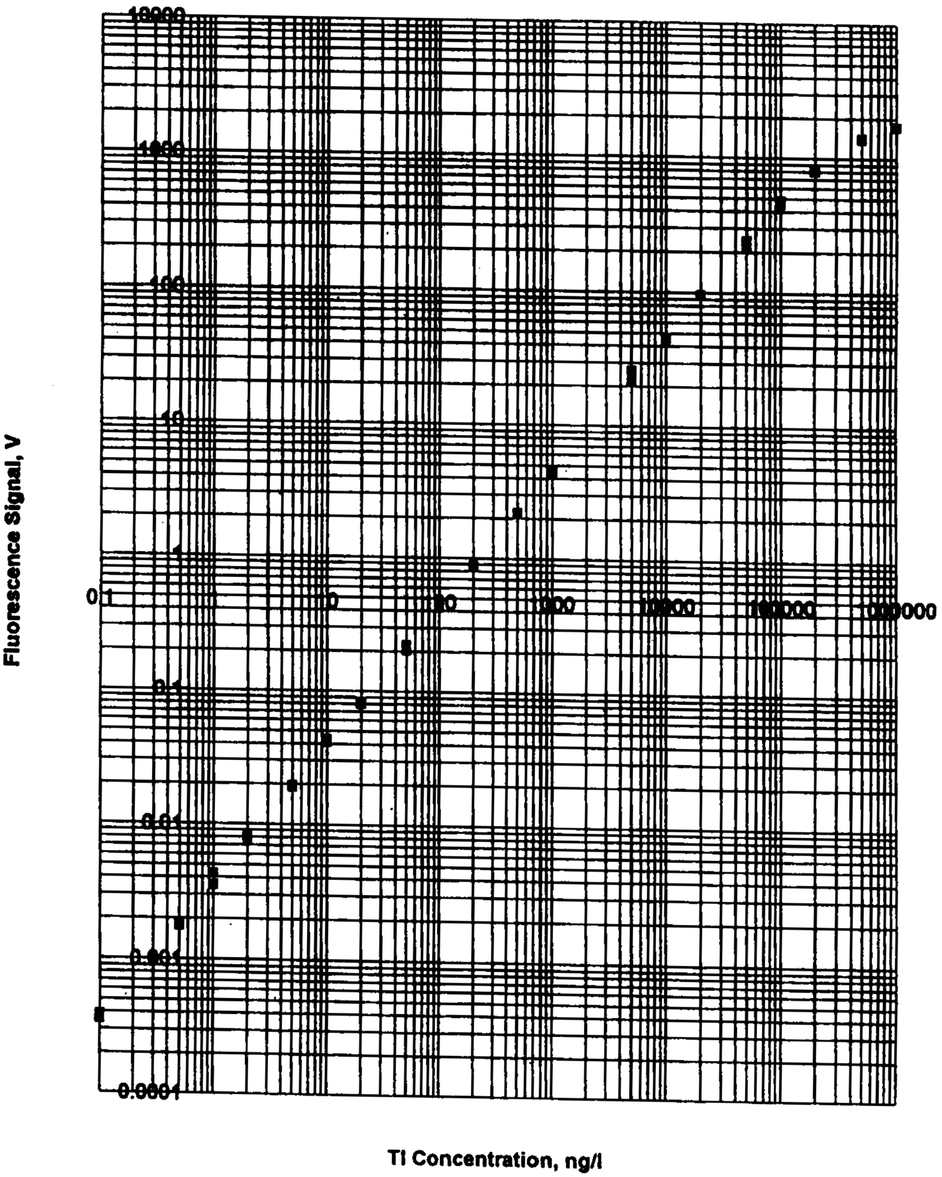

Figure 2 Thallium standard calibration curve.

of the sample on the graphite tube, thus resulting in a more diluted atom cloud and fewer excited atoms. It could also be that the high acidity attacks the graphite tube which results in sensitivity decrease. Without acidity-matching, the traditional standard calibration curve will bias the results, particularly when the sample acidity differs from the standard acidity by more than 0.5% (Figure 4). On the other hand, the *in situ* known addition technique effectively compensates for this acidity difference.

Background signals produced by sample matrices may interfere with analyte fluorescence responses[21] and were determined as follows. Signals for standards and filtered or unfiltered natural samples were obtained at ±0.05 nm away from the

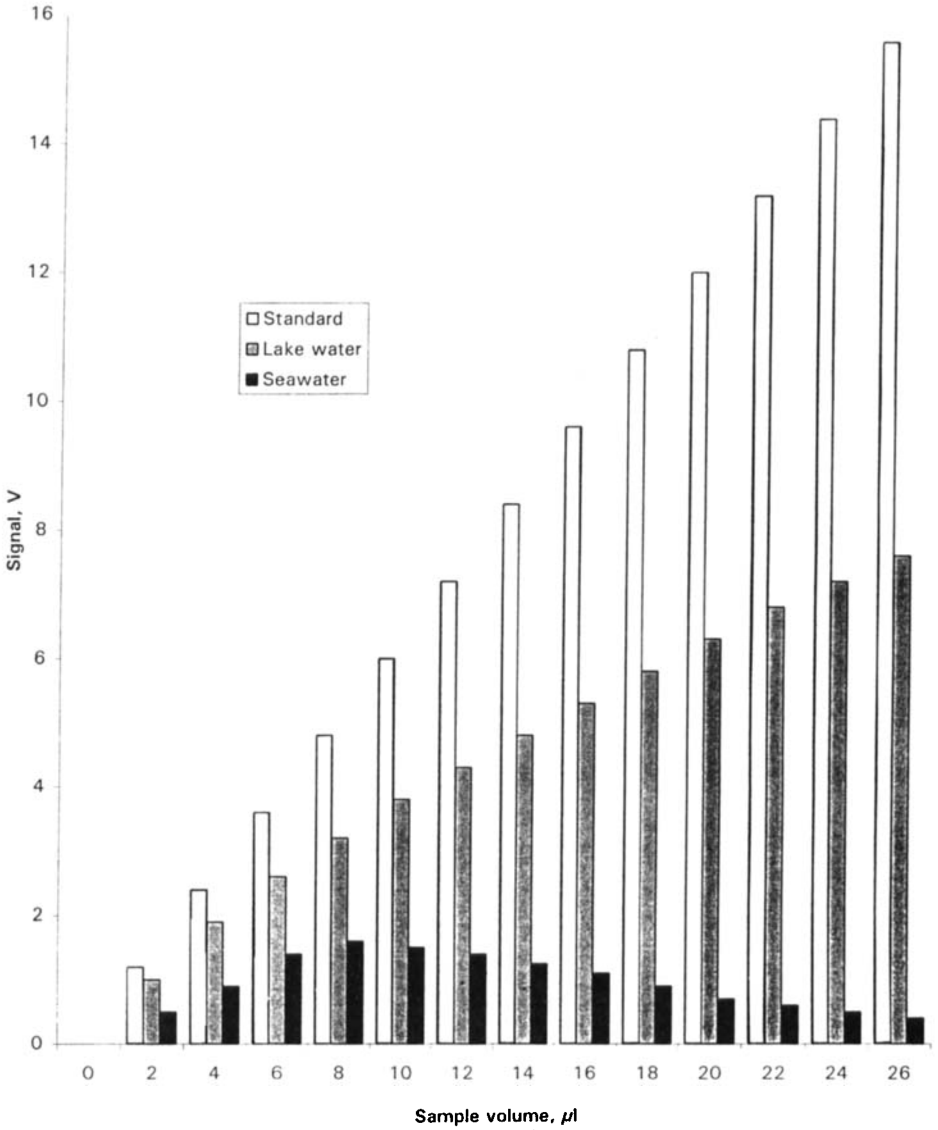

Figure 3 Signal dependence on sample volume in a constant injection volume of 26 μl (sample + MQW = 26 μl).

analytical line and were found to be insignificantly different from one another. Also, they are statistically the same as that of MQW, which is extremely small.

Figures of merit

More than forty different measurements of 20 μl of blank (MQW acidified to 0.2% HNO_3) were made during a period of 4 months, resulting in a mean value of 0.02 ng Tl/l with a standard deviation of 0.01 ng/l. According to the IUPAC criterion, the detection

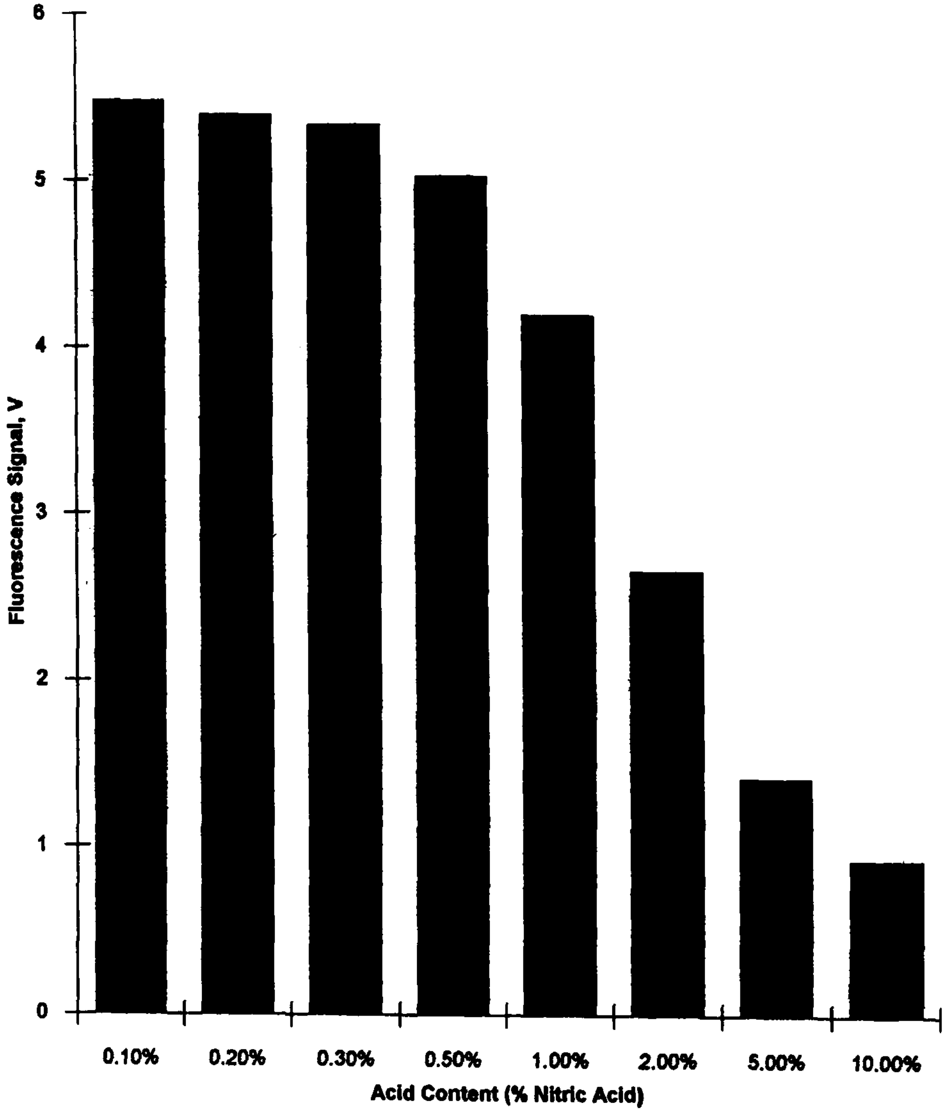

Figure 4 Tl signal dependence on acid content.

limit was 0.03 ng/l (0.6 fg absolute). Other outstanding detection limits have been reported earlier: 0.7 fg by Falk *et al.*[18], 0.3 fg by Michel *et al.*[31] and 0.1 fg by Smith *et al.*[32]. However, the process of determining each of these limits, though similar, was different from one another. For example Falk *et al.* extrapolated their calibration graphs to the signal/noise = 3 (n = 10 measurements), whereas Michel *et al.* extrapolated theirs (after subtraction of the blank signal) to signal/s = 3, s being the standard deviation of 16 measurements of the blank noise. Smith *et al.* equated the detection limit to 3 σ; the authors did not specify how σ was obtained but it apparently referred to the standard deviation of the blank. Since the blank value was not given[18,31,32], it is rather difficult to assess an objective comparison of the detection limits. Also it seems that the determination of detection limit should be based on data taken over a period of time, but not on the basis of a single-day or single-set of data.

Further improvement to our system can be likely achieved by using the detailed optical considerations given by Smith *et al.*[32] or by using a pierced ellipsoidal mirror (instead of a pierced first surface mirror coupled with the usual focusing lenses) thus minimizing the fluorescent light losses caused by aberrations and optical alignement[33]. Vera *et al.*[34], however, obtained a slightly poorer detection limit when they used an off-axis ellipsoidal mirror. Also, according to Wei *et al.*[31], if only the narrow bandpass filter is used without the spectrometer, the detection limit will further improve. However, there is no requirement for us to further improve the detection limit. A practical detection limit was determined as we usually do by making several replicate analyses of a natural sample containing a concentration 5–10 times greater than the lowest concentration that can be detected[35]. We used a sample containing 0.25 ng Tl/l and made 12 replicate analyses giving a standard deviation of 0.05 ng/l, which results in a practical detection limit for the method of 0.1 ng/l.

Figure 5 shows actual data of sixteen groups of replicate analyses of various samples, indicating that very precise results can be achieved. The relative standard deviation ranges from 1 to 8% for these groups of analyses, with an average of 4% for the whole set of data.

The accuracy of the method was demonstrated by several recovery tests using a NIST certified reference material (the only one available with a Tl value) and six

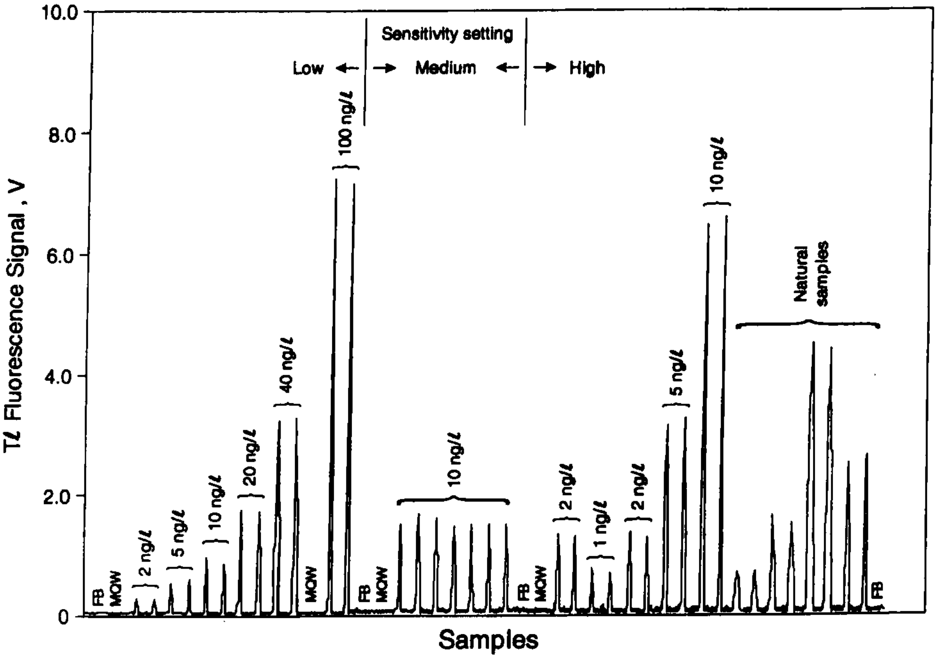

Figure 5 Replicate fluorescence responses of various samples. (FB = furnace blank; MQW = 0.2% HNO_3 Milli-Q water blank).

Table 1 Comparison of analytical results (ng/l) determined by direct and MSA analyses of SRM and lake-related waters (n > = 6).

*Sample**	*Values by direct analysis*	*MSA Values*[a]	*Certified value*
NIST SRM 1643c	4.18 ± 0.36	N.A.	(3.95)[b]
Hamilton Harbor nearshore, uf	32.71 ± 1.74	33.46	N.A.
Macfarlane Lake – 4 m, f	7.48 ± 0.60	7.39	N.A.
Macfarlane Lake – 4 m, uf	7.62 ± 0.65	7.59	N.A.
Lake Ontario nearshore, uf	7.47 ± 0.42	7.73	N.A.
Burlington tapwater, uf	3.98 ± 0.29	4.32	N.A.
Lake Ontario – 33 m, f	6.42 ± 0.35	6.25	N.A.

* Hamilton Harbor is a harbor of the Great Lakes; Macfarlane is a lake in Sudbury mining area in Northern Ontario; Lake Ontario is one of the Great Lakes; uf = unfiltered; f = filtered.

[a] Msa = Multiple Standard Addition; N.A. = not applicable.

[b] Value calculated after a 2000-fold dilution.

different natural samples related to lake waters. Table 1 summarizes the test results, which show that the values obtained by direct analysis agree well with the certified value and those derived from the multiple standard addition technique (MSA). Three levels of concentrations overlapping the concentration originally present in each sample were used in the MSA. The percent recoveries were also calculated and given in Table 2 showing acceptable recoveries, which are well within 100 ± 10%.

Total and dissolved thallium

To further ensure that the direct determination of Tl in unfiltered samples represents the total amount, a proven digestion procedure[28] was used to digest unfiltered samples followed by a LEAFS analysis. Table 3 shows good agreement between the results for undigested and digested samples, which indicates that the direct analysis of unfiltered samples gives total Tl values. The blank values were negligeable. As additional tests, the unfiltered samples were also spiked, digested and analysed. The 4th column of Table 3 give these results, which indicate complete recoveries of the original total and spiked amounts. The analytical results for filtered samples refer to dissolved concentrations of thallium. Knowledge of the dissolved and total amount of a metal in natural waters is very useful for bioavailability/toxicity studies.

Table 2 Summary of % recoveries for natural samples related to lake waters.

*Sample**	*Average % recovery*	*No. of determinations*
Hamilton Harbor nearshore, uf	101 ± 3	8
Macfarlane Lake – 4 m, f	100 ± 4	7
Macfarlane Lake – 4 m, uf	100 ± 4	6
Lake Ontario nearshore, uf	100 ± 5	10
Burlington tapwater, uf	102 ± 5	9
Lake Ontario – 33 m, f	102 ± 5	9

* Same footnote as in Table 1

Table 3 Comparison of total Tl, ng/l, determined from direct injection of undigested and digested unfiltered samples, and recovery of digested spiked-samples (mean ± sd, n > = 6).

Sample	*Undigested*	*Digested*	**Total recovery of Digested Spiked-sample*
Lake Ontario nearshore, uf	7.47 ± 0.42	7.57 ± 0.68	[a]17.66 ± 1.15
Hamilton Harbor nearshore, uf	32.71 ± 1.74	32.32 ± 4.08	[b]52.41 ± 3.86
Lake Erie – 22-10 m, uf	9.18 ± 0.42	8.92 ± 0.64	Not sufficient sample

* Unfiltered sample was spiked[a,b] and then digested

[a] 10 ng/l was spiked to Lake Ontario nearshore, uf, resulting in total % recovery of 101%

[b] 20 ng/l was spiked to Hamilton Harbor nearshore, uf, resulting in total % recovery of 99%

Thallium distribution in Hamilton Harbor water

Figure 6 shows the location of Hamilton Harbor with respect to some key sites such as steel companies and our laboratory (CCIW). The Van Dorn bottle was used to collect water samples from ten different stations selected to give a fair representation of the whole Harbor. Field blanks were obtained as follows. Right before and after sample collection, one liter of doubly deionized distilled water was used to rinse the Van Dorn bottle, and the rinsing solution was saved and used as blank. Four such blanks were collected and analysed giving an average of 0.22 ± 0.06 ng Tl/l. (The concentration of doubly deionized distilled water was << 0.2 ng Tl/l). Filtration was done in class 100

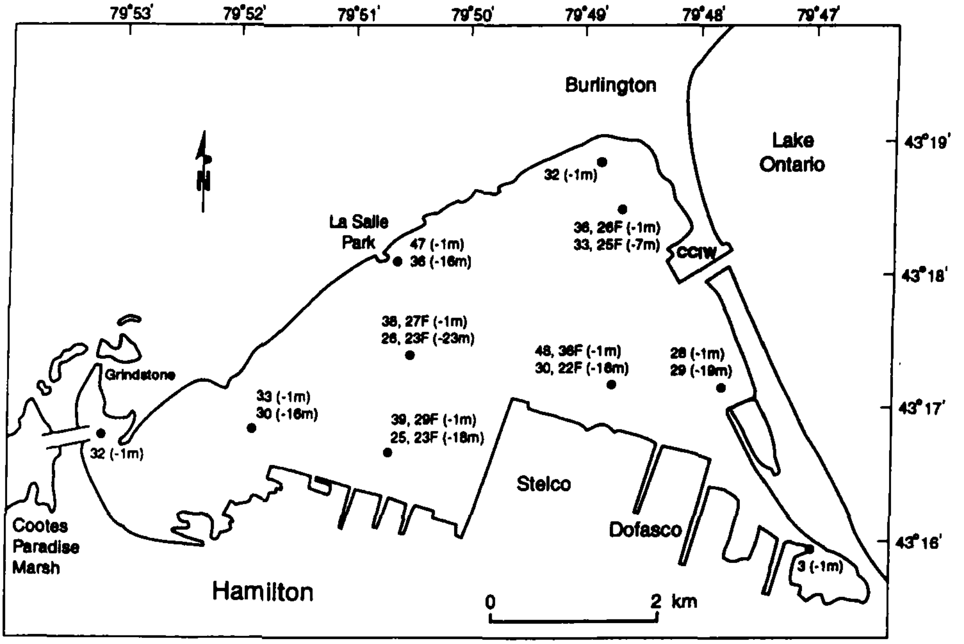

Figure 6 Thallium distribution in Hamilton Harbor water. [38, 27 F (-1 m) = 38 ng/l total Tl, 27 ng/l dissolved Tl (1 m deep)].

clean hood, and the blank concentration was as low as the concentration of the ultrapure water itself.

The distribution of total Tl in the Harbor's water is shown in Figure 6. Average concentrations of 38 ± 7 ng/l and 30 ± 4 ng/l were found respectively at 1 m from the surface and at 1 m from the bottom of the main water body (7 deep stations in the middle). This amounts to a 27% concentration difference between the top and bottom water. Also the stations with the highest surface concentrations are near the steel companies and La Salle Park, where numerous recreation activities take place daily.

Furthermore eight different water samples were subdivided then filtered, analysed and the results shown in Figure 6 along with the unfiltered ones. An average of 30 ± 5 ng Tl/l for the top water and 23 ± 2 ng Tl/l for the bottom water was observed, giving a concentration difference similar to that for the unfiltered samples. Thus the dissolved fraction with respect to total Tl ranges from 71% to 92% with an overall mean of 80 ± 8%, which is much higher than Pb dissolved fraction (work in progress).

CONCLUSION

A LEAFS method has been developed for direct determination of dissolved and total thallium in lake waters. It is a superior alternative to the conventional indirect method for determination of total metal which involves filtration/centrifugation and acid digestion. The LEAFS method is also ideal for small-volume samples as it is ultrasensitive. It appears that the particulate fraction of Tl in lake waters is small compared to Pb's.

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