

This article was downloaded by:

On: 18 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

Direct Determination of Thallium in Natural Waters by Laser Induced Fluorescence in a Graphite Furnace

O. Axner^a; N. Chekalin^{ab}; P. Ljungberg^a; Y. Malmsten^a

^a Department of Physics, Chalmers University of Technology, Göteborg, Sweden ^b Vernadsky Institute for Geochemistry and Analytical Chemistry, Moscow, Russia

To cite this Article Axner, O. , Chekalin, N. , Ljungberg, P. and Malmsten, Y.(1993) 'Direct Determination of Thallium in Natural Waters by Laser Induced Fluorescence in a Graphite Furnace', *International Journal of Environmental Analytical Chemistry*, 53: 3, 185 – 193

To link to this Article: DOI: 10.1080/03067319308045988

URL: <http://dx.doi.org/10.1080/03067319308045988>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

DIRECT DETERMINATION OF THALLIUM IN NATURAL WATERS BY LASER INDUCED FLUORESCENCE IN A GRAPHITE FURNACE

O. AXNER, N. CHEKALIN*, P. LJUNGBERG and
Y. MALMSTEN

*Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden
and *Vernadsky Institute for Geochemistry and Analytical Chemistry, 117975 Moscow,
Russia*

(Received, 2 June 1992)

The thallium content in some natural waters (lakes, rivers and drinking water) in South-West Sweden has been determined by Laser-Induced Fluorescence in a Graphite Furnace (LIF-GF). The high sensitivity of the LIF-GF technique eliminated the need for any sample pre-treatment or sample pre-concentration (except for acidification with small amounts of HNO_3), thus reducing the number of sources of contamination. It was found (by the standard addition technique) that the Tl content of the samples investigated ranges from 8 ppt for drinking water up to 56 ppt for water from the Viskan river. No matrix interferences from concomitant elements in the samples could be detected with the present experimental set-up. This allowed for a calibration against matrix-free reference solutions.

KEY WORDS: Thallium, natural waters, laser-induced fluorescence, graphite furnace.

INTRODUCTION

The problem of monitoring the metal content of natural and sewage waters has in recent years become more important due to the increasing human and industrial activity. A major interest lies in monitoring various heavy metals, such as Hg, Pb, Cd and Tl. The natural content of these metals in environmental samples lies in or below the ppb (ng/ml) region. For Pb in natural waters, for example, the background content varies from 0.1 to 0.8 ppb¹; for Tl it is significantly lower. At the same time the high toxicity of Tl demands a careful control of its presence in the environment. Examples of previous determinations of Tl in various environmental, chemical and biochemical samples are the determination of Tl in urine down to a detection limit of 0.5 ppb²; in marine soil and sand sediments down to a range of a few hundred ppb³; and in atmospheric particulate matter collected on filters⁴.

Unfortunately, the sensitivity of most spectral methods of analysis is insufficient for the direct determination of concentrations in the *sub*-ppb range. The lower limit of detection of Tl by Atomic Emission Spectrometry in an Inductively Coupled Plasma (ICP-AES) is 4.4

ppb⁵, while Graphite Furnace Atomic Absorption Spectrometry (GF AAS) is capable of detecting concentrations down to 0.4 ppb⁶. Consequently, for the detection of sub-ppb concentrations some method of preconcentration, e.g. chelation, separation or extraction, must be used together with these techniques⁷. It is well known that such procedures can lead to uncontrolled contamination and additional interferences even for elements of relatively low abundance. In many cases chemical modifiers are used as well, which gives some further side effects and increases the risk of contamination⁸. Examples of the use of such techniques are pre-concentration and extraction for the determination of Tl in rocks⁹, extraction and matrix modification for Tl determination in rocks¹⁰, extraction and reextraction for the determination of Tl in digested soils¹¹.

The Inductively Coupled Plasma Mass Spectrometry technique (ICP-MS) with its detection limit in the ppt (pg/ml) range today is the only commercially available technique capable of direct analysis of Tl in ultra-low concentrations⁵. However, in order to validate the results from analyses involving the determination of ultra-low concentrations of various elements in a variety of samples, it is essential to have at least two different ultra-sensitive techniques available. This makes the development of alternative methods of detection important.

In order to avoid contamination problems related to various pre-treatment and pre-concentration procedures there is today an extensive development of techniques possessing improved qualities, such as higher sensitivity and selectivity, as compared to conventional techniques. Laser-based spectroscopic techniques do possess such qualities. Examples of highly sensitive and selective laser-based spectroscopic analytical techniques under development in various laboratories around the world are Resonance Ionization Spectroscopy (RIS), Laser Enhanced Ionization (LEI) and Laser Induced Fluorescence with Graphite Furnace (LIF-GF)¹—techniques which all give the opportunity of direct metal determination at the ppt level or below¹²⁻¹⁴ for a number of elements.

It has previously been found¹⁵ that LIF-GF is particularly suitable for Tl determination, giving a limit of detection in aqueous solutions as low as $5 \cdot 10^{-3}$ ppt. The LIF-GF technique has also been used for the determination of Tl in alloys¹⁶ and organic material¹⁷. Consequently, it is of great interest to investigate to what extent this powerful technique can be used for the direct determination of Tl in environmentally interesting samples. In this paper we report on the results of a Tl determination by LIF-GF in natural waters from lakes and rivers in South-West Sweden, in the vicinity of Göteborg.

EXPERIMENTAL SET-UP AND PROCEDURES

The experimental set-up used for the experiments is schematically shown in Figure 1. The experimental set-up has previously been described in detail¹⁸, so only its basic concepts will be discussed below.

The furnace is a spatially and temporally isothermal two-step graphite furnace designed

¹Often also referred to as ETA LEAFS, Laser-Excited Atomic Fluorescence Spectroscopy with graphite furnace Electro-Thermal Atomization.

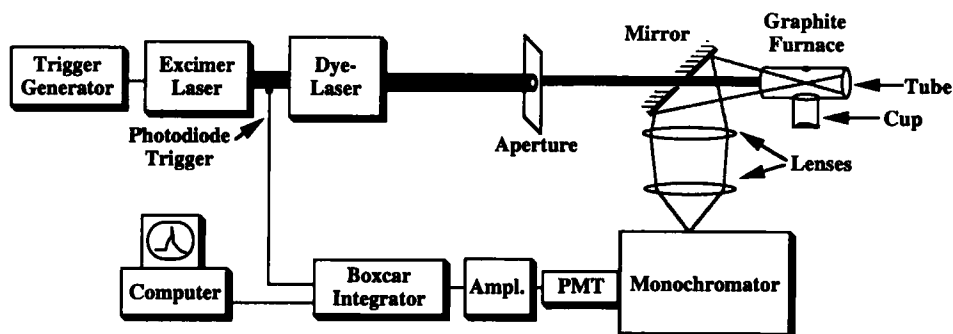


Figure 1 Experimental set-up of LIF-GF.

by Frech¹⁹ with separately controlled temperatures of the cup and the tube. Because of its spatial and temporal isothermality, the furnace is very suitable for diagnostic purposes. The samples were introduced into the cup using a 5 μL pipette and dried at 95°C for 45 s. The temperatures of the cup and the tube during atomization were 1840 K and 2080 K, respectively, with the heating of the cup delayed a few seconds with respect to the tube. The exact atomization temperature is not a crucial parameter, since the atomization efficiency of Tl has been shown to be virtually independent of temperature²⁰.

The laser system consists of an excimer laser run at 50 Hz, which pumps a dye laser (Lambda Physik, LPX 210I pumping an FI 2003). The excimer laser was filled with XeCl, thus providing light pulses of 308 nm with a duration of roughly 25 ns and an energy of about 200 mJ. The dye laser provided light with a wavelength of 276.79 nm using a Coumarin 153 dye and a BBO frequency doubling crystal, the beam having a diameter of 3 mm and an energy of about 15 μJ (measured at the exit of the graphite furnace) so as to optically saturate the transition. The laser excited atoms from the $6p\ ^2P_{1/2}$ ground state to the $6d\ ^2D_{3/2}$ level at $36\ 118\ \text{cm}^{-1}$.

The fluorescence light was collected at a 180° angle with respect to the illuminating laser beam in a front-surface illuminating scheme. The fluorescence light was attenuated by neutral density filters when necessary in order to avoid saturation of the photomultipliers. The monochromator was adjusted to select the 351.92 nm fluorescence line, between the $6d\ ^2D_{5/2}$ level (at $36\ 200\ \text{cm}^{-1}$) and the metastable $6p\ ^2P_{3/2}$ level (at $7\ 793\ \text{cm}^{-1}$), with a bandwidth of approx. 1 nm, so as to collect parts of the 352.94 nm fluorescence light from the $6d\ ^2D_{3/2}$ level (at $36\ 118\ \text{cm}^{-1}$) to the $6p\ ^2P_{3/2}$ level as well. The light selected by the monochromator (Jobin Yvon HR20UV) was detected by a photomultiplier (Hamamatsu R2027), whose signal was fed to a boxcar module (Stanford SR 250). The data were stored in an ordinary PC-type lab-computer.

A stock solution of 1000 mg/L of Tl was prepared from a Tl_2SO_4 reference solution (Fixanal; Riedel-de Haën) and distilled and deionized water (produced by a Milli Q Plus system; Millipore). Reference water solutions were prepared by successive dilutions of the stock solution with the distilled and deionized water with the addition of high-purity HNO_3 (Suprapur; E. Merk) to a concentration of 0.32%. The same concentration of acid was also added to all samples.

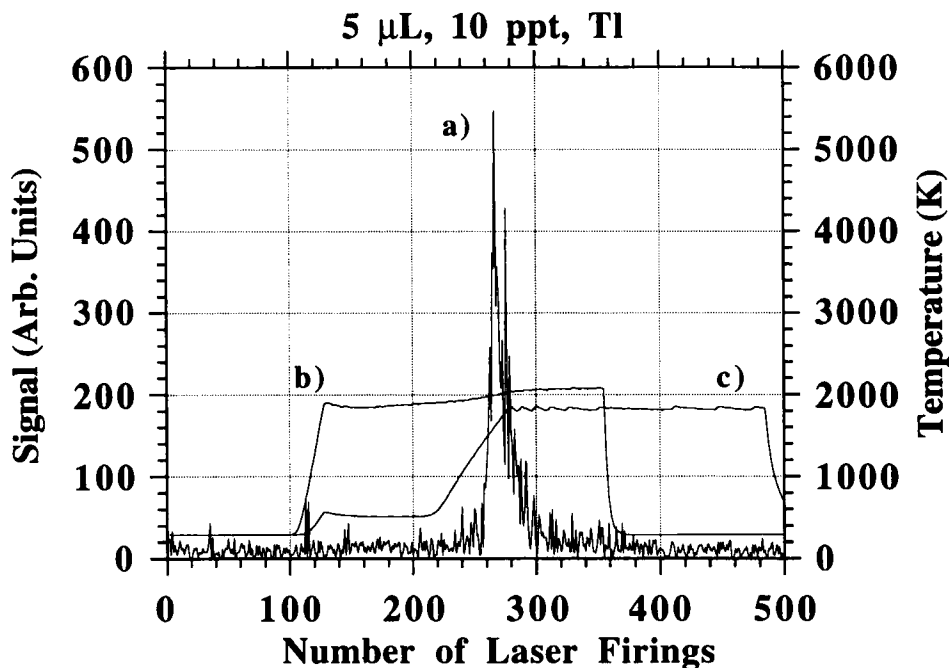


Figure 2 LIF-GF signal (*a*) from 5 μ l of a 10 ppt solution (50 fg) during one heating cycle of the graphite furnace, together with temperature curves for the tube (*b*) and cup (*c*), respectively.

The samples were collected in plastic bottles which had been cleaned with 0.32% HNO_3 for an extensive period of time. When collecting the water samples the bottles were immersed well below the surface of the water before being opened in order to avoid contamination from the surface layer. Each bottle was filled twice with the water under investigation in order to rinse out any impurities from the distilled water. Upon return to the laboratory the bottles were acidified to 0.32% HNO_3 .

RESULTS AND DISCUSSION

A typical Tl signal acquired by the LIF-GF technique from a 10 ppt Tl solution is shown in Figure 2. The curve labelled *a* represents the actual LIF signal while the two curves labelled *b* and *c* show the temperature of the tube and the cup during the heating cycle, respectively. Each individual data point in the figure—the points being connected by a solid line for easier visualization—corresponds to the signal obtained from a single laser shot. For each heating cycle, all the measured data points were integrated in order to yield a final value of the amount of Tl contained in the injected sample.

Using reference water solutions, prepared by successive dilutions of a 1000 mg/ml stock solution in doubly deionized water, to concentrations in the 0–100 ppt range, a calibration curve for Tl in deionized water was constructed. This calibration curve was linear in the

whole concentration range studied. This curve (see Figure 3) was then used to estimate the limit of detection of Tl in deionized water (corresponding to 3 standard deviations of a number of consecutive measurements of Tl when deionized water was introduced into the furnace) for the present experimental set-up. The limit of detection of Tl in deionized water was found to be approx. 1 ppt for the present set-up. This was significantly higher (almost three orders of magnitude) than the best detection limit published¹⁵ but, on the other hand, low enough for analyzing all our samples.

The detection limit, in our case, was restricted by several factors, such as: a low throughput of the monochromator (high $f/\#$ of the monochromator, $f/4.2$, not fully matched to the optical light-collection system); a blank signal originating from contamination of samples, deionized water, sample-handling equipment (pipettes, etc.) and/or the graphite material of the cup and tube; a background signal from scattered laser light; and, to some extent, the detection system noise. In addition, to achieve the best detection limit, the alignment of the spectrometer as well as the light-collection system has to be very carefully adjusted with respect to the furnace in order to ensure that the collection of the fluorescence light is as efficient as is possible. For the spectrometer, this requires a careful adjustment of six degrees of freedom (the position of the entrance and exit slits). With the rather simple light collection system used in our set-up, such a careful and precise operation was difficult to achieve at the time of the measurement. With an optimization procedure such as described in²¹, and using more appropriate experimental equipment, we envision a major improvement of the detection limit.

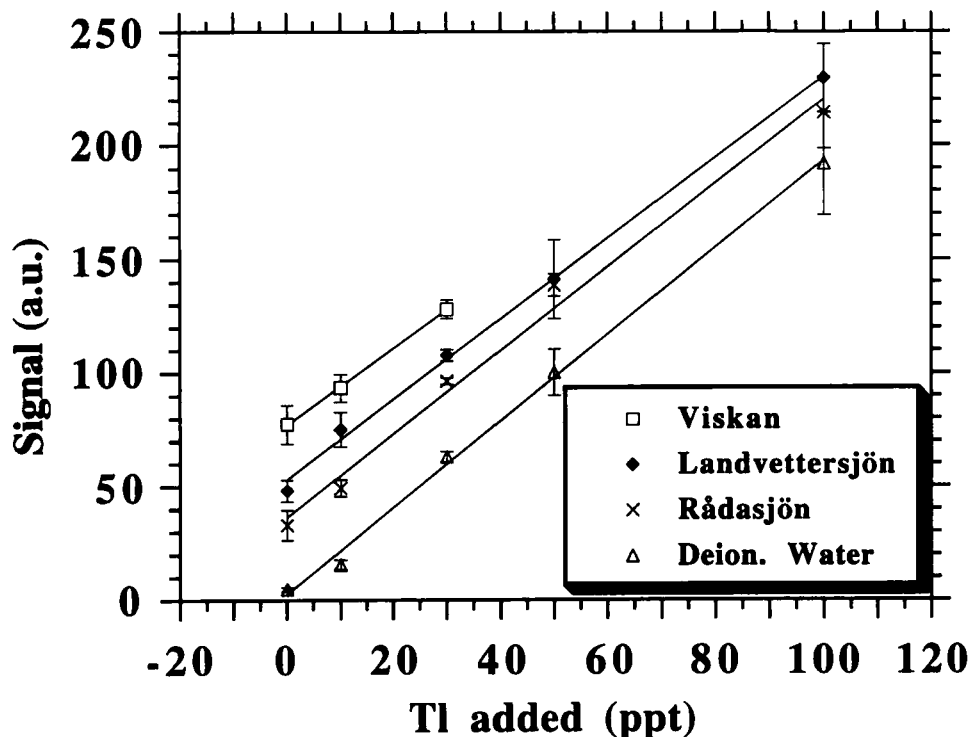


Figure 3 Standard addition curves for Viskan, Göta Älv, Rådasjön, and deionized water.

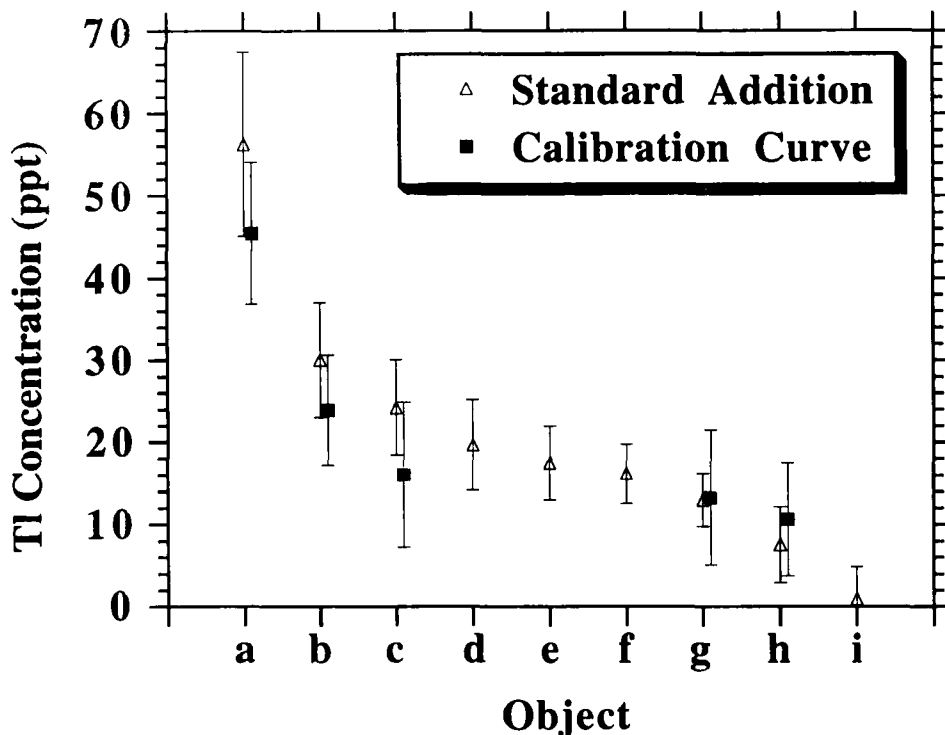


Figure 4 A compilation of the Tl contents found in the objects studied. The objects are: a—Viskan; b—Landvettersjön; c—Göta Älv; d—Rådasjön; e—Lilla Delsjön; f—Stora Delsjön; g—Stora Nedern; h—tap water; and i—deionized water. The errors represent ± 2.1 standard deviations, which give limits for the actual value of the Tl content in the various objects with a degree of confidence of 95%.

Water of two rivers and five lakes in Göteborg and its vicinity, as well as the drinking water of Göteborg city, was investigated. In order to relate the measured signals to the Tl concentration of the sample two methods were used: (i) standard addition and (ii) use of a calibration curve obtained from a set of reference Tl solutions (in deionized water).

The samples were first analyzed by the standard addition technique which is generally expected to give a correct value of the Tl content of a sample since it automatically accounts for many types of matrix interferences. The disadvantage of the technique is that it is rather time consuming. Some typical standard addition curves are presented in Figure 3, while Figure 4 and Table 1 show the results obtained by the standard addition technique for all the samples. The error bars in Figure 3 represent ± 1 standard deviation from the measurements performed at that particular concentration, while the error limits presented in Fig. 4 and Table 1 represent a 95% confidence interval for the sample, based on the statistical fluctuations of all the measurements performed on the complete set of samples under the above-mentioned experimental procedures.

The confidence intervals were obtained by a procedure based on the fit of a linear function to all the measured samples including the propagation of statistical errors and uncertainties in all measurements to a final value of, as well as a confidence interval for, the intercept of

Table 1 Summary of Tl contents in some natural waters in South-West Sweden determined by LIF-GF.

<i>Sample of analysed</i>	<i>Tl content (ppt)*</i>	
	<i>Calibration curve method</i>	<i>Standard addition method</i>
Viskan	46 ± 9	56 ± 11
Stora Nedern	13 ± 8	13 ± 3
Göta älv	16 ± 9	24 ± 6
Landvettersjön	30 ± 7	24 ± 7
Rådasjön		20 ± 6
Stora Kåsjön		16 ± 4
Lilla Delsjön		18 ± 4
Drinking water	11 ± 7	8 ± 5

* Error limits correspond to 95% confidence interval for the samples under the actual experimental conditions.

the curve with the X-axis, i.e. the Tl content of the samples²²⁻²⁴. This statistical evaluation technique is comprehensively presented in ref. 24.

In addition, in order to check the accuracy of the results, the samples were also analyzed by the calibration curve technique, which is less time-consuming than the standard addition technique. On the other hand, since the technique relies on an assumption that the sensitivity of Tl in the samples does not vary—i.e. is not affected by concomitant elements—its applicability is somewhat limited. Consequently, it is useful as long as no or small matrix interferences exist for the sample investigated.

From the previously mentioned calibration curve a sensitivity factor of the experimental set-up was derived. This sensitivity factor was then used to directly convert various measured signals from the samples to an estimated Tl concentration. However, due to fluctuations and long-term drifts for various experimental parameters (primarily laser intensity and wavelength) the calibration curve method could only be used in the cases where the actual calibration curve data was collected in close conjunction with the data of the analyzed samples. Consequently, since the measurement procedure was mainly determined by the requirements of the standard addition technique, the calibration curve method was in this study only applicable for five out of the eight samples.

As is clear from Table 1, the data correlation between the two methods is rather good, though not overwhelmingly so. This means that there are no or only small matrix influences, since these would have affected the signals from the standard addition measurements. The differences between the two series of measurements are believed to originate mainly from alterations in experimental parameters between the time of measurement of the calibration curve and the samples. Thus, the differences provide an estimate of the effect of long-term drifts and fluctuations in the experimental set-up and indicate that these effects do not particularly affect the repeatability of the method.

CONCLUSIONS

It is well known that LIF-GF offers high sensitivity and selectivity, and good precision and accuracy, and can be used for the analysis of a large range of environmental objects, such as water samples, oils and tissue samples. In this paper we report the results of the determination of the thallium content of natural waters (rivers and lakes) in South-West Sweden by LIF-GF. The Tl content of the samples investigated varied from 8 to 56 ppt—the lowest value reflecting the concentration in the drinking water of the city of Göteborg, and the highest one originating from the Viskan river some 150 km south of Göteborg.

The Tl concentration of the various samples was determined by the conventional standard addition technique. When analyzing the water samples, no matrix interferences were observed. This allowed a calibration against a matrix-free reference solution. Comparison of the two sets of data showed the correlation to be satisfactory.

The present experimental set-up which, however, was not the most optimum configuration for practical reasons (such as limited availability of optimum experimental equipment), gave a practical limit of detection for Tl for direct analysis of natural waters of around 1 ppt. In conclusion, a two-step isothermal LIF-GF allows the direct determination of Tl in water samples at the ppt level using a simple heating programme and without matrix-modifying and/or pre-concentration techniques.

Acknowledgements

This work was supported by grants from the Swedish Natural Science Research Council. One of the authors (N.C.) acknowledges support from the Royal Swedish Academy of Sciences.

References

1. H. Borg, *Vatten*, **44**, 145–147 (1988) (In Swedish).
2. D. C. Pascal and G. G. Bailey, *Anal. Toxicol.*, **10**, 252 (1986).
3. J. W. McLaren, D. Beauchemin and S. S. Berman, *Anal. Chem.*, **59**, 610–613 (1987).
4. R. J. Thompson, G. B. Morgan and L. J. Purdue, *At. Abs. Newsl.*, **9**, 53 (1970).
5. *The Guide to Techniques and Applications of Atomic Spectroscopy* (no. L-655E), Perkin-Elmer, 1991.
6. D. Nygaard and F. Bulman, *Spectr. Intern.*, **2**, 44–47 (1990).
7. B. Griepink, M. Sager and G. Tölg, *Pure Appl. Chem.*, **60**, 1425–1436 (1988).
8. B. Wetz, G. Schlemmer and J. R. Mudakavi, *J. Anal. Atom. Spectr.*, **3**, 695–701 (1988).
9. R. Kiel, *Z. Anal. Chem.*, **309**, 181–185 (1981).
10. N. T. Voskresenskaya, N. F. Pchelintseva, and T. I. Tsekhonya, *J. Anal. Chem USSR*, **36**, 667 (1981).
11. W. Schmidt and F. Dieltl, *Z. Anal. Chem.*, **308**, 129–132 (1981).
12. M. A. Bolshov, in: *Laser Analytical Spectroscopy* (V. S. Letokhov, ed., Adam Hilger, Bristol, 1986), pp. 52–94.
13. O. Axner and H. Rubinsztein-Dunlop, *Spectrochim. Acta*, **44B**, 835–866 (1989).
14. S. Sjöström, *Spectrochim. Acta Rev.*, **13**, 407–465 (1990).
15. H. Falk, H. J. Paetzold, K. P. Schmidt and J. Tilch, *Spectrochim. Acta*, **43B**, 1101–1110 (1988).
16. R. Irwin, D. Butcher, J. Takahashi, G. Wei and R. Michel, *J. Anal. Atom. Spectr.*, **5**, 603–610 (1990).
17. D. Butcher, R. Irwin, J. Takahashi, G. Su, G. Wei and R. Michel, *Appl. Spectr.*, **44**, 1521–1533 (1990).
18. S. Sjöström, *J. Anal. Atom. Spectr.*, **5**, 261–267 (1990).
19. E. Lundberg, W. Frech, D. C. Buxter and A. Cedergren, *Spectrochim. Acta*, **43B**, 451–457 (1988).

20. O. Axner, M. Norberg and S. Sjöström., submitted to *Spectrochim. Acta. B.*
21. B. W. Smith, P. B. Farnsworth, P. Cavalli and N. Omenetto, *Spectrochim. Acta*, **45B**, 1369–1373 (1990).
22. J. N. Miller, *Spectr. Intern.*, **3**, No. 5, 43–46 (1991).
23. J. N. Miller, *Spectr. Intern.*, **3**, No. 7, 45–47 (1991).
24. J. N. Miller, *Spectr. Intern.*, **4**, No. 1, 41–43 (1992).