Laser-excited atomic fluorescence spectrometry in a graphite furnace with an optical parametric oscillator laser for sequential multi-element determination of cadmium, cobalt, lead, manganese and thallium in Buffalo river sediment

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It is demonstrated, for the first time, that solid-state lasers based on optical parametric oscillation (OPO) allow relatively rapid sequential multi-element analysis of samples by laser-excited atomic fluorescence spectrometry (LEAFS) in a graphite furnace. These lasers are tunable by facile computer keyboard control over the wavelength region 220–2000 nm. A method is described for the sequential multi-element determination of cadmium, cobalt, lead, manganese and thallium in a river sediment standard reference material (NIST SRM 2704) by graphite furnace LEAFS. With a slow rate of 0.125 nm s⁻¹, the OPO laser could be tuned to cover the wavelength range needed for these elements, from 228 to 304 nm, in 15 min. This allowed each element to be determined sequentially with the analysis time determined primarily by the slow heating cycle of the furnace rather than the laser wavelength tuning. Detection limits in the multi-element mode were 545, 111, 28, 445 and 24 fg for cadmium, cobalt, lead, manganese and thallium, respectively, limited primarily by the low repetition rate of the laser (10 Hz). The multi-element detection limits were within a factor of 2–4 of those in the single element mode. Higher excitation energies, by a factor of 2–5, were required to optically saturate the transitions of the analytes in the sediment sample solution compared with aqueous standards. By use of several aliquots of one sample solution, and simple aqueous calibration, it was possible to analyze the sample, accurately, for the five elements over a concentration range between 1 ng ml⁻¹ for thallium and 460 ng ml⁻¹ for manganese. Different dilutions were not necessary owing to the long calibration range of the technique. The high sensitivity of LEAFS allowed sufficient initial dilution to remove an interference on thallium that is normally caused by fluorescence quenching in the sample. In the 1980s, the use of graphite furnaces allowed extremely low absolute detection limits in the femtogram range to be routinely achievable by laser-excited atomic fluorescence spectrometry (LEAFS). Other advantages provided by graphite furnace LEAFS include high spectral selectivity, a high dynamic range of the calibration curves, typically 5–7 orders of magnitude, only small sample volumes are required for analysis (μl or mg) and the technique has direct solid sampling capabilities for some samples. Use of the autosamplers and furnaces developed for electrothermal atomic absorption spectrometry (ETAAS) allows automation for graphite furnace LEAFS. However, with dye lasers, LEAFS in a graphite furnace has been considered to be a single element technique, because it is expensive and impractical to automate the dye solution changes needed to reach the different wavelengths required for each analyte element. This paper demonstrates that the use of a wavelength tunable optical parametric oscillator laser system permits automated, rapid, sequential, multi-element analysis by graphite furnace LEAFS.

For LEAFS, the laser must provide high peak energy above a few tens of microjoules, wavelength tunability from the ultraviolet (UV) to the near infrared (NIR) region and linewidths <0.2 cm⁻¹ to match the collisionally broadened linewidth of atomic spectral lines in atmospheric pressure atom cells. Until now, dye lasers have provided the closest fit to these requirements for LEAFS. Recent improvements in organic dye technology have allowed a single dye to cover 20–30 nm in the UV region after frequency doubling but even this is still a limited tuning range. Also, problems exist with the disposal and storage of potentially hazardous, flammable and toxic dye solutions, the limited lifetime of the dyes and the physical awkwardness and impracticality of the dye change itself. Although some of these issues are being addressed by the development of dye-doped host materials for solid-state dye lasers, the tunability of solid-state dye lasers is still as limited as traditional dye lasers, and the host materials have thermal susceptibility and degradation problems.

In an attempt to facilitate multi-element analyses by LEAFS, Schütz et al. developed a dual-wavelength dye laser system by use of an additional tuning mirror in the dye oscillator. Two of those systems were then combined for the simultaneous determination of cadmium, manganese, nickel and lead by graphite furnace LEAFS. The tuning of the separation between the two output wavelengths was restricted to within the gain profile of the same dye. Although this was feasible for the elements tested, it is not feasible for random, rapid selection of greater numbers of elements. When more elements need to be determined, a more complicated, impractical system with multiple lasers would be required.

Diode lasers are an alternative to dye lasers, and are attractive for atomic spectroscopy because of their low cost, simplicity, small size and potential for very narrow spectral linewidths. Niemax and co-workers demonstrated the simultaneous determination of lithium and rubidium by atomic fluorescence in a graphite furnace with two laser diodes for excitation. These elements were accessible to laser diodes.
because their transitions are in the visible spectrum, but the low diode laser output powers (5 mW at 670.78 nm and 40 mW at 780.03 nm) could not optically saturate the lithium resonance line at 670.78 nm, while only partial optical saturation was observed for rubidium at 780.03 nm. In common with other laser types, the lack of availability of UV diode lasers means that various harmonic generation techniques are necessary to generate the UV wavelengths for excitation of atomic fluorescence of the elements. Both extra-cavity second harmonic generation (SHG)\textsuperscript{5,10} and intra-cavity harmonic generation\textsuperscript{11} of diode lasers have been demonstrated for the generation of the near blue wavelengths that are useful for atomic absorption and molecular fluorescence, but the diode-SHG configuration suffers from very low conversion efficiencies of the order of 10\textsuperscript{−3}.\textsuperscript{9} This results in low output power which is most likely not sufficient for optical saturation in LEAFS applications. For multi-element applications of diode lasers, a practical implementation would involve multiple laser diodes arranged with multiple harmonic generation systems to provide simultaneous emission of many wavelengths, or sequential harmonic generation of the radiation from multiple diodes to provide sequential access to multiple wavelengths in the UV region. These options are feasible and should be tested to determine their design advantages and limitations. Such systems could be useful in atomic absorption where the excitation source energy is not critical, but they would be less useful for atomic fluorescence where high peak energies are necessary to ensure both excellent detection limits and optical saturation.

Various types of tunable solid-state lasers have evolved to the point where rapid tunability over a wide spectral range can be achieved, of which those based on optical parametric oscillation (OPO) are the most promising.\textsuperscript{12} Spectroscopic applications of OPO laser systems have been demonstrated for coherent anti-Stokes Raman spectroscopy \textsuperscript{13} thermal lens spectrometry\textsuperscript{14,15} and atomic spectrometry.\textsuperscript{15} In the last case, for flame LEAFS, Zhou \textit{et al.}\textsuperscript{15} characterized a tunable, 10 Hz repetition rate, OPO laser system and explored its potential for the rapid sequential multi-element determination of cobalt, copper, lead, manganese and thallium in a river sediment standard reference material. It was shown that rapid, sequential, multi-element analysis was feasible with OPO-based flame LEAFS instrumentation. Including all calibration curves, 400 measurements were made in 4.5 h during the accurate determination of the five elements in the river sediment sample. Within such a short time period, this would not have been possible with a dye laser owing to the necessity for dye changes.

In this work, for the first time, an OPO-based laser system was used to demonstrate the sequential, multi-element capability of graphite furnace LEAFS by the determination of five elements in the same river sediment reference material that was used by Zhou \textit{et al.}\textsuperscript{15} There is environmental and geological interest in the determination of major, minor and trace elements in sediment samples.\textsuperscript{16–20} ETAAS has been a convenient, effective and sensitive analytical approach for most of the elements in sediment samples.\textsuperscript{16,19} However, the complex matrix of the typical sediment sample has been shown to interfere seriously with the determination of lead,\textsuperscript{21} zinc\textsuperscript{2} and copper and made it impossible for thallium to be accurately determined by ETAAS.\textsuperscript{19} It is shown here that the selectivity, sensitivity and sequential multi-element capability of the graphite furnace LEAFS technique permitted a relatively rapid, accurate and precise determination of cadmium, cobalt, lead, manganese and thallium in a Buffalo river sediment standard reference material.

Cadmium was a special case in that it was determined for the first time here by thermally assisted stepwise line fluorescence. Owing to the inherent structure of cadmium's atomic energy levels, there are no direct connections between the transitions for laser excitation and fluorescence. Determination of cadmium by graphite furnace LEAFS was first reported by Omenetto \textit{et al.}\textsuperscript{22} who used a two step excitation scheme to address this issue. Efficient excitation was achieved by use of two dye lasers tuned to 228.902 and 643.847 nm, with thermally assisted fluorescence detection at 361 nm. A detection limit of 18 fg was measured. Bolshov \textit{et al.}\textsuperscript{23} adopted a classical right-angle resonance excitation-detection scheme at 228.8 nm to achieve a detection limit of 3.5 fg for water samples, but serious scatter problems were reported, as might be expected for resonance fluorescence. Such scatter problems are too serious to consider the use of resonance fluorescence for detection at 180° to the laser beam, which is the preferred method of detection for graphite furnace LEAFS. Here, excitation was at 228.8 nm and fluorescence detection was at 361 nm through a thermally assisted stepwise line fluorescence scheme. This avoided the use of two lasers or the use of resonance fluorescence, and allowed sequential multi-element graphite furnace LEAFS to be performed with fluorescence detection at 180° to the laser beam. This is the first report of the use of this scheme for the determination of cadmium by LEAFS.

**EXPERIMENTAL**

**OPO laser system**

An OPO laser (Model MOPO 730–10; Spectra Physics, Mountain View, CA, USA) based on \textit{Ó}barium borate (BBO) crystals and equipped with a frequency doubler was used. It was pumped by an injection seeded, 10-Hz, Q-switched Nd:YAG laser (Model GCR-250; Spectra Physics). Two detailed descriptions and reports of the performance of this laser system can be found in the literature.\textsuperscript{23,25} The temporal pulse width was about 6 ns. The OPO laser system had a scanning speed of up to 0.125 nm s\textsuperscript{−1} and a computer-controlled, wavelength tuning range from 220 nm in the UV region to 2000 nm in the near IR region. It was possible to scan the wavelength range used here, 228–304 nm, in 15 min, which meant that the speed of analysis was limited by the graphite furnace rather than the laser. The laser output pulse energies were of the order of millijoules throughout the UV spectrum with a typical spectral linewidth of 0.2 cm\textsuperscript{−1}.

**OPO–graphite furnace–LEAFS instrumentation**

The experimental arrangement for LEAFS is shown in Fig. 1. The UV output beam, which was approximately 7 mm in diameter at the OPO laser output, was passed through a UV-grade beam attenuator with a 3 mm aperture (Model 935–3; Newport, Irvine, CA, USA), which provided an attenuation of 2–40 dB. To provide beam shaping, a further circular aperture was inserted into the light path, which was adjustable from 0.5 mm diameter to about 3 × 6 mm, determined by the aperture of the beam attenuator. A 90°, off-axis ellipsoidal mirror with a diameter of 89 mm and 140.00 and 260.00 mm focal lengths (Aero Research Associates, Port Washington, NY, USA), was used to collect the fluorescence. It had a 6 mm diameter hole in the center through which the laser beam was...
passed, and it was placed in front of the furnace at an angle of 45° with respect to the excitation axis. The fluorescence was collected from the mirror at 180° to the direction of the laser beam and focused on to the entrance slit of an f/3.5 monochromator (8 nm mm⁻¹ dispersion, Model H-10; Instruments SA, Metuchen, NJ, USA). To reduce further the stray light and blackbody emission from the furnace, 10 nm bandpass filters centered at the detection wavelength of each element were placed near the entrance slit. The signals from the photomultiplier tube (PMT) (Model R212 UH; Hamamatsu, Middlesex, NJ, USA) were passed through a delay line of about 80 ns, preamplified (Model VV100 BTB preamplifier; LeCroy, Chestnut Ridge, NY, USA) and processed with a boxcar integrator (Stanford Research Systems, Sunnyvale, CA, USA) at a gate width of 10 ns, a delay time setting of 70 ns and the 'last sample' output mode. The 'last sample mode' records the average signal in the last gate. Data were collected by use of a 12-bit data acquisition system (27.5 kHz digitization rate, Model DT2801-A; Data Translation, Marlboro, MA, USA) through software developed by use of Microsoft Visual Basic. The computer was an IBM PC compatible (Model P5–60; Gateway 2000, North Sioux City, SD, USA). The atomizer was an HGA-500 graphite tube furnace equipped with an AS-40 autosampler (Perkin-Elmer, Norwalk, CT, USA).

For sequential multi-element analyses, the laser was slew scanned between excitation wavelengths at the maximum slew rate of approximately 0.125 nm s⁻¹. At each excitation wavelength in turn, the determination of each element in the Buffalo river sediment was performed, including the construction of saturation curves, calibration curves and sample measurements.

Reagents
The water used was both de-ionized and sub-boiled in a quartz still (Quartz et Silice, Paris, France), and ultrapure acids (Baker, Jackson, TN, USA) were used for the preparation of all the aqueous standards and sample solutions. A commercially available 1000 mg l⁻¹ cadmium solution was used (J. T. Baker, Phillipsburg, NJ, USA) together with cobalt, lead, manganese and thallium stock solutions prepared from cobalt powder, lead metal, manganese flake and thallium(n) nitrate (Puratrace grade; Alfa Products, Danvers, MA, USA) on a class 100 (US Federal 209b) clean bench. Stock solutions of 1000 μg ml⁻¹ magnesium nitrate [Mg(NO₃)₂] and ammonium dihydrogenphosphate [(NH₄)H₂PO₄], for use as chemical modifiers, were prepared by dissolution of magnesium nitrate and ammonium dihydrogenphosphate in 2% nitric acid (99.999% pure; Aldrich, Milwaukee, WI, USA). A commercially available 1000 μg ml⁻¹ palladium solution (J. T. Baker) was also employed as a chemical modifier. Aqueous standard solutions of cadmium, cobalt, lead, manganese and thallium were made by serial dilution with 2% nitric acid. A 2% solution of nitric acid served as the blank for cadmium and thallium, while the same blank for the remaining elements also contained the appropriate chemical modifier. All glassware and plasticware were soaked in 20% nitric acid (reagent grade; J. T. Baker) for 24 h, and then rinsed with sub-boiled, de-ionized water prior to use.

Sample preparation
Buffalo river sediment standard reference material (SRM 2704) was obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Multiple dried sediment samples of about 0.08 g were weighed into polycrystal fluoroethylene beakers, to which were added 10 ml of hydrochloric acid and 10 ml of nitric acid. The solutions were heated at 60–80 °C for several hours to dryness. The addition of acids and evaporation were repeated three times followed by the addition of a minimum amount of hydrochloric acid to dissolve the residue. The solution was then transferred into a 100 ml calibrated flask. This process a small residue remained, which was rinsed several times with water, and the resultant solution was combined with the previous solution. Nitric acid was added to the digested sample so that the final acid concentration was approximately 2% v/v. The concentrations of filters centered at the detection wavelengths were 361.2, 341.2, 403.3, 405.8 and 352.9 nm, respectively. First, a stoichiometric air-acetylene flame was used to optimize the detection system parameters. The five excitation–fluorescence wavelength pairs were used to check the calibration of the OPO laser wavelength readout. After installation of the graphite furnace atomizer, excitation scans were performed over a narrow wavelength range (about 20 pm) to locate the exact position of the optimum excitation wavelengths. Graphite furnace heating regimes under stabilized temperature platform furnace (STPF) conditions were then optimized. It was not necessary to use a chemical modifier for either cadmium or thallium. The chemical composition temperatures used were 400/2100, 1000/2200, 1000/2200, 900/1800 and 700/1800 °C for cadmium, cobalt, manganese, lead and thallium, respectively. The atomic fluorescence signals were maximized by optimization of the excitation laser beam size, slit-width of the detection monochromator and appropriate alignment of the optical axis of the monochromator. A beam pointing error existed from wavelength to wavelength, which could be controlled by use of the Pellin-Broca prism that is used to separate the frequency doubled radiation from the fundamental wavelengths at the output of the OPO. The pointing error was minimized by adjustment of the prism for each element's excitation wavelength by use of a far field target about 4 m away from the OPO output window. Thereafter, the resultant 'look-up' table was stored in the laser's computerized controller system, which then minimized the beam pointing error throughout the wavelength tuning range of 220–345 nm.

A sample volume of 20 μl was used throughout the graphite furnace experiments. Calibration graphs were constructed with aqueous standards across a concentration range of at least four orders of magnitude. Chemical modifiers of magnesium nitrate, palladium plus magnesium nitrate, and ammonium dihydrogenphosphate were contained in the cobalt, manganese and lead solutions, respectively. Instrumental detection limits were measured by extrapolation from the analytical calibration curves to a concentration equivalent to a signal-to-noise ratio of 3. The lowest point on the calibration curve was within an order of magnitude of the detection limit. The instrumental noise level was determined by the standard deviation of 16 measurements of the blank at a wavelength 100 pm away from the corresponding analytical line. A detection limit based on the procedural blank was not measured.

RESULTS AND DISCUSSION
The primary aim of the experiments was to demonstrate the sequential multi-element capability of graphite furnace LEAFS by use of a tunable laser system based on an OPO. The experimental conditions were first optimized to obtain the best signal-to-noise ratio for each element, then analyses were
performed by tuning the laser sequentially between the chosen elements. Analytical characteristics such as detection limits, interference effects and accuracy and precision for the sediment analysis were explored.

First, the optimum conditions for each element were determined. By use of the adjustable circular aperture shown in Fig. 1, the excitation beam diameter was optimized for maximum signal-to-background-noise ratio (SNR) while just maintaining saturation of the optical transitions. For all elements, a variation in SNR of a factor of 3–5 was experienced as a function of beam diameter, with an optimum beam diameter at about 2.5 mm. The beam diameter was limited primarily by reflection of the bottom part of the beam off the graphite platform, which degraded the signal-to-noise ratio. The beam could be masked to avoid this, but this was not tried here. Table 1 lists the spectrometer slit-widths that gave the optimum SNR for each analyte, together with the optimized laser excitation energies that were required for saturation of the atomic transitions for the various elements in aqueous standards and in solutions of the SRM 2704 sediment. The saturation energies listed in Table 1 were applied throughout the experimental concentration range for each element. Optical saturation ensures a maximum linear dynamic range and reduced interference. On the other hand, avoidance of the use of excess excitation energy helps to minimize the noise caused by scattered laser radiation. Example saturation curves, for manganese, in an aqueous standard and in the sediment sample solution are shown in Fig. 2. Both saturation curves displayed slopes of close to unity at low excitation energies: 0.98 and 0.99 for aqueous standard solutions and sediment sample solutions, respectively. Optical saturation, as evidenced by the onset of a plateau in the excitation curve, for the sediment sample solution occurred at an excitation energy three times larger than that required for the aqueous standard solution. This indicated that the sediment sample solution attenuated the excitation radiation by the prefilter effect. A factor of 2–5 increase in excitation energy was found to be necessary to optically saturate the transitions of cadmium, cobalt, lead, manganese and thallium in the sediment sample solution compared with simple aqueous standards. This does not cause any particular analytical inconvenience, but it does highlight that the correct excitation energy must be known for a successful analysis to be achieved. The increase in energy required for different real samples, relative to aqueous standards, merits further study to discover the extent by which the laser energy needs to be varied between different types of samples.

Detection limits for all five elements were obtained in a sequential multi-element mode. The system parameters were optimized, including laser beam position, detection system alignment and monochromator entrance slit width at each element’s excitation wavelength. Neutral density filters were used (Fig. 1) to control the amount of light that fell on the photomultiplier tube to prevent electrical saturation of the tube. The OPO laser was tuned to each excitation wavelength and detection limits were then measured. Table 2 compares the detection limits obtained in the sequential multi-element mode with those reported in the literature. Even though the laser alignment procedure that was used included the use of a far field target, laser beam pointing error still existed from wavelength to wavelength. Consequently, the detection limit degraded in the sequential mode compared with the single element mode. An improvement of a factor of 2–4 was obtainable in the single element mode where the experimental parameters were fully optimized for each individual element. Also, after taking into account that the detection limits improve

Table 1  Optimum monochromator slit-widths and laser excitation energies required for saturation of the atomic transitions of five elements in aqueous standards and SRM 2704 sediment solutions. Excitation laser beam diameter: 2.5 mm

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Monochromator slit-width/mm</th>
<th>Laser excitation saturation energy/μJ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Aqueous standards</td>
</tr>
<tr>
<td>Cadmium</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Cobalt</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>Lead</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Manganese</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>Thallium</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

Fig. 2 Saturation curves for manganese in a 500 ng ml$^{-1}$ aqueous standard (a) and 460 ng ml$^{-1}$ in river sediment sample (●). Optical saturation started at laser excitation energies of about 8 and 24 μJ, respectively.

Table 2 Comparison of detection limits with those reported in the literature

<table>
<thead>
<tr>
<th>Element</th>
<th>Literature $^*$</th>
<th>This work $^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>3.5$^*$ (25 Hz)</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>18$^*$ (100 Hz)</td>
<td></td>
</tr>
<tr>
<td>Cobalt</td>
<td>20$^*$ (500 Hz)</td>
<td>100</td>
</tr>
<tr>
<td>Lead</td>
<td>0.2$^a$ (80 Hz)</td>
<td>30</td>
</tr>
<tr>
<td>Manganese</td>
<td>1$^b$ (80 Hz)</td>
<td>400</td>
</tr>
<tr>
<td>Thallium</td>
<td>0.3$^c$ (80 Hz)</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>3$^c$ (80 Hz)</td>
<td></td>
</tr>
</tbody>
</table>

$^*$ Ref. 23, obtained with resonance fluorescence detection; $^+$ ref. 22, obtained with a two-step excitation scheme; $^a$ ref. 27; $^b$ ref. 28, obtained with non-dispersive detection system; $^c$ ref. 28, obtained with dispersive detection system.

$^+$ Laser repetition rate in parentheses.

$^*$ Obtained in a sequential mode with a laser repetition rate of 10 Hz.
predictably as the square root of a pulsed laser’s repetition rate, the results reported here for cobalt, lead, manganese and thallium are comparable to those published in the literature. Detection limits for cadmium, cobalt, lead, manganese and thallium in the river sediment sample solution were also measured. No significant detection limit differences between aqueous standards and the sample solutions were found.

For cadmium, a monochromator entrance slit-width of 2 mm was used with the wavelength set at 361.2 nm to detect the cadmium fluorescence. The monochromator spectral band-width permitted the simultaneous detection of three cadmium transitions, 361.1, 361.2 and 361.4 nm (Fig. 3). It was found that an improvement in detection limit by almost an order of magnitude resulted from a 2 mm compared with a 1 mm slit-width, because the wider slit encompassed more fluorescence transitions. Fluorescence detection at 326.1 nm was also studied. Although the transition probability of the 326.1 nm line, at 0.0014, is theoretically much less than that of the 361.1 nm line, at 12, a detection limit within a factor of 3 of the 361.2 nm fluorescence detection was obtained, presumably because the upper level of the 326.1 nm transition is efficiently populated by the fluorescence transitions from the states at 361 nm. There may also have been some reduced noise caused by detection at a wavelength deeper into the UV region where there is less blackbody radiation. The cadmium detection limit reported here was over one order of magnitude less sensitive compared with the values in the literature.22,23 This was expected because the chosen excitation process for cadmium involved inefficient, thermally assisted, stepwise mechanisms from $^1P_1$ to $^1D_2$ and from singlet state $^1D_2$ to triplet states $^3D_{1,2,3}$ (Fig. 3). Calculation revealed that an energy gap of about 0.3 µJ exists between the $^1P_1$ and $^1D_2$ states, while a Boltzmann thermal energy of only about 0.03 µJ is available at a furnace temperature of 2100 °C. The difference of about an order of magnitude indicates a low probability of excitation to the $^1D_2$ state, but even this allowed a reasonably good detection limit. It was not the best achievable for the atomic fluorescence of cadmium, but it was sufficient for the analysis of the sediment sample, and allowed for a sequential multi-element determination. A chemical modifier was not necessary for cadmium, and the temporal profile indicated that the 10 Hz repetition rate of the laser provided good sampling of the relatively rapid transient, owing to the excellent pulse-to-pulse stability of the laser.21

Virtually no interference was experienced for thallium concentrations of less than 1 ng ml$^{-1}$ in the diluted sediment sample solution. For thallium the high sensitivity of the LEAFS technique allowed dilution of the sediment solution to the point where matrix interferences no longer existed. This is in contrast to the atomic absorption experience with this sample where severe background signals and multiple peaks occur that probably result from the higher concentration of the matrix in ETAAS.21 From the ETAAS literature, it appears that problems with the accurate determination of thallium in this sample cannot be solved by changes in furnace conditions or by optimization of the use of chemical modifiers, while the standard addition approach has provided little improvement in accuracy.21 There appear to be no studies that have elucidated the source of the interference in ETAAS. The effect of dilution of the sediment sample solution on the accuracy and precision for thallium is shown in Fig. 4 for LEAFS. The accuracy of the analysis improved with dilution of the sample solution and reached an optimum beyond which no further improvement in accuracy was achieved, while the precision degraded. This optimum was at a thallium concentration of about 0.12 ng ml$^{-1}$.

Manganese had a concentration in the sediment solution (461 ng ml$^{-1}$) which would be too high for many other techniques to determine without further dilution of the dissolved sediment sample. For example, for ETAAS, a concentration of 500 ng ml$^{-1}$ of manganese is well past the upper limit of calibration linearity of the technique, but graphite furnace LEAFS can provide the long linear calibration range that is desirable for multi-element analysis where multiple levels of dilution are not convenient. Here, the same sample solution with 0.83 mg ml$^{-1}$ of sediment was used to determine both the highest concentration, manganese at 461 ng ml$^{-1}$, and lowest concentration, thallium at 1 ng ml$^{-1}$. A chemical modifier, consisting of palladium and magnesium nitrate, was used to

Fig. 3 Energy level diagram for cadmium. Broken lines indicate a thermally assisted stepwise excitation process.

Fig. 4 Effect of the river sediment sample solution on the accuracy and precision of the determination of thallium. The accuracy for each datum is indicated by the difference between the thallium concentrations found and the reference value. The precision is represented by the vertical error bars, at ± 1 standard deviation.

Fig. 5 Temporal profile of 10 ng of manganese in an aqueous standard with (●) and without (○) modifier (see text).
improve the atomization process for manganese. Fig. 5 shows the temporal shape of the manganese furnace signal with and without the chemical modifier. Neither peak shape was ideal. The amount of modifier used was much higher than that normally used for ETAAS, which was not surprising because the manganese concentration determined by LEAFS was well out of the normal ETAAS linear dynamic range. The optimum amount of chemical modifier was 10 µg of palladium and 6 µg of magnesium nitrate. The modifier was added to the sediment sample, and improved the accuracy of the determination of manganese by about 10% (Fig. 6), with calibration by aqueous standards that contained the same amount of modifier. Other modifiers, such as ammonium dihydrogenphosphate, were also tested but showed no significant effect on the determination of manganese. Experiments were also carried out to investigate the effect of different modifiers on the determination of cobalt and lead. Optimum amounts of 10 µg of magnesium nitrate and 5 µg of ammonium dihydrogenphosphate were found to be adequate chemical modifiers for the determination of cobalt and lead, respectively.

The analytical performance of the sequential multi-element analysis for cadmium, cobalt, lead, manganese and thallium in the SRM 2704 river sediment is shown in Table 3. Student’s t-test performed at a 95% confidence level showed no significant difference between the certified and the experimental values. A total analysis time of about 12 h was required for the work, which included about 130 measurements for three replicates of aqueous standard calibration curves, blank solution measurement and sample measurement for five elements. The analysis speed was dominated by the graphite furnace heating regimes.

CONCLUSIONS

For sequential multi-element analyses to be possible for real samples in graphite furnace LEAFS, a convenient wavelength-tunable laser source is the critical component. Once this is available, the high sensitivity, low absolute detection limits at the femtogram level, small sample size, high spectral selectivity and long linear dynamic range of the calibration curves provide significant advantages for real sample analyses. The only remaining disappointment is that the technique cannot at present be a simultaneous multi-element technique when a scanning laser is used. High energy lasers that emit multiple simultaneous wavelengths for a wide range of elements are still not available.

The all-solid-state OPO laser system proved to have excellent tuning characteristics in the UV region, including high output energies at all wavelengths, narrow spectral linewidths suitable for atomic spectrometry and high reliability in routine use. The use of an OPO laser together with graphite furnace LEAFS exploited the tunability of the laser and the excellent analytical characteristics of graphite furnace LEAFS. The sequential determination of cadmium, cobalt, lead, manganese and thallium in the river sediment sample clearly demonstrated the multi-element capability of the technique. Compared with the use of dye lasers, significant improvements in the throughput of the technique for real sample analyses were achieved. For a five-element task across an excitation wavelength range of nearly 80 nm, 12 h were sufficient for the entire analysis. This was a major improvement over the use of dye lasers, where a change in dye to achieve a change in wavelength to reach another element has never been done lightly. Indeed, wavelength changes have always been measured in hours, days and weeks, rather than the minutes achievable with an OPO laser system.

Many early OPO laser systems were unstable in energy as a function of time over the full wavelength range. We have previously described the excellent stability of the laser used in this work.15 The manufacturers of these types of laser are now marketing products that appear to show improvements in beam pointing stability and beam divergence of the YAG pump laser, such that the output energy stability can be maintained over an even greater range of flashlamp energies than we experienced. This will extend the lifetime of the flashlamps and give greater continuous periods of operation of the laser without significant losses in energy. Even with the technology used here, no significant optical realignment or flashlamp changes were necessary over a period of about 4 months.

Theoretically, there is no upper limit to the number of elements that can be analyzed with the LEAFS set-up described here. Excitation of over 65 elements can be covered with the current wavelength tuning range of the frequency doubled output. Further extension of the laser wavelength into the deep UV region below 220 nm will extend the coverage to over 15 more elements, although this latter region of the spectrum has not yet been fully tested for OPO laser systems.

The use of thermally assisted stepwise excitation for cadmium gave a detection limit that was no better than that with ETAAS. This was offset by the relatively simple instrumentation required, compared with two color excitation, which requires two lasers. Additionally, sequential multi-element analyses can be performed. Thallium in the sediment sample proved to be determinable by graphite furnace LEAFS, but it cannot be determined by atomic absorption in the same furnace. This was possible because the high sensitivity of LEAFS for thallium determination allows dilution that is sufficient to remove the matrix effects, an approach that contributes to the generally accepted high selectivity of this technique. This project has also shown that it is important to

| Table 3 | Analytical performance of sequential multi-element determination of cadmium, cobalt, lead, manganese and thallium in SRM 2704 river sediment sample |
|-------------------|----------------------------------|-------------------|-------------------|
| Element           | Certified/ mg g⁻¹ | Experimental¹/ mg g⁻¹ | Chemical modifier |
| Cd                | 3.45±0.22          | 3.54±0.18          | None              |
| Co                | 14.0±0.6           | 14.2±0.9           | Mg(NO₃)₂         |
| Mn                | 555±19             | 538±26             | Pd+Mg(NO₃)₂      |
| Mn                | 161±17             | 163±4.6            | (NH₄)H₂PO₄       |
| Tl                | 12.2±0.2           | 12.2±0.1           | None              |

¹ Mean ± s (n = 3).
test rigorously optical saturation of the analyte while it is in the real sample, rather than through aqueous standards. Otherwise, insufficient laser energy and possibly inaccurate analyses could result. Finally, this project demonstrated the utility of the long linear calibration range of LEAFS, as only one sample solution was used to determine all five elements that covered a concentration range of several orders of magnitude.

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