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Simultaneous determination of the Lanthanides by tungsten coil atomic emission spectrometry

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The fourteen Lanthanides are determined by tungsten coil atomic emission spectrometry. Twenty-five microlitre sample aliquots are placed directly on the coil. A simple constant current power source carefully dries the sample prior to analysis. During this dry step, the voltage is monitored to prevent over heating. This allows for shorter atomization programs, while improving sensitivity and coil lifetime. During the 5 s high temperature atomization step, the emission signals for as many as seven Lanthanides are determined simultaneously in the same 55 nm spectral window. The analytical figures of merit for all 14 natural Lanthanides are reported and compared with nitrous oxide flame atomic emission spectrometry. Tungsten coil atomic emission concentration detection limits are in the range 0.8 (Yb) to 600 (Pr) $\mu\text{g l}^{-1}$, and are lower than those for the flame in most cases. The absolute detection limits are near or below the ng level: significantly lower than the flame detection limits due to the smaller sample volume required. A three-fold improvement in detection limit may be realized by combining the signals for multiple emission lines for a single element. The method is applied to the determination of seven Lanthanides in a soil sample acquired from the National Institute of Standards and Technology. After a simple acid extraction, the measured values agree with the reported values with 95% confidence in all cases but one, Yb. Finally, a conditioning program for new tungsten coils enhances reproducibility and maximizes the emission signal.

Introduction

Conventional atomic spectrometry using flames, furnaces, or plasmas may be considered a mature technique, and most recent publications report routine developments rather than novel instrumental arrangements.¹ One exception to this generalization is the continued interest in metal speciation, and the search for a better understanding of the role of these species on biological organisms. Accordingly, *in situ*, low sample volume methods are of considerable interest.² Similarly, field methods continue to be developed.³ Flames, furnaces, and plasmas have limited portability due to their gas, power, and/or cooling requirements. Traditional atomic spectrometers also have considerable bulk. Laser-induced breakdown plasmas have met with some success in field applications, especially for the direct analysis of solids.⁴ In addition, open tungsten coil atomizers have been employed in portable battery-powered atomic absorption spectrometers.^{5,6} Atomic absorption devices, however, usually require a separate light source for each element to be determined, so portable applications are limited.

More recently, Rust *et al.* presented a new method with high potential for field applications.^{7,8} Tungsten coil atomic emission spectrometry (WCAES) employs a simple, inexpensive tungsten filament, as both atomizer and excitation source for trace metal determinations. The coil is extracted from a mass-produced, commercially available 150 W, 15 V light bulb. Power is supplied by a small, solid-state constant current source, and atomic emission lines are detected with a high resolution Czerny–Turner monochromator with a charge coupled device (CCD) detector. Since the method is based on atomic emission rather than absorption, simultaneous multi-element determination of eleven metals at the $\mu\text{g l}^{-1}$ level is reported. Clearly, a portable WCAES spectrometer could be devised by replacing the high resolution detection system with a much smaller one.

This work represents the first steps towards a portable WCAES device. A small, 156 mm focal length monochromator replaces the 1.33 m device reported previously.^{7,8} While the new device allows for the collection of more of the atomic emission signal, it also passes a higher proportion of the blackbody radiation emanating from the high temperature filament during the atomization step. This interference is reduced by employing a light blocking aperture. The smaller system also provides a broader wavelength window, so more metals may be determined simultaneously. In addition to the change in detection system, improvements in the atomizer are described. A conditioning program for new coils improves the filament-to-filament reproducibility of the atomizer. In

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addition, a new atomization heating program is employed. The program is composed of sequentially decreasing current steps, whose lengths are determined by monitoring the voltage across the coil as the sample dries. Improved reproducibility and increased tungsten coil lifetimes are observed.

The system is evaluated for the determination of the fourteen Lanthanide elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) in aqueous solution, and seven of the metals are determined in a commercially available soil sample following simple acid extraction. The Lanthanides are often present in fertilizers,⁹ or used as feeding markers in nutritional and agronomic studies.^{10,11} These elements have also been used as fingerprint markers for cement and concrete,¹² and in geological,¹³ or palaeontology studies.¹⁴ Clearly, a field instrument could find applications in these areas. While some of the Lanthanides have been determined by tungsten coil atomic absorption spectrometry (WCAAS),^{15,16} the more portable WCAES approach should be easier to deploy.

Experimental

Instrumental

A schematic diagram of the WCAES system is presented in Fig. 1. The atomizer is the tungsten coil filament produced for a 150 W, 15 V commercially available slide projector light bulb (Osram Xenophot 64633 HXL, Pullach, Germany). The fused silica bulb envelope was removed leaving the filament and bulb base intact. A microscope (Model Z45L, Leica Inc., Buffalo, NY, USA) was used to observe the surfaces of both new and used tungsten coils. The bulb base was mounted in a standard ceramic two-pronged power socket. The bulbs are mass produced to strict optical specifications, so the positioning of the filament from bulb to bulb was

highly reproducible. Power was provided by a programmable, constant-current, solid state DC power source (BatMod, Vicor, Andover, MA, USA). The filament was housed inside a glass atomization cell with fused silica windows, and a 1.1 l min⁻¹ purge gas composed of 10% H₂-Ar, served to prevent coil oxidation and to cool the atomizer. The atomization cell and tungsten coil atomizer have been described in detail elsewhere.^{17,18} The atomic emission arising from the atomization cloud at high temperature was collected with a 25 mm diameter 75 mm focal length fused silica lens. The lens formed a 1 : 1 image of the cloud on a light blocking baffle containing an adjustable aperture set to 2 mm (Fig. 1 inset). The aperture was positioned to block the blackbody radiation emitted from the coil surface, with the image of the coil approximately 1 mm away from the opening. The radiation passing through the aperture was collected with a second identical fused silica lens, and imaged (1 : 1) onto the entrance slit of a crossed Czerny-Turner monochromator (MonSpec 18, Scientific Measurement Systems Inc., Grand Junction, CO, USA). The monochromator was equipped with a 2400 gr mm⁻¹ grating (110 × 110 mm), resulting in a reciprocal linear dispersion of 2 nm mm⁻¹ at 400 nm. Based on a slit width approximately the size of a single detector pixel (20 μm), the theoretical spectral bandpass of the system was 0.04 nm. In practice, the observed atomic emission lines had full width at half maximum (FWHM) of approximately 2 detector pixels, so the practical system resolution was 0.08 nm (see the Yb peak at 398.8 nm in Fig. 2). The monochromator had a 156 mm focal length and the collection optics were *f*/3.8. The detector was a thermoelectrically-cooled charge coupled device (CCD, Spec-10, Princeton Instruments, Roper Scientific, Trenton, NJ, USA). The CCD detector consisted of a two-dimensional array of 1340 × 100 pixels. Each pixel was 20 × 20 μm in size, so the image area on the CCD camera was 26.8 × 2 mm. The system provided a spectral window of approximately 55 nm,

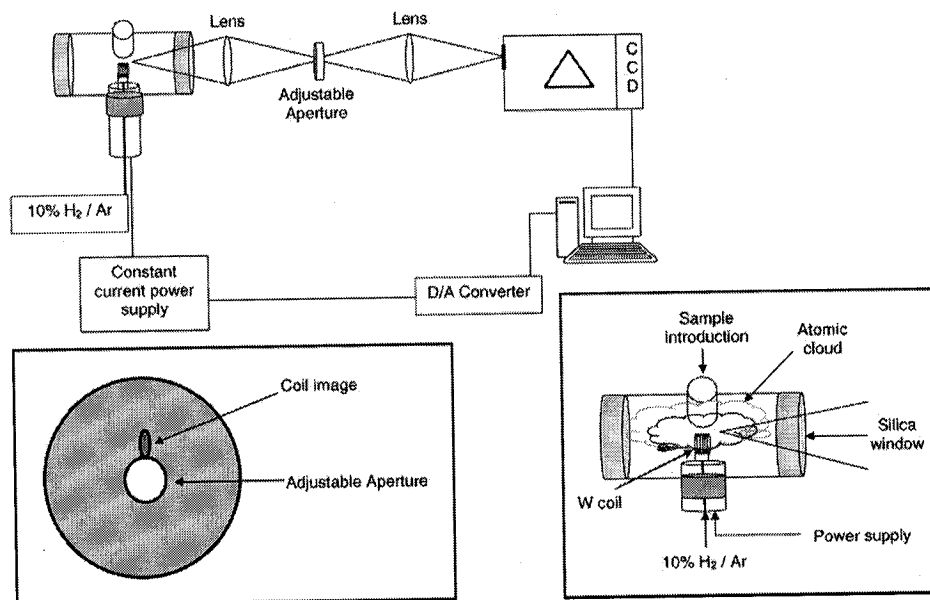


Fig. 1 Schematic diagram of WCAES instrument. Inserts show alternate views of the atomization cell and the coil image on the adjustable aperture.

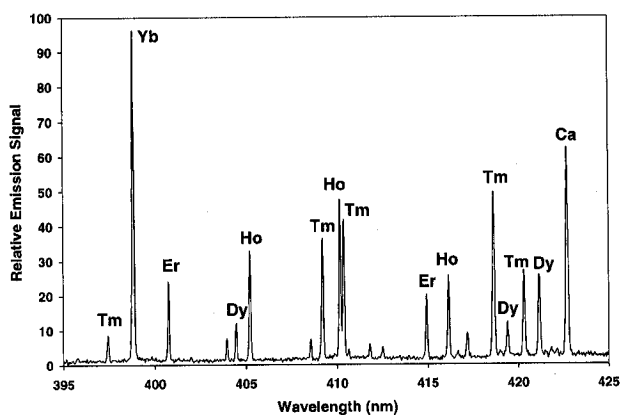


Fig. 2 Simultaneous multi-element WCAES determination of Yb (1 mg l^{-1}), Dy and Tm (2 mg l^{-1}), Ho and Er (5 mg l^{-1}).

depending upon the selection of the central wavelength. A $25 \mu\text{m}$ fixed entrance slit width was employed throughout.

The CCD detector had user selectable integration times as low as 1 ms. For the WCAES system, the greatest signal to noise ratio (S/N) for the Lanthanides was observed with an integration time of 500 ms. Ten successive spectra therefore covered the entire 5 s atomization time. All elements reached maximum emission levels during the third spectrum, and all signals returned to zero by the seventh spectrum. Therefore, the summation of six successive spectra resulted in a total integration time of 3 s, and ensured that all emission signals were captured.

Reference solutions and sample preparation

All reference solutions were prepared from dilution of single element stock solutions (1000 mg l^{-1} , SPEX CertPrep, Metuchen, NJ, USA) with 2% v/v HNO_3 . The blank solution (2% v/v HNO_3) was prepared from dilution of concentrated (14 mol l^{-1}) trace metal grade HNO_3 (Fisher Scientific, Pittsburgh, PA, USA) with distilled-deionized water (Milli-Q, Millipore Corp., Bedford, MA, USA). A soil sample from the National Institute of Standards and Technology (Montana soil, SRM # 2711) was used to check the method accuracy.

The soil sample was submitted to extraction with concentrated HNO_3 (Fisher). Approximately 1 g of soil was weighed accurately into a plastic extraction container, and a 1 ml aliquot of acid was added. The mixture was left to react for 1 min, then 1 ml of distilled-deionized water was added. The plastic container was placed in an aluminium hot block at 100°C and the extraction was carried out for 1 h. To prevent the sample from drying, 3 aliquots (1 ml each) of distilled-deionized water were added to the sample at different intervals during the extraction procedure.

The extracted sample was allowed to cool for 20 min and submitted to filtration with coarse filter paper (Fisherbrand). The filtrate was diluted to a total of 50 ml with distilled-deionized water. This procedure was carried out in triplicate.

Safety considerations

Material safety data sheets were consulted before using each chemical reagent. Essential safety precautions were taken in

each step of the analysis. Aqueous waste was stored in glass containers prior to disposal.

Atomization programs

A $25 \mu\text{l}$ volume was adopted as solution aliquot for all WCAES measurements. A micropipette (Eppendorf 20–200 μl , Brinkmann Instruments Inc., Westbury, NY, USA) was used to place the aliquot directly onto the tungsten coil. A 1.1 l min^{-1} purge gas flow rate was used to protect the coil during the atomization step. Also acting as the atomizer coolant, the 10% H_2 -Ar purge gas provided a reducing atmosphere for generation of the atomic cloud and protection (from oxidation) of the tungsten coil. The atomization program consisted of seven heating steps (Table 1). The two first steps accounted for gradual solvent volatilization. The coil reached dryness at the end of step 2, as evidenced by an increase in the applied voltage necessary to maintain a constant current during the last few seconds of this stage. The dry coil reached a higher temperature than the wet coil for a given current. Therefore, the ashing stage of the program, steps 3 and 4, employed lower currents. Using progressively lower current prevented the coil from glowing red prior to atomization, and thus reduced the potential to lose analyte. A cooling period (step 5) ensured a reproducible high temperature atomization step, since the beginning temperature was always the same (near room temperature). Finally, the high current (10 A) atomization step generated the atomic cloud and provided energy sufficient to excite atomic emission. The detector was triggered at the beginning of the atomization step (step 6) and six successive spectra were collected automatically within the 55 nm spectral window. The final cooling step readied the coil for the deposition of the next sample aliquot.

New tungsten coils were subjected to two different heating programs in order to improve the analytical signal. The conditioning program (Table 1) served to “break in” the new coil, presumably by etching the smooth surface of the tungsten wire. This program was employed outside of the atomization chamber in air, so coil oxidation was promoted.

Table 1 Tungsten coil heating programs

Step	Sample atomization ^a		New coil conditioning ^b		New coil cleaning ^c	
	Current/A	Time/s	Current/A	Time/s	Current/A	Time/s
1	2.5	45	3	10	3.5	250
2	2	35	5	5	4.5	250
3	1.7	15	0	10	5.5	300
4	1.5	15	5	5	7.0	150
5	0	10	0	20	10	35
6	10	5 ^e			0	40
7	0	25				

^a Atomization program for a $25 \mu\text{l}$ aliquot of an aqueous solution under a 1.1 l min^{-1} flow rate of 10% H_2 in Ar. ^b Conditioning program for a new dry tungsten coil in open air. ^c Cleaning program for a newly conditioned coil under a flow rate of 1.4 l min^{-1} of 10% H_2 in Ar (for oxide removal). ^d The approximate temperature (T) in Kelvin of the dry coil surface may be estimated from the current (I) in amps: $T \approx 309 I + 325$.¹⁷ While the current associated with each step is fixed, the actual temperature will depend upon the age of the coil, and the presence of liquid or salt on the coil surface. ^e Tungsten coil atomic emission was collected during this step.

The coil was then placed in the atomization chamber with a reducing atmosphere for a cleaning program (Table 1), with a 1.4 l min^{-1} purge gas flow rate (10% H_2 -Ar). This program served to remove the oxidation products adhering to the coil after the air heating.

Results and discussion

Background emission signal

WCAES measurements are susceptible to interference from the continuum background radiation emanating from the coil surface, which is acting as a blackbody emitter.⁸ Care must be taken to isolate this bright background signal from the emission arising from the gaseous analyte atoms near the coil surface. To minimize this problem, a radiation-blocking aperture was placed midway between the focusing lenses (Fig. 1). After optimizing the coil position, a significant reduction in the background signal permitted the collection of relatively intense analytical signals. The signal to background ratio (S/B) was maximized with a 2 mm aperture and a viewing height 1 mm above the upper surface of the coil. Also, as described before,⁸ S/B was higher when the image of the coil was positioned approximately 1 mm to the side of the monochromator entrance slit, so the final viewing position was 1 mm above and 1 mm to the right of the upper surface of the coil.

Heating program optimization

As described above, the tungsten coil is heated by a constant current power supply. The sample aliquot wets the coil, so during the dry step the resistance is lower than during the ashing and atomization steps. A given drying current will begin to evaporate the liquid sample, and as the amount of liquid on the coil is reduced, the resistance rises, producing an increase in the temperature for the resistively heated filament. Even at a relatively low drying current, if the coil is allowed to heat to dryness, the temperature will begin to rise rapidly. Without careful control of the end time for the drying step, the coil may rise in temperature enough to cause significant loss of analyte atoms. Coil temperatures briefly as high as $700 \text{ }^\circ\text{C}$ have been observed in this step, resulting in the poor recovery of relatively volatile elements.¹⁹ Furthermore, small changes in analytical sample volume may cause the point of coil dryness to occur at slightly different times from run to run, so a fixed drying time length may result in different ending temperatures and a varying degree of sample loss. These sources of error, while potentially small, will clearly affect analytical precision.

To counteract these effects, the potential across the coil was monitored during all heating steps. As the coil dried, the resistance rose and higher voltage was necessary to maintain the constant current. Thus, the degree of dryness of the sample was monitored by observing the potential across the coil. The rate of increase in potential with time was low while liquid remained on the coil, and then abruptly increased upon total dryness. This point of abrupt potential change was used to signal the end of the dry step, rather than a fixed time. In a 60 s dry period designed to completely dry the coil in a single step for example, repetitive runs typically reached the potential change in the range $58 \pm 2 \text{ s}$. Ending the dry step at the

potential change, rather than the fixed time, took the guess work out of the equation.

To further improve precision, the drying program was divided into multiple steps, having incrementally smaller constant currents (Table 1). This insured that the completely dry coil state was reached gradually, reducing the risk of sample loss and splattering. In addition, the probability of beginning the ashing or atomization stages with a wet coil were greatly diminished. Sending the coil to high current, even for an instant, while liquid water was still present, resulted in severe oxidation and coil damage. Previously published works typically employed multi-step programs with gradually increasing currents,^{7,8,18,20} but the optimized program presented here produced higher analytical signals, longer coil lifetimes (~ 200 runs), and lower background signals, when compared to a conventional program.

Coil surface and sensitivity

Using a new, untreated coil, the atomic emission signal observed for a test solution increased slowly during the first few dozen atomization programs, before leveling off at a maximum stable level after approximately 100 firings. The analytical signal using a fresh coil was typically 50% lower, on average, than the signal observed for a seasoned coil. Microscopic comparisons of new and used coils in the past have indicated that the surface of a new filament was smooth when compared to a seasoned one that was pitted.²¹ The tungsten coils in the current work were also examined with a microscope. As expected, new coils were clean and smooth, while seasoned ones were rougher on the surface, and also contained tiny crystals which resembled tungstate (though no further analysis was employed to verify the composition). One possible explanation for the crystalline material may be found in the literature.²² Non-stoichiometric compounds with the general formula M_xWO_3 were prepared at high temperature under a H_2 atmosphere during the production of tungsten bronzes. These crystals were characterized as metal-like and yellow in color, with high conductivity. While detailed studies on the effects of chemical modifiers have been reported for tungsten coil atomic absorption spectrometry,^{23,24} a reasonable first approximation may be that the increased surface area resulting from these crystals may allow for better adhesion of analyte atoms during the heating program. While the investigation of the exact role of the surface effects on emission signal is beyond the scope of this manuscript, a conditioning program for new coils was developed. Initially, a current was applied to a new dry coil under exposure to air. During this brief program (Table 1) the outer surface of the coil was oxidized. Then a second program was applied under a 10% H_2 -Ar atmosphere (Table 1) to remove the oxidation products, resulting in a clean, seasoned coil. Reproducible, maximized signals were then obtained throughout the lifetime of the coil.

Multi-element WCAES spectra

The 55 nm spectral window provided by the detection system facilitated the simultaneous determination of up to 7 Lanthanide elements by WCAES. Fig. 2 and 3 present portions of two

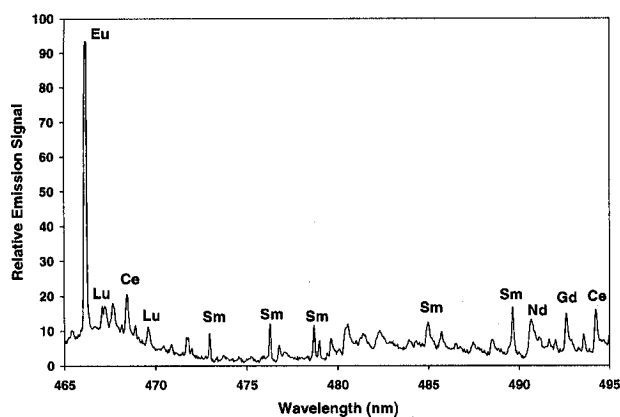


Fig. 3 Simultaneous multi-element WCAES determination of Sm and Eu (1 mg l^{-1}), Lu (5 mg l^{-1}), Ce (10 mg l^{-1}), Nd and Gd (20 mg l^{-1}).

different spectral windows. Within the 30 nm region centered around 410 nm (Fig. 2), sharp atomic emission lines for five different Lanthanide elements were observed: Tm (2 mg l^{-1}), Yb (1 mg l^{-1}), Er (5 mg l^{-1}), Dy (2 mg l^{-1}), and Ho (5 mg l^{-1}). In addition, the Ca line at 422.7 nm was visible. The Ca was always present as a low level contaminant in the blank ($\sim 1 \text{ mg l}^{-1}$). Even though the WCAES spectra were rich, little overlap occurred.

An example of the resolving power of the detection system is demonstrated by the near baseline resolution of the Ho and Tm peaks at 410.38 and 410.58 nm, respectively. The full width at half maximum for the La peak at 398.80 nm is 0.08 nm. Since the resolution is limited by the spectrometer, all of the peaks in Fig. 2 have nearly the same 0.08 nm FWHM (2 pixel widths). Fig. 3 shows a slightly more complicated region of the spectrum. Signals due to six Lanthanides are present: Eu (1 mg l^{-1}), Lu (5 mg l^{-1}), Ce (10 mg l^{-1}), Sm (1 mg l^{-1}), Nd (20 mg l^{-1}), and Gd (20 mg l^{-1}). The spectrum

also seems to contain an underlying molecular band in the region 465 to 470 nm.

Analytical figures of merit

Analytical figures of merit were determined with aqueous solutions of the Lanthanides (Table 2). Limits of detection (LOD) were calculated as 3 times the standard deviation in the blank signal ($n = 20$), divided by the slope of the calibration curve. The observed LODs range from $0.8 \mu\text{g l}^{-1}$ (Yb) to $600 \mu\text{g l}^{-1}$ (Nd and Pr). These values compare quite favorably to traditional flame emission detection limits using N_2O as the oxidant.²⁵ In fact, these data suggest that nitrous oxide flame emission detection limits could be used to predict WCAES LODs to within approximately an order of magnitude. The WCAES LOD is lower than the flame LOD in all but 3 cases: Er (LODs are equal), Eu (flame LOD lower by a factor of 2), and Pr (flame LOD lower by a factor of 9). In addition, the WCAES system simultaneously monitors a 55 nm spectral window, so multiple lines for a single element falling in the window may be used for calibration purposes.⁸ Summing the signals at multiple wavelengths lowers the detection limit in most cases, by roughly a factor of 3. Finally, the sample volume for WCAES is quite small ($25 \mu\text{l}$) compared to the amounts required for traditional flame analysis (approximately $500 \mu\text{l}$), so the absolute detection limits ($0.02\text{--}15 \text{ ng}$) compare even more favorably. Ref. 25 reports flame LODs for 68 elements, suggesting that WCAES might find wide applications outside of the Lanthanides. Other, more recent publications, report similar detection limits in the nitrous oxide acetylene flame.²⁶

The precision of the method was calculated as the relative standard deviation (RSD, $n = 10$) for each element (Table 2). Aqueous solutions providing WCAES emission signals in the mid-range of the calibration curve were used for these measurements: $25 \mu\text{g l}^{-1}$ (Eu, Yb), $200 \mu\text{g l}^{-1}$ (Tm), $500 \mu\text{g l}^{-1}$ (Sm, Ho, Lu), 1 mg l^{-1} (Dy, Er), 5 mg l^{-1} (Ce, Pr, Gd, Tb), and

Table 2 WCAES analytical figures of merit

Emission wavelengths/nm	Limit of detection/ $\mu\text{g l}^{-1}$					Montana soil content/ $\mu\text{g g}^{-1}$	
	WCAES ^a	WCAES ^b	Flame ^c	LDR ^d	Precision ^e	Reported	Found
Ce 465.1 478.2 479.2 480.2 488.0 494.3 ^g 569.9 ^h	400	100	10 000	2.0	3.9		
Dy 404.6 ^h 418.7 419.5 421.2 ^g	30	10	50	2.3	6.7	5.6	5.6 ± 0.7
Er 386.3 397.4 400.8 ^g 408.8 415.1	70	30	70	1.9	8.4		
Eu 459.4 ^g 462.7 466.2	1	0.7	0.5	2.2	6.5	1.1	0.92 ± 0.12
Gd 440.1 ^h 461.6 ^g 463.4 490.0 491.9	500	200	5000	2.0	4.8		
Ho 404.1 405.4 410.4 ^g 416.3 417.3	30	10	100	2.3	2.4	1.0	1.0 ± 0.2
La 533.2 550.1 ^h 559.6 560.2 ^g 564.8 565.5	80	30	6000	1.8	8.2	40	51 ± 15
Lu 451.9 ^g 453.1 454.5 455.9	80	40	1000	1.7	4.4		
Nd 469.6 489.7 490.2 492.5 ^g 494.5 495.5	600	200	700	2.0	4.7	31	55 ± 17
Pr 495.1 ^h 602.6 ^g	600	NA ⁱ	70	1.5	4.9		
Sm 472.8 476.0 ^h 478.3 484.2 488.4 ^g 491.0 491.9	30	7	200	2.2	5.7	5.9	6.8 ± 0.4
Tb 432.7 ^h 534.1 ^g 534.8 535.7 537.5 542.8 546.0	300	90	500	2.3	2.4		
Tm 371.8 ^h 409.4 410.6 418.8 ^g 420.4	10	5	80	2.0	3.9		
Yb 398.8 ^g	0.8	NA ⁱ	6	1.8	6.9	2.7	1.0 ± 0.1

^a Detection limit determined using the signal at the primary wavelength only. ^b Detection limit determined using the combined signals at all listed wavelengths within the 55 nm window. ^c Flame atomic emission detection limits reported for a nitrous oxide acetylene flame.²⁵ ^d Linear dynamic range in decades, beginning at the detection limit. ^e Precision (repeatability) reported as % relative standard deviation for an aqueous solution in the midrange of the calibration curve ($n = 10$). ^f NIST Standard Reference Material 2711. NIST does not certify the reported Lanthanide values in SRM 2711. Found values are the mean ± 1 standard deviation ($n = 3$). ^g Primary emission wavelength for WCAES. ^h Primary emission wavelength for flame emission (if different from WCAES). ⁱ Not available. Only one emission line in available spectral window.

10 mg l⁻¹ (La, Nd). The RSD was always below 10% and often below 5%.

The performance of the WCAES method was evaluated using a moderately complex sample. Seven Lanthanides were determined in a commercially available soil sample (Montana soil, NIST SRM #2711). The sample was prepared with a simple nitric acid extraction technique that could be employed in the field. Table 2 presents the recovery values observed for each of the elements present in the sample above the WCAES detection limit. The Lanthanides were reported by NIST to be present in the solid sample at concentrations between 1 and 40 µg g⁻¹, however, NIST does not certify these reported values. The Lanthanides were determined to have concentrations in the range 0.9 to 55 µg g⁻¹ in the sample. While more rigorous sample preparation techniques like microwave digestion might improve some of the individual recovery values, clearly all of these elements could be determined at concentrations within a few µg g⁻¹ of their actual values using a field-friendly sample preparation method. The statistical *t*-test showed that the found value agreed with the NIST reported value with 95% confidence in all cases, except for Yb. The error in the Yb determination could be due to incomplete extraction, or to inaccuracy due to the relatively low amount of the metal present in the sample.

Another potential source of inaccuracy in the determination of Lanthanides by WCAES may arise from interference effects caused by concomitant elements in the sample matrix. Indeed, interference effects have been documented for atomic absorption spectrometry using metal atomizers, such as the wire loop,²⁷ and the tungsten coil.^{28,29} To date, no interference studies have been published for WCAES methods, and such a study is beyond the scope of this manuscript.

Conclusions

WCAES is a potentially portable technique for the simultaneous determination of the Lanthanides. Concentration detection limits are similar to those reported for nitrous oxide flame atomic emission spectrometry (in the µg l⁻¹ range), and WCAES LODs may be predicted using previously reported flame emission data. Absolute detection limits are at the low ng level and below, due to the low volume requirement of the WCAES technique (25 µl). Detection limits may be further improved (by approximately a factor of 3) if multiple emission lines for a single element are monitored simultaneously. The WCAES instrument is very simple, requiring only a 150 W constant current power supply. This power could be provided by an automobile battery, rendering the technique portable. In addition, a simple extraction technique for the analysis of a soil sample provides good results for seven Lanthanides present at the µg g⁻¹ level in the solid. Finally, the multi-wavelength capability of the system provides for the determination of single elements at more than one emission line. This characteristic improves the confidence level of the analysis and potentially increases the linear dynamic range of the measurement. All 14 Lanthanides may be determined by WCAES.

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