

# Thermal lens spectroscopy of plutonium using a laser diode and fiber optics

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## Abstract

A thermal lens spectrometer for the analysis of Pu(VI) in liquids is described. The use of fiber optics and a pulsed laser diode excitation source results in a compact system which can be adapted to measurements in process streams or in the field. The detection limit is  $1 \times 10^{-6}$  M Pu(VI) at 831 nm. The performance of the laser-diode-based spectrometer for Pu(VI) detection is comparable with that of dye-laser-based photothermal or photoacoustic spectroscopy.

## 1. Introduction

Optical absorption spectra of actinides in solution can be used to quantify the element, oxidation state and state of complexation [1]. The characteristic absorption bands have peak molar absorptance in the range  $8\text{--}550 \text{ M}^{-1} \text{ cm}^{-1}$ , and the actinide ions can be detected with conventional spectrophotometry at concentrations greater than  $10^{-5}\text{--}10^{-4}$  M. In solutions with neutral or basic pH values, however, the solubilities are usually less than  $10^{-5}$  M, so more sensitive techniques are required.

Thermal lens spectroscopy (TLS) is a high-sensitivity optical absorption method capable of detecting actinides at submicromolar concentrations in aqueous solution [2–4]. In dual-beam TLS, heat is deposited in the sample medium by absorption of an excitation laser beam, and the amount of heat deposited is measured through the defocusing of a second, probe laser beam [5]. Usually, the probe beam is provided by a low power HeNe laser and the excitation beam is provided by a high power dye laser system. A spectral scan is taken by tuning the dye laser output wavelength (most laser dyes have a tuning range of 30–60 nm).

The ability to perform photothermal spectroscopy of actinides in process streams or in the field is limited by the large size of the dye laser system. A laser diode system is more compact and portable, and suitable output power levels are now available in the near-IR. The use of fiber optics allows greater flexibility in the location of the source and detector units. Fiber optics

can be used to make the spectrometer more compact [6] or to make remote measurements, such as in a glove-box [7]. In this work, we report on the development of a laser-diode-based TLS system for the detection of Pu(VI) using the absorption band at 831 nm.

## 2. Experimental methods

A schematic block diagram of the TLS system is shown in Fig. 1. The excitation beam was provided by a laser diode (Spectra Diode Labs SDL-2462) coupled to an optical fiber (Fiberguide Industries Anhydroguide; core diameter, 200  $\mu\text{m}$ ). The laser diode emission spectrum is a set of 10–20 longitudinal mode lines in a spectral band of about 2 nm. The spectral resolution is sufficient for measurements of actinides in solution, which have absorption bandwidths of several nanometers. The center wavelength of the emission band was temperature tuned using the thermistor and thermoelectric cooler built into the laser diode package. The emission spectrum is a function of both the temperature indicated and the operating current, so the

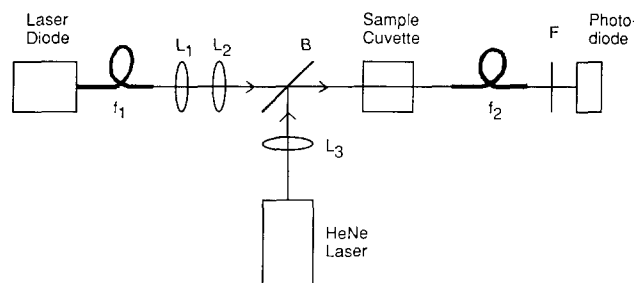


Fig. 1. Schematic diagram of set-up for laser-diode-based TLS.

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laser diode output was initially calibrated using a spectrometer (SPEX 1404) and a photomultiplier tube.

The laser diode was operated in the pulsed mode with square current pulses of width 13 ms at a repetition rate of 20 Hz. The IR radiation exiting the fiber was focused in the center of a quartz cuvette of pathlength 10 mm, using lenses L1 and L2 (focal lengths of 50 mm and 125 mm). The excitation energy delivered to the sample was about 1 mJ per pulse.

The excitation beam and the HeNe laser probe beam were made collinear with a pellicle beam-splitter B. The probe beam was brought to a focus at 80 mm past the center of the cuvette, using lens L3 (of focal length 150 mm). Thermal defocusing of the probe beam was monitored with a photodiode (UDT PIN 10DP) behind an aperture. Good results were obtained with a pinhole of diameter 350  $\mu\text{m}$  or a second optical fiber (core diameter 400  $\mu\text{m}$ ) as the aperture. An interference filter (Corion D1-633-F) was placed between the aperture and the photodiode to block excitation radiation. The photodiode was connected to the current input of a lock-in amplifier (Stanford Research Systems 510). The reference waveform was supplied by the monitor photodiode built into the laser diode package.

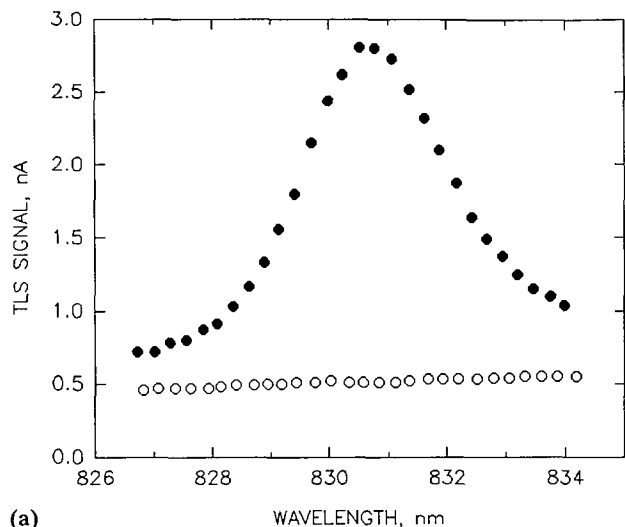
A stock solution of  $3 \times 10^{-4}$  M  $^{242}\text{Pu(VI)}$  was prepared by fuming in  $\text{HClO}_4$  and diluting to volume with 1 M  $\text{HNO}_3$ . The absorbance of the stock solution was measured with a spectrophotometer (IBM 9420) over the wavelength range 350–900 nm to confirm that the Pu was in the +6 oxidation state. Sample solutions were prepared by volumetric dilution with 1 M  $\text{HNO}_3$ .

### 3. Results and discussion

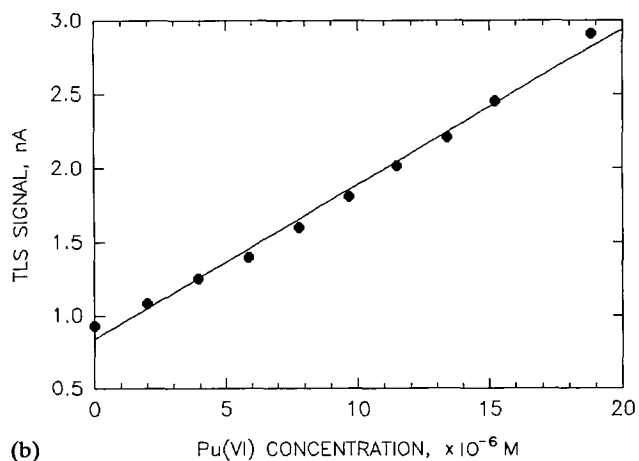
The excitation beam size has a strong effect on the TLS signal and, when using fiber optics to transfer the excitation beam, it is important to focus to a small spot size [8]. The excitation beam diameter was 300  $\mu\text{m}$  at the focus, as measured with a pinhole of diameter 25  $\mu\text{m}$  and photodiode mounted on a translation stage.

The TLS spectra of a water sample and a  $2 \times 10^{-5}$  M Pu(VI) sample are shown in Fig. 2(a). In this wavelength region, the absorption coefficient of water increases with the wavelength, while the laser diode output power decreases with the wavelength. These two effects tend to cancel one another, resulting in a nearly flat water background spectrum. The Pu(VI) absorption peak is clearly resolved in Fig. 2(a).

The peak TLS signal is a linear function of the Pu(VI) concentration (Fig. 2(b)). The detectability of actinides in solution by photothermal spectroscopy generally depends on both the molar absorptivity of the analyzed substance and the absorption coefficient of the solvent at the measurement wavelength. The Pu(VI) band at



(a)



(b)

Fig. 2. (a) Thermal lens signal for  $2 \times 10^{-5}$  M Pu(VI) solution (full symbols) and deionized water (open symbols). (b) Thermal lens signal at excitation wavelength of 831 nm.

831 nm has a relatively large peak molar absorptance ( $550 \text{ M}^{-1} \text{ cm}^{-1}$ ) but background absorption by the water is also relatively large at 831 nm. The background has not been subtracted in Fig. 2. The detection limit, defined as the concentration of the analyzed substance which gives a signal-to-noise ratio of 3, is  $1 \times 10^{-6}$  M Pu(VI). The performance of the laser-diode-based spectrometer for Pu(VI) detection is comparable with that of dye-laser-based TLS [3] and photoacoustic spectroscopy [9], which have achieved detection limits near  $10^{-7}$  M Pu(VI).

### Acknowledgments

This work was supported by Laboratory Directed Research and Development Funds at the Lawrence Livermore National Laboratory. We thank Nancy Hanink for assistance in preparing and assaying the Pu stock solution.

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