

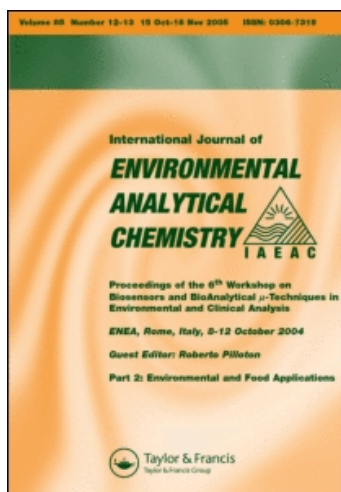
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Low-Cost Colorimetric Measurement of Phosphate Trace Levels in Water and in Soil Solutions by the Collinear Photothermal Beam Deflection Method

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LOW-COST COLORIMETRIC MEASUREMENT OF PHOSPHATE TRACE LEVELS IN WATER AND IN SOIL SOLUTIONS BY THE COLLINEAR PHOTOTHERMAL BEAM DEFLECTION METHOD

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The collinear photothermal beam deflection technique with a c.w. AlGaAs semi-conductor diode laser (790 nm) and He-Ne laser (630 nm) used as the pump and probe beam, respectively, has been combined with the molybdenum blue colorimetry to measure the level of orthophosphate in water and in soil solutions. A detection sensitivity of 0.1 mmol/m^3 of PO_4^{3-} has been achieved with the present set-up.

KEY WORDS: Photothermal beam deflection, orthophosphate, semiconductor diode, molybdenum blue colorimetry.

INTRODUCTION

Heavy use of phosphate in agriculture, industry and households for fertilization and cleaning purposes leads to a steadily increasing concentration in surface and ground waters, since the phosphate is mostly either washed off the fields or ends up in waste water. Phosphates are also a main nutrient of algae and one cause of the strong eutrophication that threatens many lakes and streams. The increasing level of phosphate concentration in ground water is also of great public concern because it endangers the quality of the drinking water supply.

An inexpensive technique capable of measuring minor amounts of phosphate in various types of water with a sensitivity sufficient to enable precise determination of the concentration gradient would be very valuable both for monitoring purposes and for modelling studies (for example, the propagation and deposition of phosphate in ground and surface waters).¹ A simple instrument based on this principle would enable farmers to fertilize the soil in a more controlled manner, which in turn would help in lowering the pollution load. A less sensitive (ca. 500 mmol/m³), low-cost device would also be helpful in optimizing the yield of several greenhouse cultivars and in reducing the run-off during the so-called closed-loop soilless (hydroponic or substrate) growth. For most applications listed above, detection sensitivity better than 10 mmol/m³ of orthophosphate is required.²

Present techniques and instrumentation for routine analysis of phosphate in water are based on either a specific colorimetric reaction, on ion-selective electrodes or on the use of a characteristic chemo- or biosensor. The well-established and widely used molybdenum blue colorimetry³ technique, the working of which relies on a colour reaction of the orthophosphate and the measurement of optical absorption using a standard spectrophotometer, is restricted to concentrations higher than 10 mmol/m³. This is primarily due to the attenuation by light scattering in the aqueous sample, which limits the precision when measuring low absorptions. Additionally, there are also technical problems associated with the reliable measurement of small intensity differences between two strong light sources. On the other hand, the detection limits of phosphate-selective electrodes and other sensors are much above 10 mmol/m³ at present.⁴ Infrared absorption spectroscopy cannot be used as an alternative for low level detection of phosphate, because broad and strong vibronic absorption bands of phosphate in the infrared (centred near 1030 cm⁻¹) overlap with the absorption bands of intrinsically strongly absorbing water.⁵

In this paper, we report on a simple, laser-based, technique, the sensitivity of which was found high enough to allow the measurement of the concentration of orthophosphate in water and in soil solutions down to a level of 0.1 mmol/m³. Well-proven molybdenum blue colorimetry was combined with laser photothermal spectroscopy, which is an ideal technique for the measurement of ultralow absorptions.

Photothermal detection techniques developed in recent years have evolved into versatile tools capable of ultrasensitive detection,^{6,7} in particular when combined with laser sources. Various photothermal schemes utilize the effects of the heat released in a sample upon the absorption of radiation. The best known is photoacoustics, where the acoustic wave generated by thermal expansion is being sensed. We recently explored the potentiality of piezophotoacoustic detection for orthophosphate colorimetry⁸ and were able to improve the sensitivity to 1 mmol/m³. Other photothermal techniques employ the photothermal effect on the optical index of refraction.^{9,10} It proved experimentally advantageous to measure the refractive index gradient in temperature fields rather than the index change itself.¹¹ For the detection of low phosphate concentrations in water we found the technical variant called "collinear photothermal beam deflection spectroscopy"

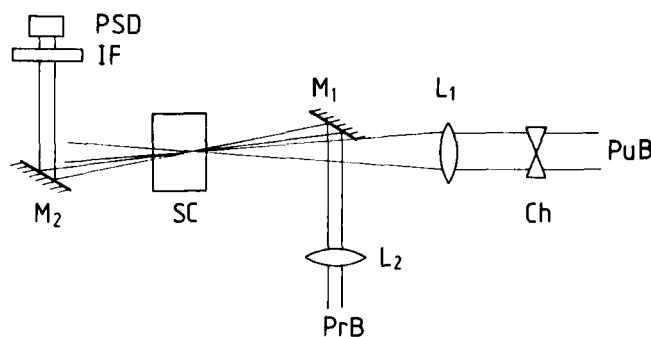


Figure 1 Experimental set-up used in this study. L_1, L_2 , focusing lenses; M_1, M_2 , plane mirrors; IF, interference filter; PSD, position sensitive detector; PrB, probe laser beam; PuB, pump laser beam; Ch, chopper; SC, sample cuvette.

(BDS) particularly suitable.¹² Before giving experimental details a brief description of BDS is given. Two different lasers are used; one provides the radiation that is absorbed (pump laser), and the other (probe laser) detects the refractive index gradient. The pump laser optically heats the excited region and changes the index of refraction, the gradient of which causes a deflection (angle which is proportional to the optical absorption) of the probe beam. We note that thermal lensing spectrometry of phosphate using sophisticated equipment (Ar ion laser pumped dye laser, digital signal averager) has been reported previously.^{13,14}

EXPERIMENTAL

Readily available continuous-wave, low-power lasers suffice for the detection sensitivity needed. A visible Uniphase 1305, HeNe laser (632 nm, 1 mW) was used for probing (PrB) and a near-infrared semiconductor laser (780 nm, 4 mW, Philips CQL20 AlGaAs) for pumping (PuB) as shown in Figure 1. The beams of these lasers have fairly well defined Gaussian profiles, the diameter of which is fitted with the appropriate lenses L_1 and L_2 . The probe beam is focussed into the sample to a tighter focus ($1/e$ diameter, ca. $50 \mu\text{m}$) than the pump beam ($1/e$ diameter, ca. $250 \mu\text{m}$).

The beams are aligned (by means of a plane mirror M_1) to cross in the middle of the sample at the smallest possible angle (about 2°) with the given optics in order to maximize the spatial overlap. The probe beam intersects the optically pumped region at the maximum of the refractive index gradient and is deflected. The vertical displacement between the pump and the probe beam was aligned by adjusting the position of the pump lens with micropositioners. Upon reflection on a plane mirror M_2 the amplitude of deflection was measured by a Centronix QD-50 quadrant position sensor PSD. The pump beam is mechanically chopped (Ch) at 14 Hz and the modulated deflection signal fed to a lock-in amplifier (Ithaco 3961A) to filter the proper ac component. A 632-nm narrow-band interference filter (IF) was used to screen the detector from scattered pump light. The set-up was

assembled from laboratory standard optical mounts on a home-made vibration insulated optical table.

For trace colorimetry the sample is optically thin, i.e., $\alpha l < 0.3$ where α is the absorption coefficient and l the sample thickness. For such a case the deflection angle, ϕ , is given by¹⁰

$$\phi = (L/n)(dn/dT) \text{ grad}(T) \quad (1)$$

where L is the path length, n is the index of refraction and T is the temperature. For a Gaussian pump beam profile the temperature gradient, $\text{grad}(T)$, i.e. the deflection signal, is proportional to the absorption provided the dc temperature, the pump laser power and the modulation frequency are constant. Note that a zero signal is observed with no absorption and that attenuation by light scattering does not interfere.

The standard procedure for the molybdenum blue reaction was used. The orthophosphate, PO_4^{3-} , present in the sample is reacted at pH 4 (buffered solution) with ammonium molybdate (Merck P.A., Darmstadt, F.R.G.) to phosphate-molybdic acid, which is subsequently reduced by ascorbic acid (Merck P.A.) and antimony (Merck P.A.) to form the blue coloured phosphomolybdenum complex. The absorption of this complex around the two bands between 700 nm and 900 nm is a measure for the amount of phosphate. This colorimetry is well proven and possible interferences of other ions and pollutants have been documented.¹⁵

Both the water itself¹⁶ and the dissolved reagents have small absorptions at the pump wavelength of 790 nm. Since these absorptions also contribute to the measured signal it is necessary to subtract the signal of a reference sample made from the reagents in distilled water. The samples were pipetted in a standard photometer cuvette (10 mm \times 10 mm) without removing it from the set-up. Disturbing turbulences and air bubbles were gone after 30 s. Several successive readings were taken from the lock-in amplifier which was set to an integration time constant of 10 s.

RESULTS

The sensitivity and linearity of the photothermally detected phosphate molybdenum blue colorimetry was tested using dilution series of a freshly-made phosphate standard solutions. The result of four different sets of measurements is summarized in Figure 2. The very low concentration range not accessible by conventional methods was deliberately chosen to show the sensitivity. The net signal is linear from 0.1 mmol/m³ to higher concentrations (correlation coefficient $r=0.99$) and at the lowest concentration shown the signal-to-noise ratio was 4. Even at lower phosphate concentrations the signal still was large enough for measurements. However, some deviation from linearity was consistently observed, possibly indicating a change in equilibrium of the colouring reaction. The reproducibility was excellent despite the mechanical instability of the experimental set-up.

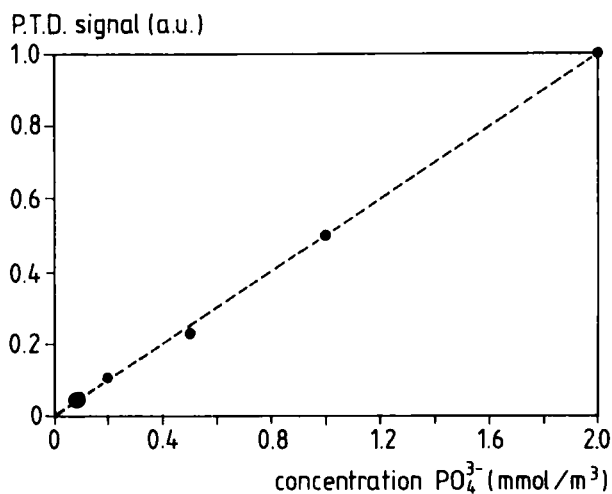


Figure 2 The lock-in signal corrected for the absorption by blank solution plotted versus the PO_4^{3-} concentration (mmol/m^3).

The photothermal colorimetry was further tested and validated by measuring the phosphate content of a soil water solution sample obtained from the soil science experimental field of Kootwijk in the nearby Veluwe district. The specimen was collected from 10 cm depth in the mineral soil using a standard 1910 high flow porous ceramic cup (Soil Moisture Corp., Santa Barbara, USA). The cup is fitted with two tubes, one serving for evacuation of the cup, the other one for removing the water collected inside. The water was brought to the laboratory in a polyethylene bottle and measured within 24 h to avoid changes in the sample.¹⁷ The phosphate concentration of the collected soil water was determined to be $0.24 \text{ mmol}/\text{m}^3$.

DISCUSSION

Reliable colorimetric determination of extremely low phosphate concentrations by means of photothermal detection is possible, because the latter is a very suitable technique for measuring weak absorptions and is not disturbed by light scattering. The results presented show that the beam deflection (BDS) technique is even more sensitive than, and has considerable practical advantages over detection with the photoacoustic effect.¹¹ In particular the immunity of BDS to the presence of small air bubbles in the sample contrasts favourably with the problems encountered in photoacoustics.¹¹ The experimental set-up is rather simple and made with inexpensive and readily available optical components. A lightweight instrument suitable for routine laboratory and field work based on this technique is feasible. The set-up could be mounted in a small solid block or frame to make it insensitive to vibrations¹⁸ and to get the mechanical stability needed for permanent alignment. The design could include two semiconductor lasers and an improved

optics layout. Simplifications on the electronics side are obvious. We note that the extension of this photothermal colorimetric detection technique to other nutrient ions is possible, provided lasers having suitable frequencies are available.

CONCLUSION

In conclusion we have demonstrated a detection sensitivity of 0.05 mmol/m^3 phosphate in water by combining the well-established molybdenum blue colorimetry with the sensitive photothermal detection technique to measure small absorptions. Such trace amounts are not easily accessible using the standard techniques. The detection limit is insensitive to moderate turbidity of the sample.

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