

## A Smart-Laser-Based Calorimeter

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Laser spectroscopy and calorimetry are certainly among the fields of science that have experienced the largest improvement in performance, due mainly to technological advances. In fact, laser-based methods are involved in fields ranging from medicine to particle physics (1), and using state-of-the-art microcalorimeters, it is possible to investigate enthalpy changes associated with several biochemical and physical chemical processes (2).

Our group has been working on the development of new methods based on laser deflection to detect heat flow coming from chemical reactions; that is, new detection schemes to be used in calorimeter instruments (3, 4). Here we propose a method that could be easily used in a physical or instrumental chemistry laboratory. It clearly demonstrates the fundamentals of thermochemistry and provides an understanding of laser-based photothermal methods. This combination is likely to increase the interest and creativity of the students. The experimental setup is simple and inexpensive, and based on components that should be readily available in physical or instrumental chemistry laboratories.

### Theoretical Background

When chemical transformations are accompanied by consumption or release of heat (i.e., enthalpic changes are involved) the generated temperature gradient ( $\Delta T$ ) causes density and refractive index changes in the surrounding medium (5). The effects of these gradients on a monitoring laser beam are the very simple basis of this calorimeter.

In the proposed method, two nonmiscible solvents are added to a sample cuvette (the reaction phase, where the chemical reaction occurs, and the monitoring phase, where the heat change is detected) (Fig. 1). Heat is generated in the reaction phase and propagates to the monitoring phase through convection. The magnitude of  $\Delta T$  is proportional to the amount of heat liberated or absorbed by the chemical reaction ( $Q$ ).  $\Delta T$  induces the formation of a refractive index gradient ( $\Delta n$ ), whose magnitude depends on  $\Delta T$  itself and on the thermo-optical properties of the monitoring phase, including its temperature derivative of the refractive index ( $dn/dT$ ) and its thermal conductivity.<sup>1</sup> A continuous  $\Delta n$  is expected; however, for illustrative purposes,  $\Delta n$  is represented

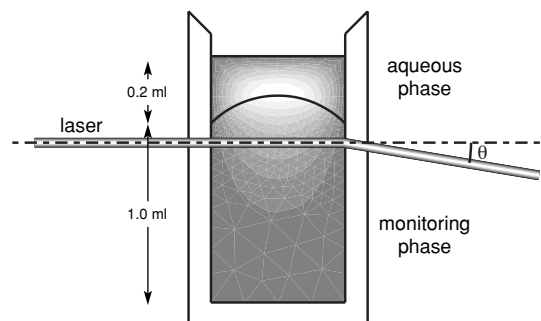


Figure 1. Schematic of the sample cuvette containing the aqueous and monitoring phases; the laser beam crosses the monitoring phase close to the interface. The different gray tones represent the refractive index gradient. Lighter gray represents higher temperatures and therefore smaller refractive index values. Because the picture has only an illustrative goal no numeric values are shown.

in Figure 1 as several gray-scale nodes. When a laser beam crosses this  $\Delta n$  perpendicularly, as depicted in Figure 1, it works as a thermal prism and the major effect is to change the deflection angle ( $\theta$ ) of the laser beam (3–6).

The role of the monitoring phase is twofold: it maximizes the deflection signal (therefore we want to choose monitoring phases that have high  $dn/dT$  values) and it prevents concentration gradients generated in the chemical reaction from passing to the monitoring phase. A concentration gradient, although being generated on a much longer time scale (it depends on molecular diffusion), would also cause a refractive index gradient and therefore would also deflect the laser beam (6b).

### Apparatus and Methods

The heat sensor based on laser deflection is similar to ones that have been described before (3, 4, 6). It is schematically depicted in Figure 2. The beam from a 1.4-mW CW He–Ne laser (Oriol-79309) is focused in the 1-cm quartz sample cuvette in the monitoring phase, 3 mm below the interface with water. A knife-edge blocks around 50% of the laser beam at the outset of the experiment (Fig. 2) and a converging lens

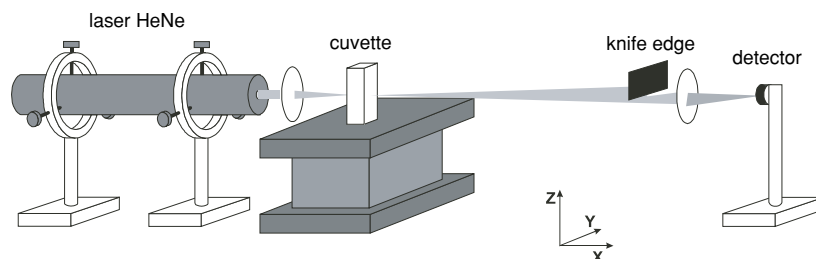


Figure 2. Schematic of the laser deflection calorimeter.

is used to refocus the beam in the photodiode (PIN 10DP, UDT). The signal is digitalized by a 12-bit A/D board (CIO-AD08, Computer Boards) installed in a 386 PC (TRI). The laser beam passing through the monitoring phase senses this refraction index gradient, which acts as a thermal prism and causes the deflection of the laser beam (Fig. 1).

The laser light intensity is monitored by a photodiode (Fig. 2). Because this detector is not sensitive to the position of the laser beam, the change in the deflection angle has to be converted into a change in light intensity, which can be accomplished by adding a knife-edge to the laser beam pathway. Depending on the intensity of deflection, the laser beam is more or less blocked by the knife-edge, which is sensed by the photodiode as more or less light intensity. Another instrumental configuration that works is to use a position-sensitive detector, which allows direct measurements of the deflection angle without using the knife-edge. This laser-based detection method differs fundamentally from the ones in commercial calorimeters, which are usually based on the responses of thermistors.

It is important to emphasize that it is not necessary that the laser beam have a Gaussian shape. In fact other lasers, including laser pointers, will work as well. The total volumes of the aqueous and monitoring phases are 0.2 and 1.0 mL, respectively. Carbon tetrachloride is chosen initially because of its large  $dn/dT$  value, which maximizes the refractive index gradient generated (5). However, other solvents that have good thermo-optical properties and are not miscible with water can also be used (hexane, cyclohexane, chloroform, etc.). The only restriction for choosing reaction and monitoring phases is that they should not mix. Even aqueous solutions containing high-concentration substrates (sucrose 50%, w/w) can be used. The high-viscosity sucrose solution is able to keep a distinct phase with the aqueous solution for some time (see below).

## Hazards

Poisoning may occur by inhalation or ingestion of  $\text{CCl}_4$  and cadmium compounds, or by skin contact.

## Results

### Determination of Sign of Enthalpy Changes

Figure 3A shows typical laser deflection signals obtained after the addition of 15  $\mu\text{L}$  of hot and cold water to the aqueous phase (200  $\mu\text{L}$ ) equilibrated at 23  $^\circ\text{C}$ . Note that just after the addition of 1.5 J of heat to the aqueous phase,<sup>2</sup> the voltage measured in the photodiode starts to decrease, indicating that a higher percentage of the laser beam is being blocked and therefore that the laser beam is being deflected. The signal reaches its maximum value at about 20 s and then returns to the original value at about 80 s. The temperature change induced in the aqueous phase works as an instantaneous heat source and the signal profile depends on the heat conduction in the monitoring media. The spikes at the start of the signal are due to the meniscus moving when the sample is manually injected. Note that removing 1.3 J from the aqueous phase (by adding cold water) causes a laser deflection in the opposite direction. This reversal of sign in the deflection signal can be explained considering that a positive temperature gradient generates a negative refractive index gradient ( $dn/dT$  of the organic phase is negative [5]) and the opposite happens when the negative temperature gradient is induced.

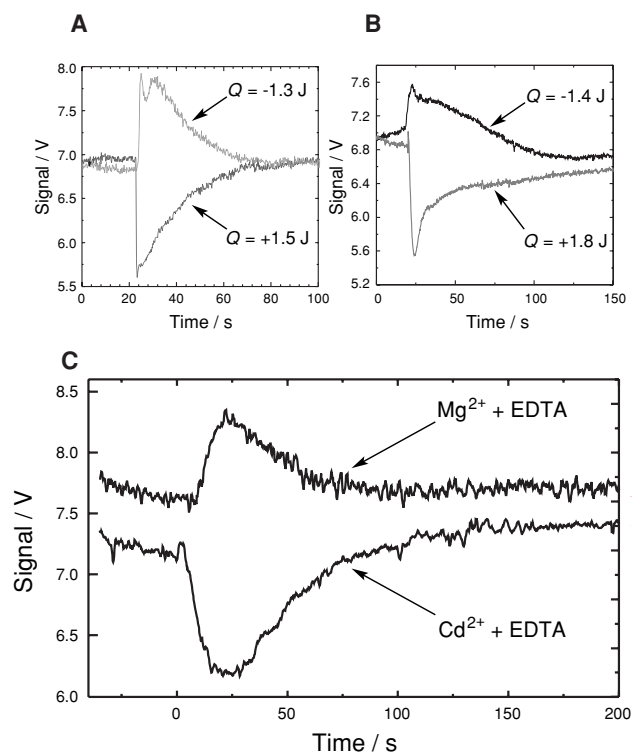


Figure 3. Deflection signals obtained after equilibrating the aqueous phase (200  $\mu\text{L}$ ) at 23  $^\circ\text{C}$  and adding (A) 15  $\mu\text{L}$  of water at different temperatures (47.5  $^\circ\text{C}$ , bottom; 2.5  $^\circ\text{C}$ , top) (monitoring phase, 1 mL of  $\text{CCl}_4$ ); (B) 15  $\mu\text{L}$  of water at different temperatures (53  $^\circ\text{C}$ , bottom; 0.5  $^\circ\text{C}$ , top) (monitoring phase, 1 mL of 50% [w/w] sucrose solution); (C) 15  $\mu\text{mol}$  of 1 M  $\text{CdCl}_2$  and 1 M  $\text{MgCl}_2$  solutions to the aqueous phase containing 1 M EDTA (monitoring phase, 1 mL of  $\text{CCl}_4$ ).

The similar profiles obtained for the mixture sucrose–water show the possibility of using nonorganic solvents in the monitoring phase (Fig. 3B). In the case of 50% (w/w) sucrose solution, there is a 10-minute window where mass transport between the phases is not observed (data not shown). After that time the solution mixing can be visualized by the laser beam deflection, which is caused by a concentration gradient, deteriorating the baseline of the thermal response. This instrumental setup may in principle be used to study mass transport in heterogeneous systems!

Deflection profiles similar to the ones induced by adding hot and cold water are observed when cadmium and magnesium solutions, respectively, are added to the aqueous phase containing EDTA (Fig. 3C). In the  $\text{Cd}^{2+}$ –EDTA reaction, the laser light is deflected to the same direction as when a positive temperature jump is induced; that is, heat is liberated in the surroundings. The opposite is observed for the  $\text{Mg}^{2+}$ –EDTA reaction—heat is removed from it. This can be explained if the processes of complexation of cadmium and magnesium with EDTA are exothermic and endothermic, respectively. In fact, that is in agreement with some results obtained using other calorimetric methods (7, 8).

### Quantitative Determination of the Enthalpy Change

Although the experiment with water is useful to show the sign of an enthalpy change, it is difficult to calibrate the instrument using this method because there is little control

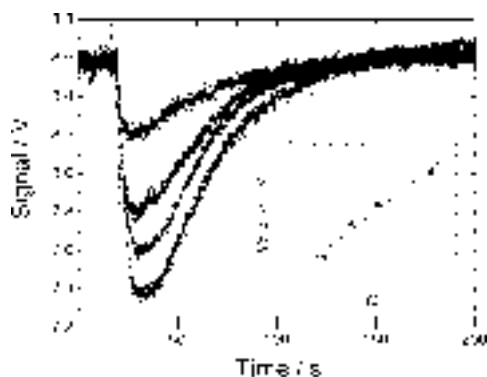


Figure 4. Deflection signals obtained after the addition of 15  $\mu\text{L}$  of 0.2, 0.4, 0.6, and 0.8 M HCl solutions (equivalent to 3, 6, 9, and 12  $\mu\text{mol}$  of HCl) to the aqueous phase containing 1 M NaOH. Inset:  $\Delta\text{Signal}$  (maximum deflection minus baseline) of HCl–NaOH neutralization reactions as a function of calculated heat liberated.

**Table 1.  $\Delta H$  for  $\text{Cd}^{2+}$  and  $\text{Mg}^{2+}$  Complexation with EDTA**

Ion <sup>a</sup>	Assay	Q/kJ	$\Delta H/(\text{kJ mol}^{-1})$	
			Exptl <sup>b</sup>	Lit. (8)
$\text{Cd}^{2+}$	1	-0.53	$-35 \pm 5$	-38
	2	-0.56	$-36 \pm 3$	
$\text{Mg}^{2+}$	1	0.34	$23 \pm 3$	23
	2	0.25	$17 \pm 5$	

<sup>a</sup> 15  $\mu\text{mol}$  of 1 M  $\text{CdCl}_2$  or  $\text{MgCl}_2$  solution was added to the aqueous phase containing 1 M EDTA.

<sup>b</sup> Value  $\pm$  SD for 3 injections.

over the actual water temperature in the cell. Instead, the deflection signal can be calibrated with a chemical reaction whose enthalpy value is known (neutralization of NaOH by HCl,  $\Delta H^\circ = -56.5 \text{ kJ/mol}$ ) (7). Figure 4 shows the deflection profiles after the addition of increasing amounts of HCl to the aqueous phase containing NaOH. Larger quantities of heat liberated in the aqueous phase cause increases in the deflection signal (Fig. 4, inset). The  $\Delta\text{Signal}$  values were calculated by subtracting the maximum deflection ( $\sim 20 \text{ s}$  after injection) from the baseline value. Both the maximum deflection and the baseline values were picked manually from the transient curve. The slope of this curve ( $m$ , in units of V/J) is used to correlate the deflection signal with the quantity of heat liberated or absorbed by the reaction and allow the determination of its enthalpy change ( $\Delta H$ ) as expressed by eq 2.<sup>3</sup> In eq 2, the deflection signal  $\Delta\text{Signal}$  of the reaction for which  $\Delta H$  is being calculated is divided by the moles of the limiting reactant ( $N$ , mol), which gives units of V/mol. This value is divided by  $m$ , giving finally  $\Delta H$  in units of J/mol.

$$\Delta H = \frac{\Delta\text{Signal}}{mN} \quad (2)$$

Using the same instrumental setup the deflection signal due to the  $\text{Cd}^{2+}$  and  $\text{Mg}^{2+}$  complexation with EDTA was measured twice.  $\Delta H$  was calculated following eq 2; the results are shown in Table 1. It is clear that the results obtained by

the laser deflection method agree semiquantitatively with the enthalpy values from the literature (8).

The estimated error in the final  $\Delta H$  calculation is around 10–15% (Table 1). It is a composite of several factors, including the manual dispensing of microliters of reactants into the sample cell. It is important to note that the minimum quantity of heat this instrumentation can detect is around 60 mJ (4). Any dilution heat would be too small to interfere with these measurements; that is, addition of few milliliters of 1 M HCl to the reaction phase containing only water results in no measurable signal. We are working to make this instrumentation more sensitive (4).

This experiment shows an alternative way of measuring the enthalpy change of chemical reactions, which uses a new and indirect method to detect the  $\Delta T$ . It is increasingly common to use indirect methods because it is not always possible to use a traditional device (e.g., a thermometer) to measure the temperature of a system. Therefore it is important to expose undergraduate students to this concept. Also emphasized is the idea that by performing a simple calibration of the instrument response, it is possible to obtain  $\Delta H$  values from the deflection signal without having to consider the complex physical theory that relates both variables. This concept is usually applied to analytical determinations.

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## Notes

1. A physical model that predicts the temporal behavior and magnitude of the deflection signal has been developed and will be published elsewhere.

2.  $Q$  values were estimated using the equation  $Q = mCAT$ , where  $m$  is the mass of liquid dispensed in the cuvette,  $C$  is the heat capacity of water ( $4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ ), and  $\Delta T$  is the temperature difference between the equilibrated cell and the sample dispensed in the cell.

3. Although the points of this calibration curve seem to have a nonlinear tendency, we believe it is because of random variations. A series of calibration curves shows no overall nonlinear tendency.

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