# Wall-coated open-tubular column chromatography on an organo–clay stationary phase

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## Abstract

Wall-coated open-tubular (WCOT) column chromatography is shown to be a viable tool to measure hydrocarbon interactions with an organo–clay as the stationary phase. In this paper, we report the heats of interaction for a series of hydrocarbons (*n*-alkanes of $C_6$–$C_{12}$, and cyclohexane) on a cetyltrimethylammonium bromide (CTAB)-modified Laponite-RD clay. The measurements were performed with a new WCOT method that we have developed, and also a conventional packed-column approach. Although the measurements from both techniques yield the same values of enthalpy (on the basis of our statistical analysis), we argue that WCOT column chromatography gave the more reliable results, with lower uncertainties and better chromatographic behavior.
Published by Elsevier Science B.V.

*Keywords:* Stationary phases, GC; Enthalpy of interaction; Wall-coated open-tubular columns; Organo–clay complex; Hydrocarbons; Laponite; Cetyltrimethylammonium bromide

## 1. Introduction

It was shown recently [1] that it is possible to construct a wall-coated open-tubular (WCOT) column with a clay mineral as the coating material, suitable for study and use in gas chromatography. The enthalpy of adsorption for several hydrocarbons

was measured on this column, and these data were compared with equivalent data from the more conventional technique with a packed column. We extend that work here to explore whether the WCOT procedure is a technique that can determine the relative strengths of interaction of hydrocarbons with an organo–clay. The organo–clay is of interest for a number of reasons. First, it has the potential to serve as a surrogate for natural soils that typically consist of 5–60% clay. These systems, although simplistic, are relevant for study in an environmental context, and have the potential to enhance our understanding of the pollutant–soil interaction. A spill of even a simple, single component pollutant in a soil is a complex problem. While numerous studies have

reported on sorption interactions between soils and pollutants, such as the work of Delle Site, a review of nearly 700 papers [2], relatively few studies have investigated the fundamental thermodynamics of these sorption processes [3–11]. We agree with other workers who believe that fundamental thermodynamic studies of pollutant–soil sorption processes are crucial in furthering our understanding of these complex phenomena, and that the development of a WCOT gas chromatographic technique will facilitate these necessary studies [8]. Second, because of the importance of nanomaterials (of which clays and organo–clays are a subset), an understanding of the interaction with different families of chemical compounds is not simply critical, but essential. Controlled fillers, such as the nanostructured materials that are added to polymers and coatings, must interact favorably with the parent matrix. Thermodynamic data such as the enthalpy of adsorption is a necessary parameter in the prediction of such interactions.

In this work, we measure the enthalpy of interaction, $-\Delta H_{int}$, between the *n*-alkanes $C_6$ –$C_{12}$ and cyclohexane, with an organo–clay stationary phase formed by complexing cetyltrimethylammonium bromide (CTAB) with Laponite-RD clay [12–14]. We use the term enthalpy of interaction rather than enthalpy of adsorption or enthalpy of solution in recognition of the composite mechanism that is responsible for solute hold-up on the organo–clay substrate. Laponite-RD is a synthetic clay that possesses similar physical and chemical characteristics of natural smectite clays. Since it is very well characterized, and free from the organic impurities that are typically found in natural clays, Laponite-RD is an ideal clay for use in metrology development. The box in Fig. 1 shows the molecular structure of this clay, along with the macroscopic structure of a clay particle, and the chemical structure of CTAB. The clay disks are capable of holding (by covalent bonding) approximately 417 cetyltrimethylammonium ($CTA^+$) ions on the top and on the bottom of a disk, for a total of 834 per disk [15]. In addition to these bonded $CTA^+$ ions, it is clear from this work as well as previous work that additional CTAB molecules interlayer into the bonded $CTA^+$, forming a sponge-like structure in which the polar quarternary amine moiety is outermost [15].

## 2. Theory

Assuming ideal behavior in the gas phase, and very low surface coverage (that is, infinite dilution) of the solute on the sorbent or stationary phase, values of $-\Delta H_{int}$, were obtained from the standard expression [16,17]:

$$\ln\left(\frac{V_g}{T_c}\right) = -\frac{\Delta H_{int}}{R} \cdot \left(\frac{1}{T_c}\right) + C \tag{1}$$

where $V_g$ is the isothermal specific retention volume at column temperature $T_c$, $R$ is the gas constant, and $C$ is a constant. The $V_g$ is determined at each $T_c$ from:

$$V_g = jF_c t_R \tag{2}$$

where $j$ is the Martin–James compressibility factor, $F_c$ is the fully corrected volumetric carrier gas flow-rate, and $t_R$ is the retention time of the injected solute. From these equations, a plot of $\ln(V_g/T_c)$ against $(1/T_c)$ will yield $-\Delta H_{int}$ as the slope. A more complete discussion of the theory, corrections and assumptions that were applied to the raw data are detailed elsewhere [1,16,17].

## 3. Experimental

In earlier work, we reported the production and use of a clay-coated WCOT column consisting of a 30 m fused quartz capillary with internal diameter 0.32 mm, and a packed column consisting of clay-coated 80–100 mesh (149–177 μm) spherical glass beads [1]. The same approach has been utilized here. Since the preparation of these columns, the integration of the columns into modified conventional gas chromatographs, the measurement procedures, and the data and error analysis have been described, such a discussion will not be reproduced in detail here. The preparation, however, of the CTAB–clay chromatographic stationary phase is new to this work and is discussed below.

The organo–clay complex is formed when $CTA^+$ cations (formed by the dissociation of CTAB) exchange the sodium on the Laponite-RD surfaces. Laponite-RD exists as platelets approximately 25–30 nm in diameter, with a thickness of approximately
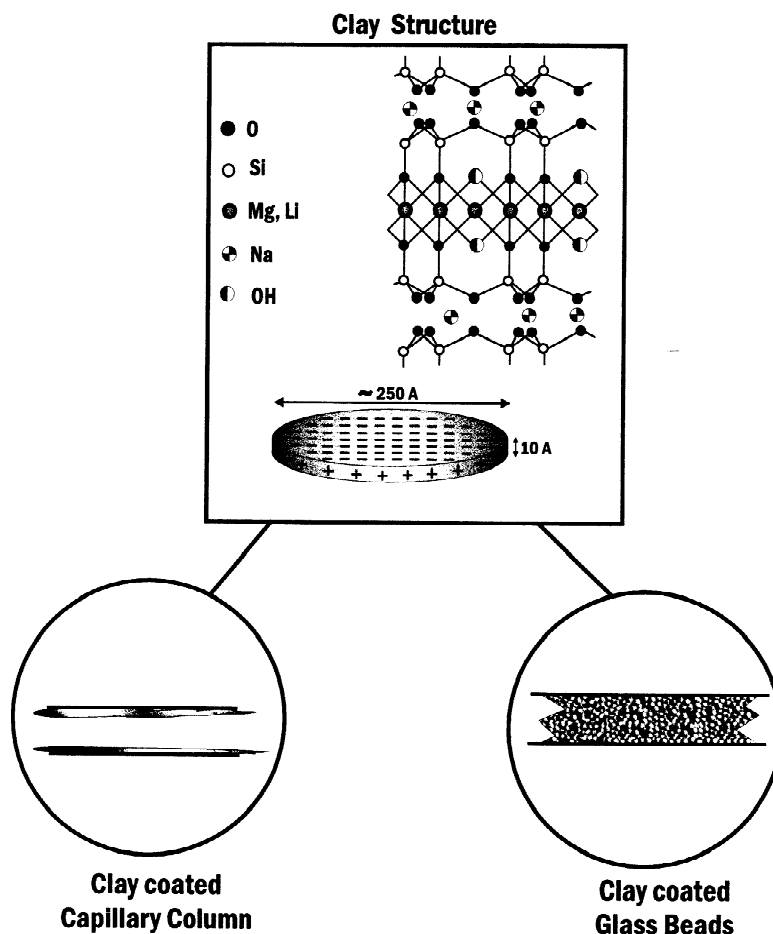
**Clay Structure**



Fig. 1. The molecular structure of the clay substrate is depicted in the box above, along with the macroscopic structure of a clay particle. The circles depict the coating of the clay on a WCOT (capillary) and packed gas chromatographic column.

1 nm [12,14]. Hence, given the cation-exchange capacity (cec) of Laponite-RD to be 55 mequiv./ 100 g [14], an aqueous 1.5% Laponite-RD suspension and an aqueous 0.05 *M* CTAB solution were mixed so that approximately 2 cec equivalents were available. The organo–clay complex was then recovered as a precipitate. Excess CTAB was removed by centrifuging and washing the precipitate, which was then dried at 100 °C overnight. Aliquots of the precipitate were re-dispersed with water for deposition on the chromatographic columns. The encircled schematic diagrams of Fig. 1 depict the deposition of the open tubular column and on the packed column, as discussed below.

### 3.1. Packed column

The packed column was prepared by depositing the organo–clay complex on spherical glass beads (80–100 mesh, 149–177 μm, commercially available chromatographic grade, washed and oven-dried). Specifically, a mass of organo–clay precipitate calculated to provide approximately 30 layers of coating on the glass beads was re-dispersed in water, and the suspension was stirred for 2 days. The suspension was then placed in a fluted flask containing the glass beads. An additional 200 ml of water was added to the flask to ensure a complete coverage of the beads by liquid. Vacuum rotary

evaporation and oven heating affected the coating on to the beads.

### 3.2. WCOT column

A mass of 0.26 g of organo–clay complex was suspended in 34 ml of 50 m*M* CTAB solution. The suspension was centrifuged, and the supernatant liquid was degassed. The prewashed WCOT capillary was filled with the supernatant. The column was then heated in increments of 25 °C, up to a temperature of 150 °C. Pure nitrogen was then passed through the column for 5 min, and the column was evacuated and maintained at 100 °C for 24 h. To ensure good surface coverage, the filling procedure was repeated at least six times for each column. Finally, the column was conditioned at 200 °C overnight under a nitrogen pressure of 1.3 atm (1 atm = 101 325 Pa). Ref. [1] gives other details of these loading procedures.

We indirectly confirmed that the organo–clay coating procedure for both the packed column beads and the WCOT capillary was successful. This was done by comparing the chromatographic data from the treated columns with those obtained from control columns (that is, columns prepared without the coatings). No measurable solute retention (above that obtained for a minimally retained marker) was observed on these control columns.

For a given solute, chromatographic runs were made on both the packed and WCOT column at 4–7 temperatures ranging between 60 and 200 °C for the packed column and between 50 and 150 °C for the

WCOT column. Research grade nitrogen was used as the carrier gas in all experiments. The hydrocarbon solutes and the CTAB used in these experiments were research grade materials (with purities ranging from 98 to 99.5%, m/m) obtained from commercial sources and were used without further purification. Of course, since the chromatographic technique is also a separation method, solute purity is a secondary concern. For the packed column measurements, a flash vaporization injector and a thermal conductivity detector were used. For the WCOT column, a split/splitless injector and a flame ionization detector were used.

Data were logged with either a commercial integrator or a computer equipped with appropriate peak processing software. Minimal quantities of solute were injected to produce peaks approximately a factor of 10 higher than the minimum detectable quantity for each measurement. This was done to satisfy the requirement of zero surface coverage and to avoid sample size dependent retention volumes.

## 4. Results and discussion

The measured values of $-\Delta H_{int}$ obtained in this study are presented in Table 1. For comparison, the $-\Delta H_{ads}$, measured earlier for the same solutes on pure Laponite-RD [1], are also provided. The respective expanded experimental uncertainties, presented with a coverage factor $k = 2$ (that is, two standard deviations) are presented with the measured enthalpies. The average deviation between the $-\Delta H_{int}$

Table 1
WCOT and packed column values of the heat of interaction, $\Delta H_{int}$, for selected hydrocarbons on the CTAB/Laponite-RD surrogate soil

| Adsorbate | $-\Delta H_{int}$ (kJ/mol) | | $-\Delta H_{ads}$ (kJ/mol), Laponite-RD WCOT |
|---|---|---|---|
| | CTAB/Laponite-RD packed column | CTAB/Laponite-RD WCOT | |
| Hexane | 43.5±0.8 | 37.4±0.1 | 55.1±1.2 |
| Heptane | 48.3±2.6 | 47.4±0.1 | 60.3±3.8 |
| Octane | 55.4±0.6 | 52.8±0.3 | 73.8±2.6 |
| Nonane | 62.3±4.0 | 60.4±0.1 | 78.5±1.2 |
| Decane | 65.7±1.2 | 64.0±0.2 | 82.7±1.0 |
| Undecane | 75.1±2.2 | 69.4±1.8 | 91.7±2.4 |
| Dodecane | 73.8±3.8 | 77.8±0.9 | 96.3±2.7 |
| Cyclohexane | 39.1±0.4 | 35.6±0.2 | 48.5±1.4 |

The enthalpy of adsorption, $\Delta H_{ads}$, values from the WCOT procedure with Laponite-RD are shown for comparison [1].

measured by the two methods (packed column and WCOT column) is 2.3 kJ/mol. This deviation is somewhat lower than that measured for the pure clay stationary phases presented previously [1].

The data obtained from the WCOT column approach have an uncertainty that is four times lower than those from the packed column. The average experimental uncertainty from the packed column measurements is 2.0 kJ/mol, while those from the WCOT approach average 0.5 kJ/mol. We ascribe this to the major experimental advantages of the WCOT approach, namely the higher chromatographic efficiency (producing sharper chromatographic peak shapes) and lower applicable experimental temperatures. As expected, both data sets correlate well with physical variables known to affect or describe sorption, for example, carbon number (for the *n*-alkanes), relative molecular mass, normal boiling temperature, critical volume and or molar volume. Pearson correlation coefficients for these correlations are provided in Table 2. Note that the correlation coefficients for the WCOT column are significantly higher than those from the packed column measurements. Fig. 2 is a representative plot of the variation of $-\Delta H_{int}$ with, in this case, relative molecular mass, $M_r$. The error bars in the figures are the expanded uncertainties as provided in Table 1. Based on the uncertainty analysis of the two sets of data, and the reproducibility of the data, we conclude that the WCOT data are the more reliable. This conclusion is consistent with our summation of the results for the Laponite-RD coated columns, discussed previously [1].

The packed column and WCOT column gave values of $-\Delta H_{int}$, that are generally within their respective estimated experimental errors, although the $-\Delta H_{int}$ obtained from the WCOT column are, generally, somewhat less negative. The agreement between the two methods was further demonstrated

Table 2
Pearson correlation coefficients of $-\Delta H_{int}$ with physical properties of the adsorbates

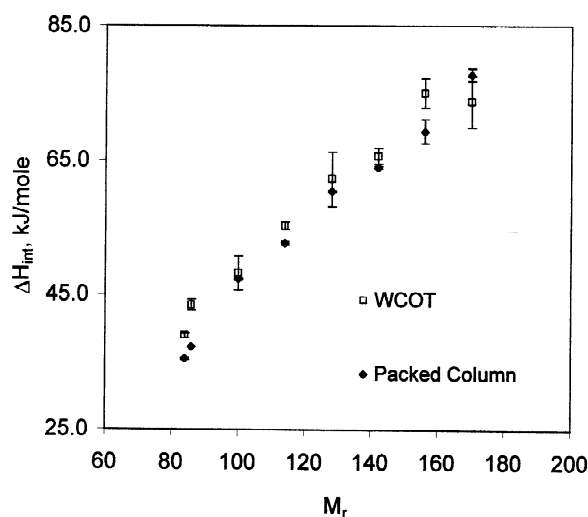|  | Packed column | WCOT column |
|---|---|---|
| Carbon number | 0.984 | 0.993 |
| Relative molecular mass | 0.984 | 0.993 |
| Normal boiling temperature | 0.987 | 0.995 |
| Critical volume | 0.986 | 0.995 |



Fig. 2. Variation of the enthalpy of interaction, $-\Delta H_{int}$, with the relative molecular mass, $M_r$, of the adsorbates. The top graph is for the WCOT column measurements; the lower is for the packed column measurements.

by a weighted regression of $-\Delta H_{int}$ against carbon number performed for each of the two sets, similar to what was done earlier for the pure Laponite-RD stationary phases [1]. Two weighted fits were performed, of the form:

$$-\Delta H_{int}^{P} = \alpha^{P} + \beta^{P} \cdot M_r \tag{3}$$

and

$$-\Delta H_{int}^{WCOT} = \alpha^{WCOT} + \beta^{WCOT} M_r \tag{4}$$

where $M_r$ is the solute fluid relative molecular mass, and $\alpha$ and $\beta$ are fitting coefficients. The superscripts "P" and "WCOT" denote the respective columns. The weighting factors were taken as the reciprocals of the individual expanded uncertainties. We then tested the null hypothesis: Ho: $\alpha^{P} = \alpha^{WCOT}$, $\beta^{P} = \beta^{WCOT}$. The null hypothesis is the mathematical statement asserting that the coefficients from the two fits are statistically the same, and therefore the two data sets are, in fact, statistically the same. Disproving the null hypothesis is an assertion that the two data sets, from the packed-column and the WCOT column, are in fact statistically different. The two coefficients are tested simultaneously; both of the coefficient equalities expressed in the null hypothesis

must be true in order to affirm (or rather, fail to reject) the null hypothesis. The $F$ test was performed on the weighted fits described above. We calculated our test statistic $F = 0.22$ at the 95% confidence level, with a $P$ value of 0.8 [18]. Since 0.8 is considerably larger than the threshold $P$ value of 0.05, we may conclude that the $-\Delta H_{int}$ values obtained by the two methods are in fact statistically the same (or more correctly, we fail to prove that they are different). This is evidence that the physical structures of the clay surfaces on both columns are the same in terms of pore sizes, pore spacings, and platelet spacings.

It is interesting to observe that the enthalpies of adsorption for the hydrocarbons on the pure clay are uniformly higher than their enthalpies of interaction on the organo–clay complex. Clearly, our data show that interaction on Laponite-RD is stronger than on Laponite-RD/CTA$^+$. We believe that the organic component of the stationary phase (in this case, CTA$^+$) effectively occupies or "ties up" the most active sites of the clay, thus rendering them inaccessible to approaching solute molecules. This kind of behavior is often seen in gas–solid chromatography, where a coating is commonly applied to a very active adsorbent to decrease or modify the retention process [19]. Hydrated cations are the most active sites on the clay for interaction with polar and nonpolar molecules. When cetyltrimethylammonium cations are present as exchangeable ions, the clay surface is modified and interactions with hydrocarbon solutes are observed to decrease. The exchange of an organic moiety on the surface of a clay can also produce the opposite effect (that is, an increase in the measured interaction with the surface). In many such cases, this is the result of greater accessibility to the clay surface (matrix expansion rendered by the presence of the organic moiety), rather than an increased interaction with the organic moiety.

Moreover, the presence of exchanged CTA$^+$ ions makes the organo–clay more non-polar than the bare clay. Thus, the alkane solutes effectively "see" a bonded-organic layer that is similar to a stationary phase composed of hexadecane or octadecane. Solute interactions with the organic fraction of the organo–clay composite material should be governed by partition mechanisms, and thus characterized by an enthalpy of solution, $\Delta H_S$. Adsorption processes

control the interactions with exposed clay surfaces not exchanged with CTA$^+$. Therefore, the net solute interaction with the organo–clay stationary phase is controlled by a combination of both adsorption ($-\Delta H_{ads}$) and partitioning ($-\Delta H_S$) processes. To illustrate how the combination of these interactions leads to the measured decrease in enthalpy between pure clay and the orgrano–clay substrates, a comparison of the enthalpies for $n$-alkanes on various substrates was performed, and is shown in Fig. 3. While $-\Delta H_S$ for pure CTA$^+$ are not used in this comparison, the representation of the cetyl moiety with hexadecane or octadecane is chemically appropriate. As in Fig. 2, the data are plotted as a function of $M_r$. Fig. 3 clearly demonstrates that the $-\Delta H_{int}$ of $n$-alkanes on the Laponite-RD/CTA$^+$ composite is lower than the $-\Delta H_{ads}$ on the pure Laponite-RD stationary phase [1]. The comparison also shows the $-\Delta H_{int}$ for the $n$-alkanes are greater than the reported $-\Delta H_S$ of $n$-alkanes on hexadecane [20] and octadecane [21] stationary phases. Thus, the measured $-\Delta H_{int}$ on the organo–clay material appears to be a combination of adsorption processes with the accessible clay surfaces (the $-\Delta H_{ads}$ contribution) and absorption processes with the CTA$+$ interlayer region ($-\Delta H_S$). Contributions from both adsorption and partitioning processes can, in principle, be determined by varying the phase loading of liquid
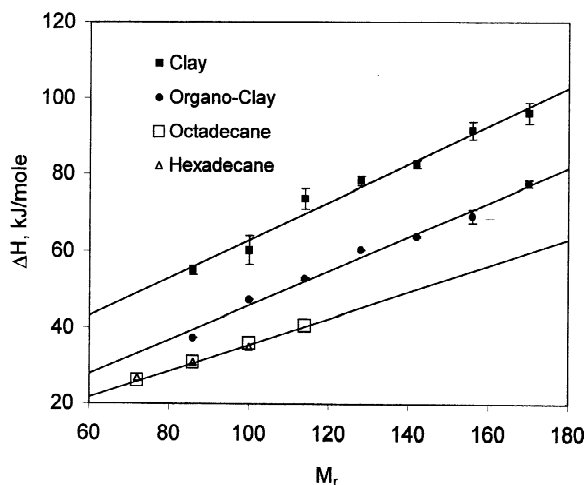


Fig. 3. Enthalpy of $n$-alkanes on various surfaces. $-\Delta H_{ads}$ on Laponite-RD (■) [1]; $-\Delta H_{int}$ on CTA$^+$/Laponite-RD (♦); $-\Delta H_S$ on hexadecane (△) [9] and octadecane (□) [10].

stationary phases [22]. This approach, however, is not practical for the organo–clay system reported here due to the unique stationary phase morphology (e.g., organic/inorganic agglomerates). Therefore, we believe that reporting the sum of these contributions, in the form of an enthalpy of interaction, is the most appropriate convention for this specific stationary phase.

## 5. Conclusions

We conclude by remarking that the WCOT approach is a viable technique to measure fluid interaction on an organo–clay complex. In fact, it is to be preferred over traditional (i.e., McBain balance) and packed column chromatographic methods. The relative uncertainties are lower than those obtained from the packed column method. The higher efficiency and increased speed of the WCOT approach allows the use of lower experimental temperatures than are required for the less efficient packed column approach. Moreover, better, more symmetric peak shapes and retention times with lower uncertainties are obtained from the WCOT column. Although the systems investigated here are somewhat simplistic in the context of environmental studies, the WCOT column approach has demonstrated considerable promise as a useful tool to measure fundamental thermodynamic interactions between pollutants and soil, and thus increase our understanding of the fate of organic pollutants in natural soils with both a high clay and a high organic content.

## Acknowledgements

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