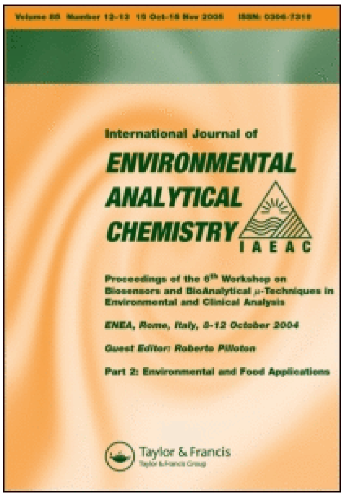

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# A Method For Measuring The Vapour Pressures Of Pah'S Adsorbed On The Surface Of Soot

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**To cite this Article** Neue, G. and Rudolph, F.(1993) 'A Method For Measuring The Vapour Pressures Of Pah'S Adsorbed On The Surface Of Soot', International Journal of Environmental Analytical Chemistry, 52: 1, 229 — 236
**To link to this Article: DOI:** 10.1080/03067319308042863
**URL:** http://dx.doi.org/10.1080/03067319308042863

*Intern. J. Anal. Chem.*, Vol. 52, pp. 229-236
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# A METHOD FOR MEASURING THE VAPOUR PRESSURES OF PAH'S ADSORBED ON THE SURFACE OF SOOT

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*(Received, 15 June 1992)*

A new method is reported that utilizes a low-temperature quartz microbalance in combination with Knudsen cells to obtain adsorption isotherms for substances with very low equilibrium pressures ($< 10^{-5}$ Pa). The method allows for the first time to measure directly thermodynamic properties of important aerosol/pollutant systems at typical environmental temperatures. Application is demonstrated by an investigation of fluoranthene and pyrene adsorbed on carbon aerosol particles ($T = 293.15$ K–302.13 K). Both PAHs are unable to form extended multilayers on the surface. Slightly above monolayer coverage the three-dimensional crystalline solid phase is thermodynamically more stable.

**KEY WORDS:** Adsorption, carbon, aerosol, fluoranthene, pyrene, PAH.

## INTRODUCTION

Many atmospheric aerosols carry adsorbed pollutants on their surfaces. The life times of such molecules on the surface is limited by either chemical reaction with other atmospheric gases or by desorption. While there is some information about chemical transformations, quantitative data for the latter process usually are unavailable. The reason is that these systems must have very low equilibrium pressures to exist for hours or days. At these low pressures classical adsorption methods[1] do not work because they require larger quantities of aerosols to observe adsorption. It is easy to estimate that at low pressures diffusion within fine powders is so slow that establishing equilibria might well last days or even years. One way to overcome this problem is to observe molecules on isolated aerosol particles with very sensitive detection methods, e.g. aerosol photoemission[3,4,5] or laser induced aerosol fluorescence[2].

Despite the impact these techniques had in aerosol science, they typically rely on complicated physical processes and interference from surfaces is likely to occur[6] (like fluorescence quenching, or additional signals from the surface itself). Obviously, also the sensitivity for different classes of molecules is very different.

The present work is aimed to provide a direct measurement of adsorption isotherms, i.e. the functional dependence of equilibrium pressures as a function of surface coverage. From sets of such data all thermodynamic properties can be derived[1].

Of particular interest to problems in the context of environmental science is the equilibrium pressure itself which allows to estimate compositions of surface phases as a function of time. Another parameter which can easily be measured from adsorption isotherms is the molar heat of adsorption which gives a measure for the strength of molecular bonds to the surface. It represents an information about how easily one adsorbed molecule can be replaced by different species.

## PRINCIPLES OF THE METHOD

The usual way to monitor adsorption as a function of pressure is only possible either at higher pressures where mass transport processes are fast enough or on surfaces directly exposed to the gas phase. The first case is the classical adsorption study, the second is the basis for a method to measure adsorption at low pressures on large single crystals[7a,7b,7c]. How to obtain adsorption isotherms of low vapour pressure materials on fine particles, e.g. soot systems, was hitherto unknown.

As we like to measure thermodynamic states it should not matter how the final state that represents a point of the adsorption isotherm was reached. A pathway that circumvents the problem of slow diffusion can easily be constructed. It consists of the following steps. 1) Heating

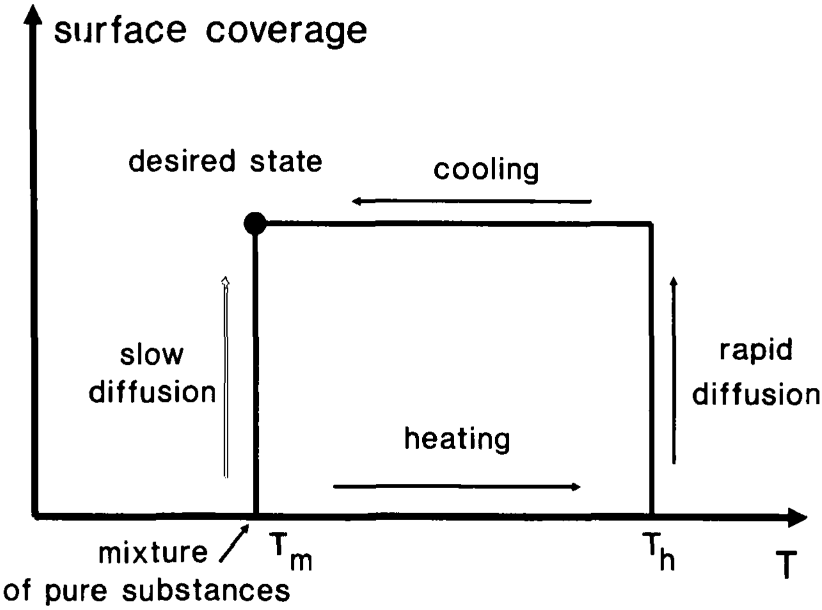

**Figure 1** As diffusion at the measuring temperature T*m* is too slow a thermodynamically equivalent path via T*h* is taken for sample preparation.

a mixture of a pure substance and the pure adsorbent. 2) Rapid equilibration at higher temperature. 3) Cooling of the adsorbate to the desired temperature for the measurements (Figure 1).

This approach needs a closer examination of the basic processes as there are some problems. The equilibration occurs by diffusion. But there are three different mechanisms, gas diffusion through small voids between the solid particles, ad/desorption causing exchange between the gas phase and the adsorbed phase, and surface diffusion. Gas diffusion is very rapid. A simple estimation using standard expressions of gas kinetics shows that even at $p = 10^{-6}$ Pa the molecules should be able to cross macroscopic sample dimensions in seconds or minutes. But at low gas densities this mechanism is very inefficient as there is no significant mass transport associated with it. In addition, gas diffusion is only slightly dependent on temperature. But raising the temperature increases desorption by a factor $\exp(-\Delta H_{ads}/RT)$. Assuming adsorption enthalpies of the order of 100 kJmole$^{-1}$ it is fairly easy to increase the gas density by some orders of magnitude by moderate temperature changes. Pressures of 1 Pa or less are sufficient to obtain useful equilibration times.

Surface diffusion also accelerates the uniform distribution of matter throughout the sample. Diffusion coefficients measured by solid state NMR for a variety of PAHs adsorbed on carbon particles[8,9,10] showed indeed unexpectedly high mobilities even for large PAH molecules and characterize the surface phases at least partially as fluids at room temperature. Nevertheless, with typical values of $D_{tr} = 1 \cdot 10^{-11}$ m$^2$s$^{-1}$ this mechanism is a rather slow process for sample dimensions of 10 mm.

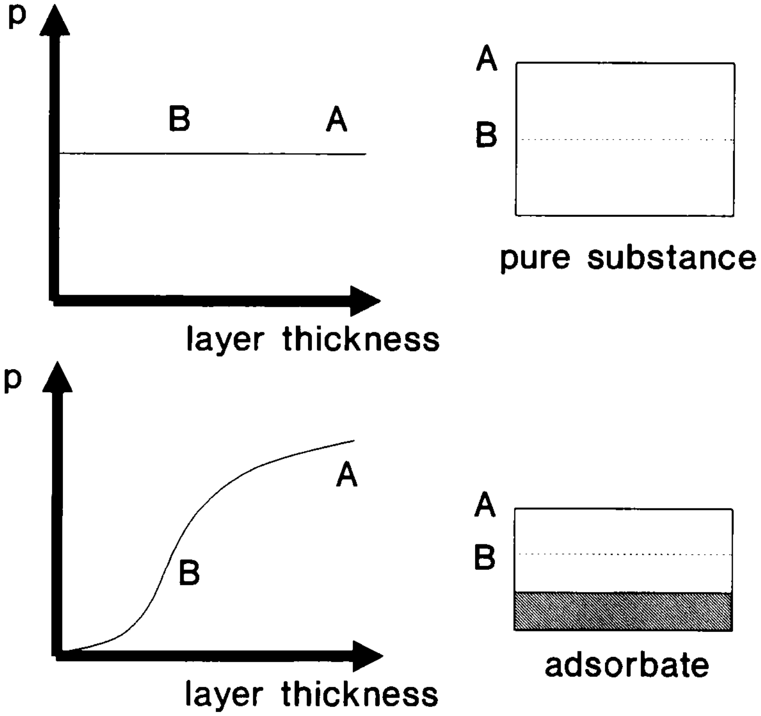

**Figure 2** In contrast to pure substances, the equilibrium pressure of adsorbates depends on the amount of mass taken from the system.

Limitations for the temperature arise from the fact that materials must not decompose or react. Also the solid may change its composition of surface groups by heating.

The cooling step presents two other difficulties. During temperature changes the distribution of the molecules between the gas and the adsorbed phases changes, too. If the pressure is kept at 1 Pa, as mentioned above, and the sample volume during preparation is small, then the fraction of molecules in the gas phase is negligable and cooling is essentially an isosteric process under those conditions. Thus, the final surface coverage is already obtained at the higher temperature. There might also be objections concerning the equilibration. But it has to be observed that lowering of the temperature is not accompanied by a significant mass transport. The density of the gas phase at 1 Pa is already so low that voids between particles with a diameter of 100 nm (typical for many diesel soots) contain only 0.2 particles. Hence, equilibration means local thermal equilibration of the adsorbed layer and not a large scale exchange with gas phase molecules.

The above discussion shows that it should indeed be possible in most cases to prepare samples with a well-defined surface loading.

Measurement of small equilibrium pressures also deserves some attention. Direct determination in a closed volume system suffers from the existence of background gases ($H_2O$, $H_2$,CO, air etc.) that desorb from walls and other surfaces. Selective detection methods like mass spectrometry usually require careful calibration for each individual substance. In view of unknown vapour pressures of many solid materials this might not be the ideal choice. A second constraint is the fact that adsorbates change their vapour pressure according to the adsorption isotherms if material is taken from the system. This contrasts with pure substances that show constant vapour pressures irrespective of their amount (Figure 2).

A standard method to determine low vapour pressures is to use Knudsen cells[11a,11b,11c]. They are simply small sample containers with a small well-defined hole through which some molecules of the gas phase can escape. If placed in a high vacuum apparatus the hole translates small pressures inside the container into mass losses.

Because of the constraints mentioned above a temperature controlled quartz microbalance placed above the Knudsen cell is an ideal detector. For larger molecules like PAHs its easy to find a quartz temperature where they condense completely but the background gases don't. The additional mass changes the vibration frequency of the quartz which is part of an electronic oscillator (Figure 3). As frequencies can be measured with high accuracy this type of balance allows to detect mass changes that are small enough to leave the equilibrium pressure of the adsorption system virtually unchanged.

## EXPERIMENTAL

Measurements were carried out with fluoranthene (vapour pressure: $p_0$ (298K) = $1.23 \cdot 10^{-3}$ Pa) and pyrene ($p_0$ (298K) = $6 \cdot 10^{-4}$ Pa). Both substances were purified by sublimation to remove high vapour pressure contaminants that might otherwise disturb the determination of equilibrium pressure. Impurities of low vapour pressure material is not so important as long as it does not cover a large fraction of the surface.

The commercially available carbon black "Spezialschwarz 350" (SS350, Degussa, Frankfurt, specific surface area S = 59 $m^2g^{-1}$) was chosen as a substitute for diesel soot. The

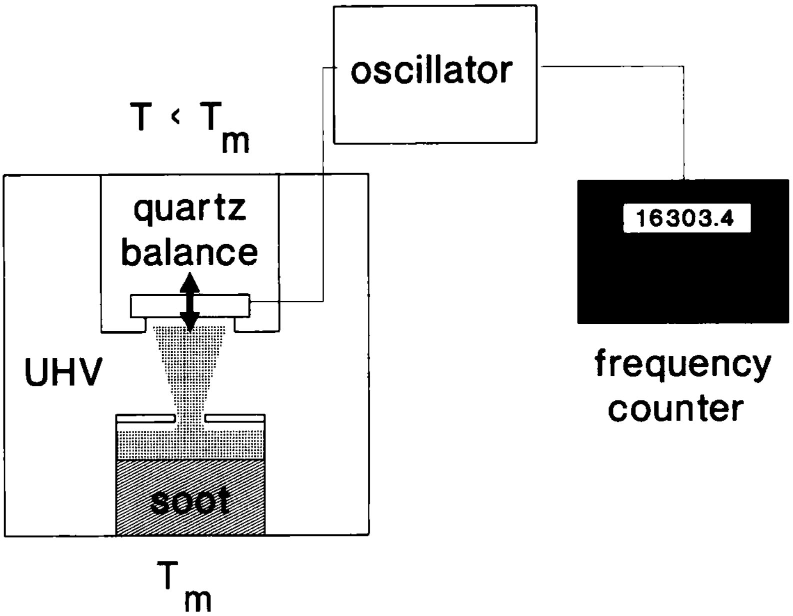

**Figure 3** Schematic representation of the experimental setup.

selection was from several carbon blacks with a wide range of surface properties. The carbon blacks were characterized by macroscopic (pH-value, oxygen content, surface area, particle morphology, chemical analysis of surface groups) as well as spectroscopic techniques (FTIR, $^{13}$C CP-MAS NMR). These were compared with NBS reference material SRM 1650 as well as with several diesel soot samples obtained under different engine load conditions. The above mentioned carbon black turned out to be very similar to typical diesel soot particles but has the advantage of beeing available in large quantities. As a well defined industrial product its properties are highly reproducible even in different batches.

Sample preparation started with heat treatment of the carbon black under vacuum ($\leq 10^{-2}$ Pa) at 380 K for 24 hours. For each sample the required amount of PAH was added and the mixture was kept for 3 to 6 weeks in a closed glass container under vacuum at 363 K to obtain a homogeneous adsorbate. Equilibration was easily to observe by the disappearance of PAH crystals which occurred typically within a few days.

The measurement itself took place in a thermostated Knudsen cell placed in an UHV apparatus. Calibrations showed that deviations of the sample temperature from its setpoint was less than 0.1 K. Typically 1 g of adsorbate was used in a single experiment.

The quartz microbalance (Oxford Applied Research, Oxford) is constructed as a flow cryostate that can be operated between 77 K and 570 K. The temperature of the balance was set to 240 K (±1 K) to guarantee that at least 99% of the PAHs condensed onto the quartz crystal but on the other hand background gases like $H_2O$ remained in the gas phase. The low equilibrium pressures released only $10^{-5}$ of the surface coverage onto the balance during the time of measurement (a few minutes) thus guaranteeing representative values for the equilibrium pressures.

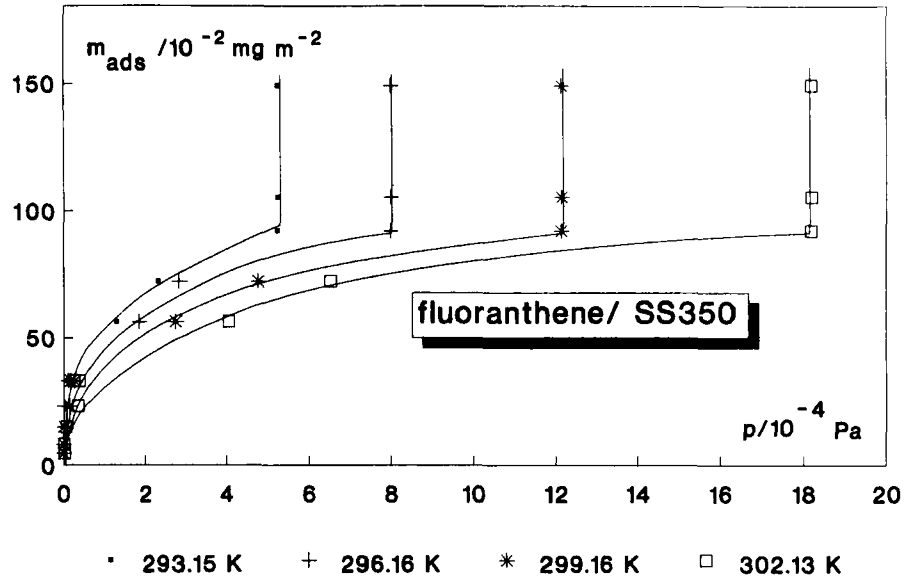

Figure 4 Adsorption isotherms of fluoranthene on carbon particles.

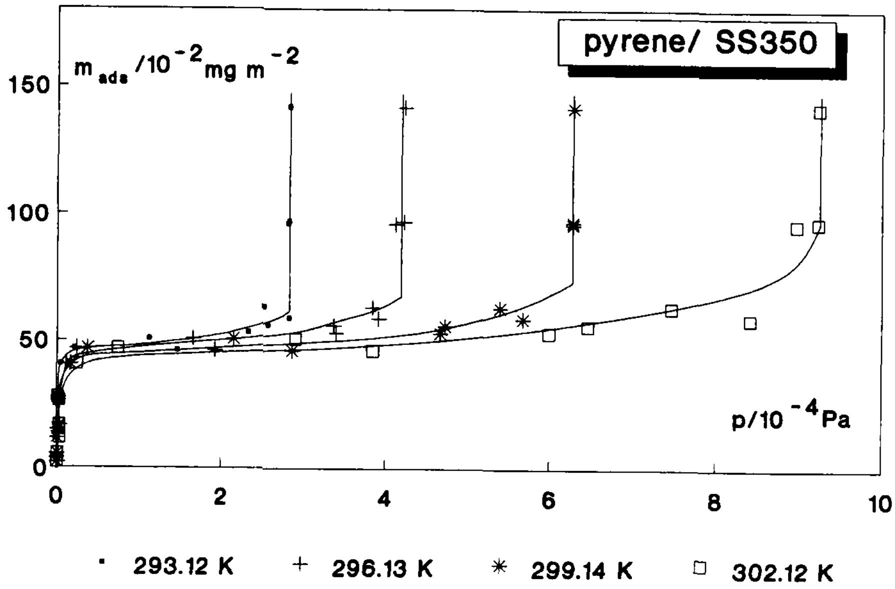

Figure 5 Adsorption isotherms of pyrene on carbon particles.

## RESULTS

Figures 4 and 5 show adsorption isotherms of fluoranthene and pyrene on SS350. All isotherms are of type I according to the classification of Brunauer, Deming, Deming and Teller[12]. The curves are characterized by a first rapid uptake at low pressures. Monolayer coverage is reached at typically less than one tenth of the vapour pressure of the pure PAH. By using the classical BET model[13], monolayer coverages were determined as 0.52 mg $m^{-2}$ (fluoranthene), and 0.48 mg $m^{-2}$ (pyrene).

Multilayer formation occurs only weakly for fluoranthene and is almost absent in the case of pyrene as can be seen from the very flat middle part of the isotherms. Higher surface coverages are characterized by $p/p_0=1$. This shows that above a critical adsorbed amount (fluoranthene: 0.9 mg $m^{-2}$, pyrene: 0.6 mg $m^{-2}$) the crystalline PAH is thermodynamically the more stable phase. Under those conditions tiny crystals grow on the surface which can be observed by solid state NMR[10].

This behaviour is also reflected by isosteric heats of adsorption ($q_{st}$) as a function of coverage. These data can be obtained by the relationship[1]

$$\left(\frac{\partial \ln p}{\partial T}\right)_{n_{ads}} = \frac{q_{st}}{RT^2}$$

As an example isosteric heats of adsorption (which are differential enthalpies of adsorption) for the system pyrene/SS350 are shown in Figure 6. Above monolayer coverage enthalpies jump down to the value of the enthalpy of sublimation for pure pyrene.

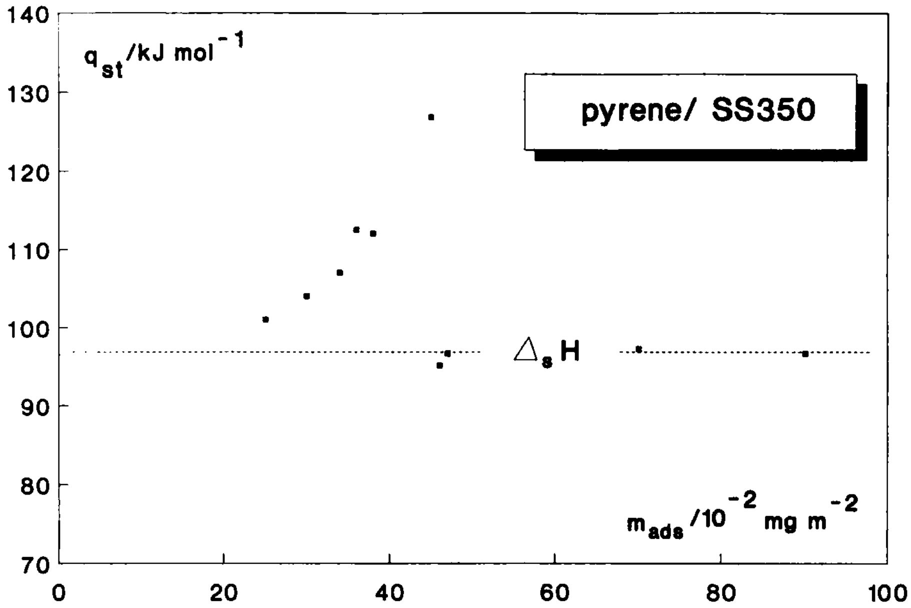

Figure 6 Isosteric heats of adsorption for pyrene adsorbed on carbon particles as a function of coverage.

## CONCLUSIONS

It has been shown that it is possible to obtain reliable quantitative thermodynamical data for adsorption systems that are relevant to problems in environmental science. The use of a very sensitive quartz microbalance in combination with Knudsen cells proved to be very efficient. Disturbance by the measurement itself can easily be kept so low that the adsorption equilibrium is maintained to such a degree of accuracy that it is well below other sources of error. As this method apparently is the first that is able to derive adsorption data for low sublimation pressure materials adsorbed on fine particles at temperatures that are relevant to environmental processes, it seems to be a very promising technique for analyzing the interaction of atmospheric aerosols with high molecular weight trace gases.

### *Acknowledgements*

The authors like to thank "Deutsche Forschungsgemeinschaft" and "Fonds der Chemischen Industrie" for financial support of the project.

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