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MICRO-ADSORPTION DETECTOR

I. PRINCIPLES OF OPERATION AND MECHANISM OF RESPONSE

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SUMMARY

A description of a commercially available micro-adsorption detector (Varian) is given. Detector response was monitored by a digital data logging system producing a paper tape. This digital data was analyzed using a DEC PDP-8/I. Investigation of the mechanism of response showed the detector response to be a complex function of both adsorption and desorption processes. This contradicts the earlier published conclusions: (a) that the peak response was merely the differential of the sample concentration profile and (b) that the positive peak was due only to adsorption processes and the negative peak was due solely to desorption processes. The investigation and results are discussed in this paper.

Correlation between sample size and (a) the first half of the positive peak area, (b) total peak area, (c) total negative peak area, and (d) total peak area were tested. Statistical analysis of the detector response showed that only the first half of the positive peak area was proportional to sample concentration. For quantitative analysis it was also shown that total peak height, or positive peak height could also be used. This work is discussed in Part II of this series.

INTRODUCTION

High pressure liquid chromatography (HPLC) has seen a flourish of activity as evidenced by the exponential increase in instrument sales and usage in the last few years. An essential part of the HPLC systems are low dead volume, sensitive detectors which allow continuous monitoring of the column effluent.

Ideally the detector response would be universal. The most widely used detec tors today, the ultraviolet photometer (UV) and the differential refractometer (RI)

have useful roles. However, the UV suffers from lack of universal response, and the RI suffers from lack of sensitivity.

The micro-adsorption detector (MAD) described by Hupe and Bayer in 1967[1] is a universal detector which has aroused considerable interest. Since the detector responds to the heat of adsorption of the solute, if the solute interacts with the stationary phase sufficiently to effect a separation this same system in the MAD should generate a response. Publications have appeared using the MAD to analyze for carbohydrates, lipids, and amino acids[2–4].

The positive peak is attributed to the heat of adsorption and the negative peak to the heat of desorption[5]. It has been reported[6] that the signal from an ideal MAD would be the differential of a Gaussian curve. Nagasawa uses a "thermal detector" to monitor ethylene glycol and its oligomers when separated on a Sephadex column[7]. The peak shape indicates that this may be a MAD, but no details are given. Heats of adsorption of organic vapors are measured by a flow calorimeter but not at levels attainable with the MAD[8–10].

Smuts *et al.*[11] modified the MAD to eliminate the troublesome negative peaks by continuously replenishing the adsorbent.

Because of its promise as a universal detector and the confusion concerning the mechanism of response and correlation of the peak shape with the mechanism it was decided to investigate the detector in detail. This paper describes the mechanism of response and related the response curve to the adsorption and desorption processes. Future publications will evaluate the detector as a universal HPLC and universal gas chromatographic (GC) detector.

EXPERIMENTAL

Equipment

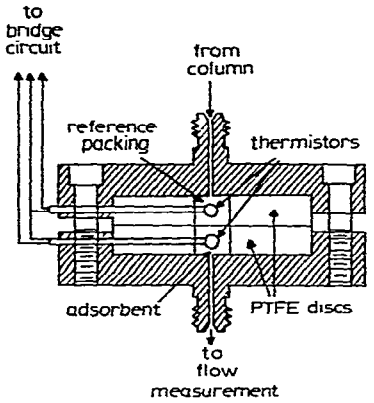
In this work the equipment utilized included the micro-adsorption detector, a pumping system, a strip-chart recorder, a digital data logger, and a computer.

Micro-adsorption detector. The basic components of the MAD are shown diagrammatically in Fig. 1. This model was purchased from Varian Aerograph (Walnut, Creek, Calif., U.S.A.)*. The detector consisted of two matched, 100,000-Ω thermistors each mounted in a 2.5-mm diameter orifice in a 34-mm diameter, 4-mm thick, PTFE disc. These were held in a stainless-steel housing having 1/8-in. Swagelok fittings. The cavities around the thermistors were packed with a non-absorbing material in the upper or reference cell, and an adsorbing material in the lower or sensing cell. The two sections were separated by 400-mesh platinum wire screens.

The detector was attached directly to the outlet of the chromatographic column, and the column effluent passed directly from the column into the reference cell. Here the reference thermistor sensed only the temperature of the flowing stream. As the effluent passed into the sensing cell, the solute adsorbed onto the packing material with the release of heat and a consequent increase in temperature. The temperature differential between the reference and sensing thermistors was measured by the Wheatstone bridge circuit.

The two thermistors formed opposing legs of a Wheatstone bridge circuit shown schematically in Fig. 2.

* This detector is no longer available from Varian.



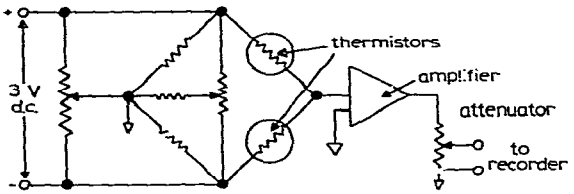


Fig. 1. Schematic diagram of the micro-adsorption detector.

Fig. 2. Schematic diagram of the MAD bridge circuit.

Pumping system. Since the MAD can detect temperature differentials of the order of 5×10^{-5} °C, a thermostated environment and constant flow-rate of the mobile phase are essential for stable operation. Thermostating was provided by immersing the detector in a stirred 2-l water bath in an insulated container. Liquid transfer lines were encased in rubber tubing. The pump was a Model D-018 Milton Roy Mini-Pump used in a system shown schematically in Fig. 3.

Degassing of the mobile phase was accomplished by passing between the mobile phase reservoir and the suction side of the pump. Off-gas from the degasser was returned to the solvent reservoir which operated under atmospheric pressure. Since trace amounts of water in the mobile phase deactivate the detector adsorbent and cause considerable loss in sensitivity, the mobile phase had to be dried. Drying was accomplished by passing the pump discharge through a bed of 60–200-mesh silica gel (Fisher, grade 950) contained in a section of 3/8-in. O.D. stainless-steel

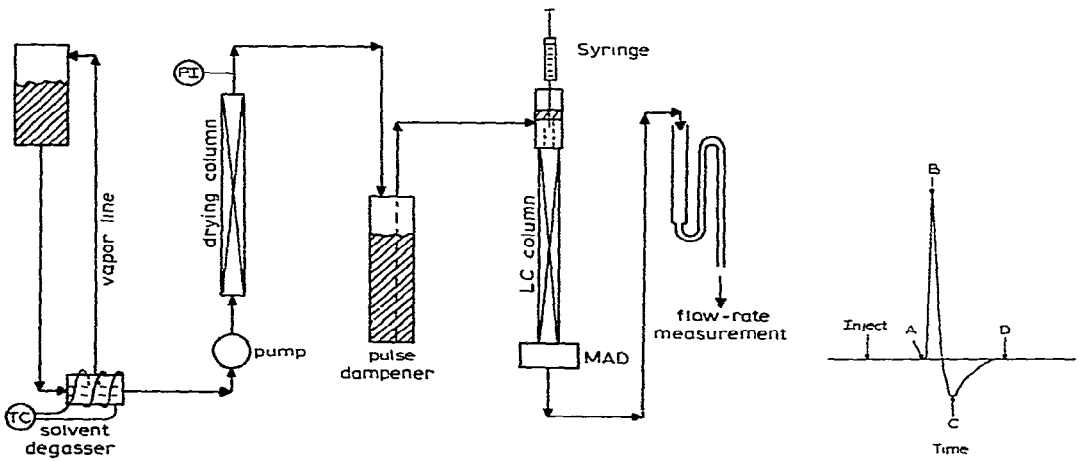


Fig. 3. Flow diagram of the HPLC system.

Fig. 4. Definition of the regions of the response from a MAD detector. A–B = positive peak height; A–C = negative peak height; B–C = total peak height.

tubing, 4 ft. long, fitted with sintered stainless-steel filters on each end. The silica gel was activated by heating for 48 h at 140°. It was changed every 48 h.

The pressure fluctuated about 10% of maximum pressure per stroke resulting in an unacceptable noise level in the MAD output signal. This pressure oscillation was damped by filling the pressure pump reservoir half full of mobile phase. In this manner the mobile phase vapor acted as a buffer against the pump stroke and damped the pressure fluctuation. The noise level was reduced from 50 μV to less than 5 μV with this buffer tank.

Data system. The output signal from the MAD was recorded on a Westronics Model LD11AD, 1-mV dual-pen recorder with disc integrator. In addition, a digital data logger was employed. The MAD analog signal was fed in parallel to the recorder and to a Keithley Model 160 digital multimeter. The output from the multimeter was a digitized millivolt signal, which was converted and printed as ASCII coded punched paper tape. The interface between the multimeter and a Teletype printer was designed and built by the V.P.I. Chemistry Department Electronics Shop. The digitized data were read into the Digital PDP 8/I computer and processed. The Focal programs used in the study are available from the authors.

The system used for this study consisted of acetone as a solute and benzene as the mobile phase with Corning porous glass beads as adsorbent in the sensing cell and Corning smooth, low-surface-area glass beads in the reference cell. This system gave a strong, well defined, and readily reproducible signal. Sample dilutions were selected such that a 10-μl liquid sample gave approx. 75% full scale recorder deflection.

Referring to Fig. 4 the positive peak height was defined as the vertical distance from A to B; negative peak heights as the distance from A to C, and total peak height as the distance from B to C. The positive peak area was defined as the area above the base-line, and the negative peak area was defined as that area below the base-line. Total peak area was taken as the sum of these two. Mechanically it was easier and more precise to measure total peak height rather than either positive or negative heights.

The total, positive, and negative peak heights and widths were measured manually from the chromatograms. The areas were determined with a disc integrator and by computer integration of the punched data tape using a Digital Equipment Corporation model PDP 8/I computor and a Simpson's rule integration procedure. The standard deviations of ten replicate runs were compared at each concentration level and tested using Fisher's F test.

RESULTS AND DISCUSSION

The sensitivity and universal response of the micro-adsorption detector make its use as an HPLC detector appear very attractive. In order to interpret the MAD response, an analysis of the phenomena causing the response was required. Scott[12] has analyzed the heat flow in packed adsorption columns. However, he has neglected the amount of heat removed by the mobile phase. This may not be serious in the case of gaseous mobile phases, but certainly cannot be neglected when using a liquid mobile phase. Smuts *et al.*[11] have attempted an analysis of the MAD output, but conclude that since the response deviates from the ideal in an unknown manner, it does not

appear possible to devise a means of converting the observed signal to an ideal signal which can be treated analytically.

Applying the observations of this work to the MAD response curve (Fig. 4) we can analyze the processes occuring in the adsorption cell under non-overloaded conditions. A component injected first encounters the adsorbent at point A; adsorption occurs and an increase in temperature begins and continues until point B is reached. At B, the maximum solute concentration has been reached, and after this point net adsorption, as opposed to dynamic exchange of solute molecules in the interfacial layer, stops, and the temperature begins to decrease, since no heat is being supplied by adsorption. As the concentration of the solute decreases, desorption of the solute begins and continues to point C. The negative temperature differential encountered prior to C is caused by the endothermic nature of the desorption process. Desorption is not complete at point C, but the maximum rate of desorption has been reached at this point; the ability of the environment to supply the energy necessary for desorption is just balanced by the heat uptake by the desorption process. At point D the desorption is completed, and the system re-equilibrates. The desorption curve differs greatly from the adsorption curve, in that the adsorption curve depends on the rate of adsorption and reaches a maximum at the maximum solute concentration, whereas the desorption process is dependent upon the ability of the environment to supply the heat for the endothermic reaction. Two assumptions are vital to this analysis: (1) the adsorption occupies only a small fraction of the adsorption sites, and is therefore not influenced by the availability of sites, and (2) only physisorption is considered.

The first assumption is probably valid up to the limit of the linear response range. Reproducibility of repeated runs verifies the second assumption. While the above analysis is applicable to non-overloaded conditions, it is reinforced and elucidated by consideration of overloaded conditions. Refering to Fig. 5 it can be seen that as larger samples are used the peak shape depends upon the sample size. The desorption peak width increases with sample size, and the shape of the desorption peak changes. As the solute concentration reaches the level which represents overloading, no further net adsorption can occur, and the temperature differential between the reference and adsorption cells decreases. The mobile phase rapidly carries

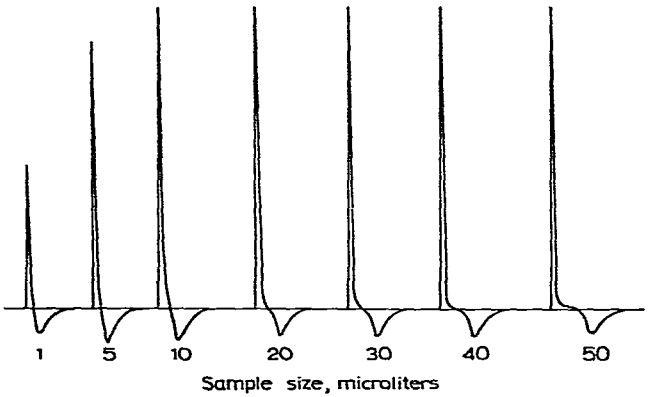


Fig. 5. Peak shape as function of sample size.

the heat away. If this concentration were maintained, the system would re-equilibrate, and the response curve would return to baseline, as indeed is shown, prior to desorption in the extreme case. If this concentration level were maintained only a single positive peak would be obtained. The origin of the broadening of the desorption peak is the increased amount of solute to be desorbed, and the limiting factor is the rate at which energy can be supplied by the environment. The delay in the negative peak is attributable to the fact that net desorption will not occur until the concentration of solute in the mobile phase has decreased to a level which will permit desorption. Saturation of the adsorption sites is indicated by the identical size and shape of the desorption peaks observed in the three largest sample sizes.

No adequate description of these processes in the adsorption cell and their relation to the observed response has been found in the literature, and certainly no attempt at a mathematical description has been found. From the complexity of the response signal, and the difficulties encountered in calibrating the negative peak, it would appear that Smuts, Richter and Pretorius[13] are correct in saying that a mathematical description in the near future is unlikely.

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