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CHEMICAL CHARACTERIZATION OF THE SURFACE SITES OF COAL

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CHEMICAL CHARACTERIZATION OF THE SURFACE SITES OF COAL

I. OBJECTIVES AND SCOPE OF WORK

We propose to do experimental studies in four related areas concerning the acid-base properties of coal surfaces; 1) develop high precision flow microcalorimetric methods for determining the concentrations and strengths of the acidic and basic surface sites of coal powders; 2) develop photo-acoustic FTIR and solid-state NMR spectral shift techniques for determination of the concentrations and strengths of acidic and basic surface sites of coal powders; 3) determine the concentrations and strengths of the acidic and basic surface sites of some of the well-characterized coal samples from Argonne National Labs, comparing the coal samples before and after demineralization treatments with HCl and HF; 4) study the effects of surface acidity and basicity on the coal/water interface, with emphasis on the role of interfacial acid-base interactions in the adsorption of ions, surfactants and coal/water slurry stabilizers.

A practical application of the new measurements of the acidity and basicity of surface sites will be to exploit acid-base contributions to preferential wettability for optimizing separation of coal pyrites from the organic components. We find that freshly ground coal pyrites are quite a bit more acidic than the the organic matter, and should be preferentially wet by a basic medium, so that pyrites separation from coal should be quite possible.

II. TECHNICAL PROGRESS

In this quarter we have concentrated on flow microcalorimetry for assessing the acidity and basicity of surface sites of coal powders, with emphasis on learning how to calibrate our Microscal calorimeter correctly. The Microscal flow microcalorimeter is by far the most sensitive calorimeter for studying the acid-base properties of the surface sites of powders, but it is difficult to calibrate with accuracy. We have used flow microcalorimetry to determine the surface concentration and the strength of acidic and basic surface sites of powders and fibers of various materials, and we have obtained repeatable results with many different kinds of powders or fibers, but we have been concerned more and more with the accuracy of the determinations. In recent studies with organic pigments we compared titrations of acidic and of basic sites with the Microscal flow microcalorimeter versus those done in a stirred suspension in a Tronac batch calorimeter, and found that the results with the flow microcalorimeter were about 60% too high. The Microscal is far more sensitive, but its calibration is not accurate. The Tronac is less sensitive, but its calibration is quite accurate. Clearly, both must be used for meaningful results.

Flow microcalorimetry of Coal Powders

In our previous research grant from DOE we developed techniques for titrating the concentrations and strengths of the acidic and basic surface sites of coal powders.¹ A main feature of this study was the use of organic solvents and acid-base probes which do not dissolve into coal. Following the lead of Larsen² and Squires³, we found that t-butyl pyridine and t-butyl phenol did not penetrate into coal as do pyridine and phenol, so that in successive adsorption-desorption cycles the amounts adsorbed from solution in iso-octane were closely matched by the amounts desorbed when pure iso-octane was

pumped through the bed. A high degree of repeatability was obtained, as evidenced in Figure 1.¹

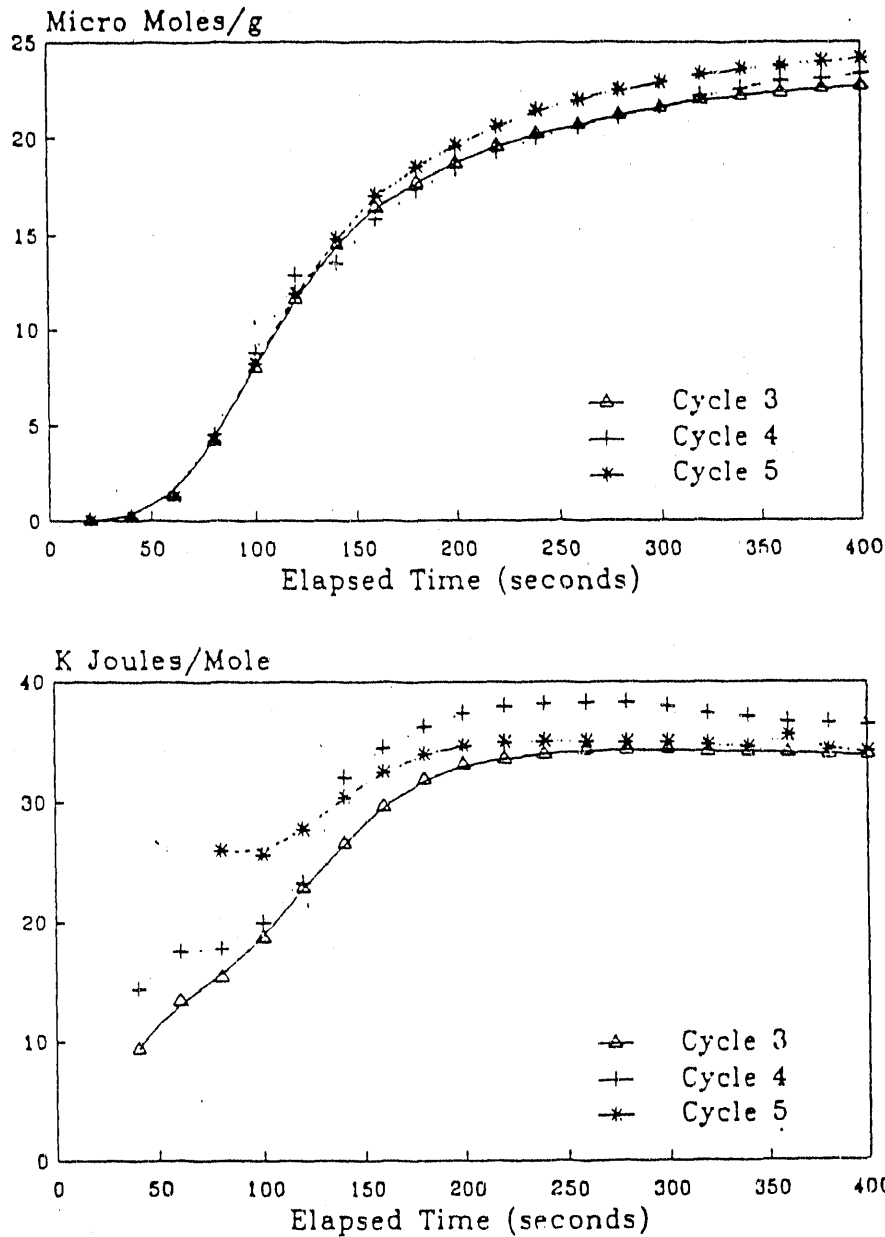


Figure 1.- Upper plot: Time dependence of the amount of 4-t-butylpyridine adsorbed onto PSOC #11 bituminous coal (in $\mu\text{mol/g}$) as solution is pumped through the adsorption bed. Lower Plot: Time dependence of the molar exothermic heats of adsorption (in kJ/mole) of 4-t-butylpyridine on PSOC #11 coal in the same three adsorption cycles illustrated above.¹

In more recent studies we have learned to plot flow microcalorimetric data like titrations, with plots of acid strength versus surface concentration, as illustrated below to show the acid strength of coal pyrite surfaces.

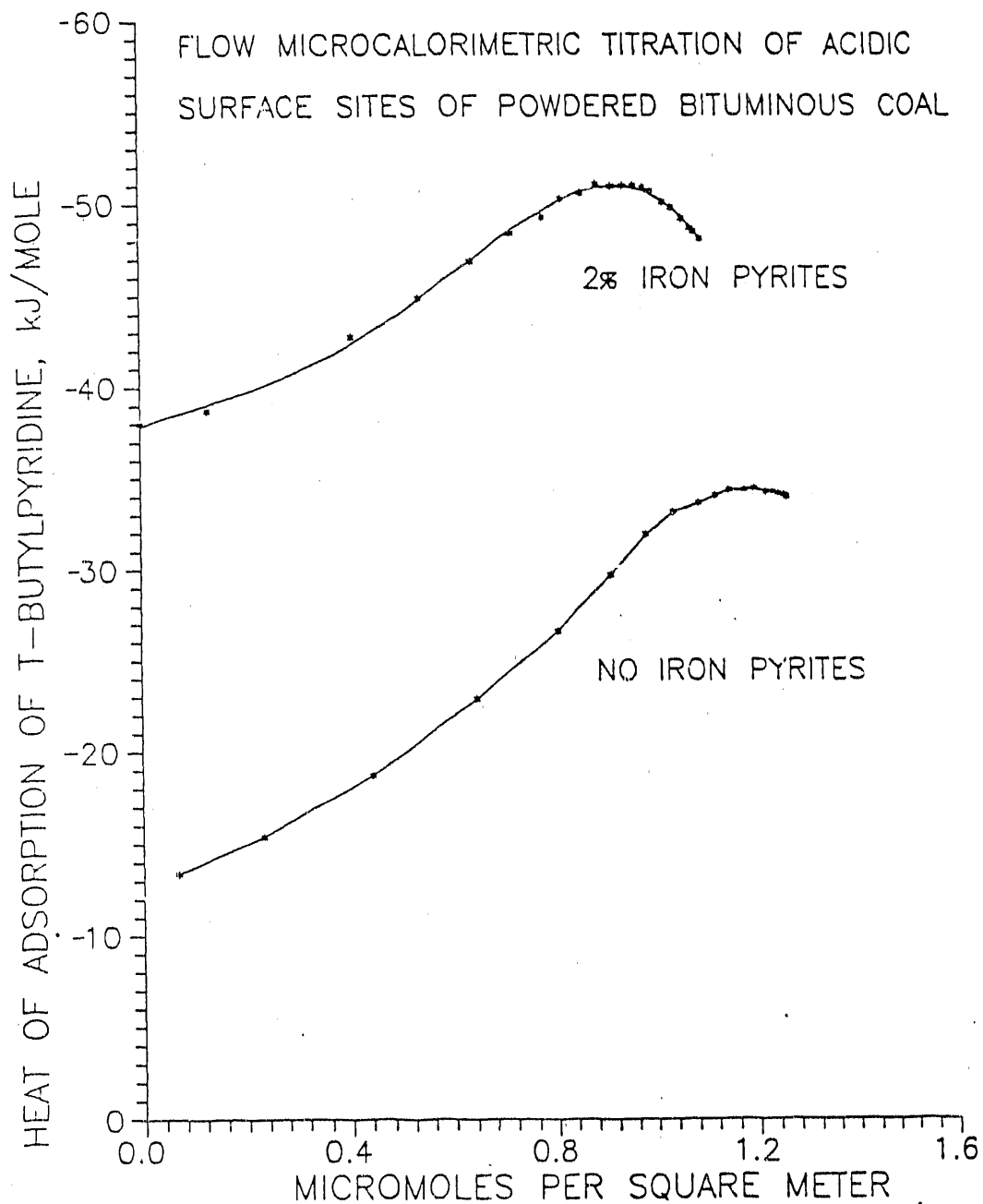


Figure 2. Cumulative exothermic heat of adsorption plots for t-butylpyridine adsorbing onto PSOC #213 bituminous coal (2% coal pyrites) and on PSOC #11 bituminous coal (no pyrites) by flow microcalorimetry.

The strong surface acidity of coal pyrites illustrated above was found only in freshly milled coal samples, and this strong surface acidity suggests that coal pyrites might be extractable with a process which could take advantage of the preferential wettability of these particles by basic media.

Our main concern in this study is to improve the analytical techniques for measuring the concentration and strength of acidic and basic surface sites, and in flow microcalorimetry the greatest current need appears to be for better calibration of the measured heats of adsorption. The magnitude of the heats of adsorption shown in Figures 1 and 2 are now known to be too high; actually the maximum heat of adsorption for the upper curve in Figure 2 is really about -30 kJ/mole rather than the -50 kJ/mole illustrated. This report concerns a study of how to correct this deficiency.

Experience with Flow Microcalorimetry with other Materials

The results of flow microcalorimetry depend very much on the kind of powder under test, particularly on its specific surface area, and on its hydrophilicity. We have had surprisingly good repeatability with glass fibers with less than $1 \text{ m}^2/\text{g}$,⁴ with magnetic iron oxide particles of $20 \text{ m}^2/\text{g}$,⁵ and with carbon blacks with $50\text{-}300 \text{ m}^2/\text{g}$.⁶ Figure 3 illustrates the results with the pyridine titration of magnetic iron oxides, showing excellent repeatability with four different loadings of the calorimeter with the same batch of oxide, and Figure 4 shows good repeatability for the titration of a carbon black (Vulcan 9; $140 \text{ m}^2/\text{g}$) with 4-t-butylphenol. The results for the magnetic iron oxides were uncorrected, but those for the carbon black were corrected, using a correction constant determined for perylene pigments ($50\text{-}75 \text{ m}^2/\text{g}$) as shown in Table 1.

Search for a Flow Microcalorimetric Calibration Standard

We have sought to develop a calibration standard for the Microscal flow

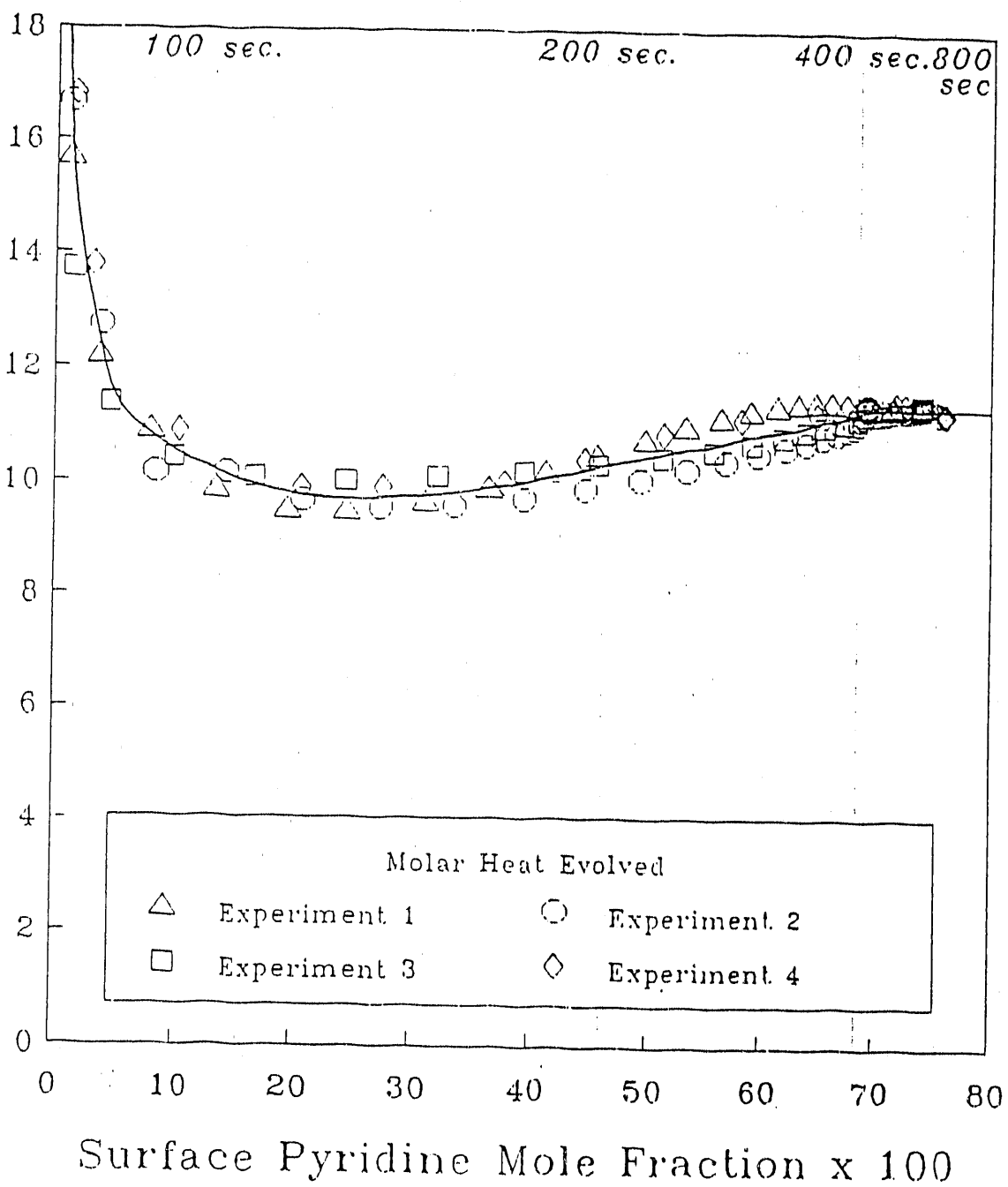


Figure 3.- Flow microcalorimetric titration of the acidic surface sites of gamma iron oxide by pyridine in cyclohexane at 30° C. Four separate runs were made with material from the same production lot.⁵

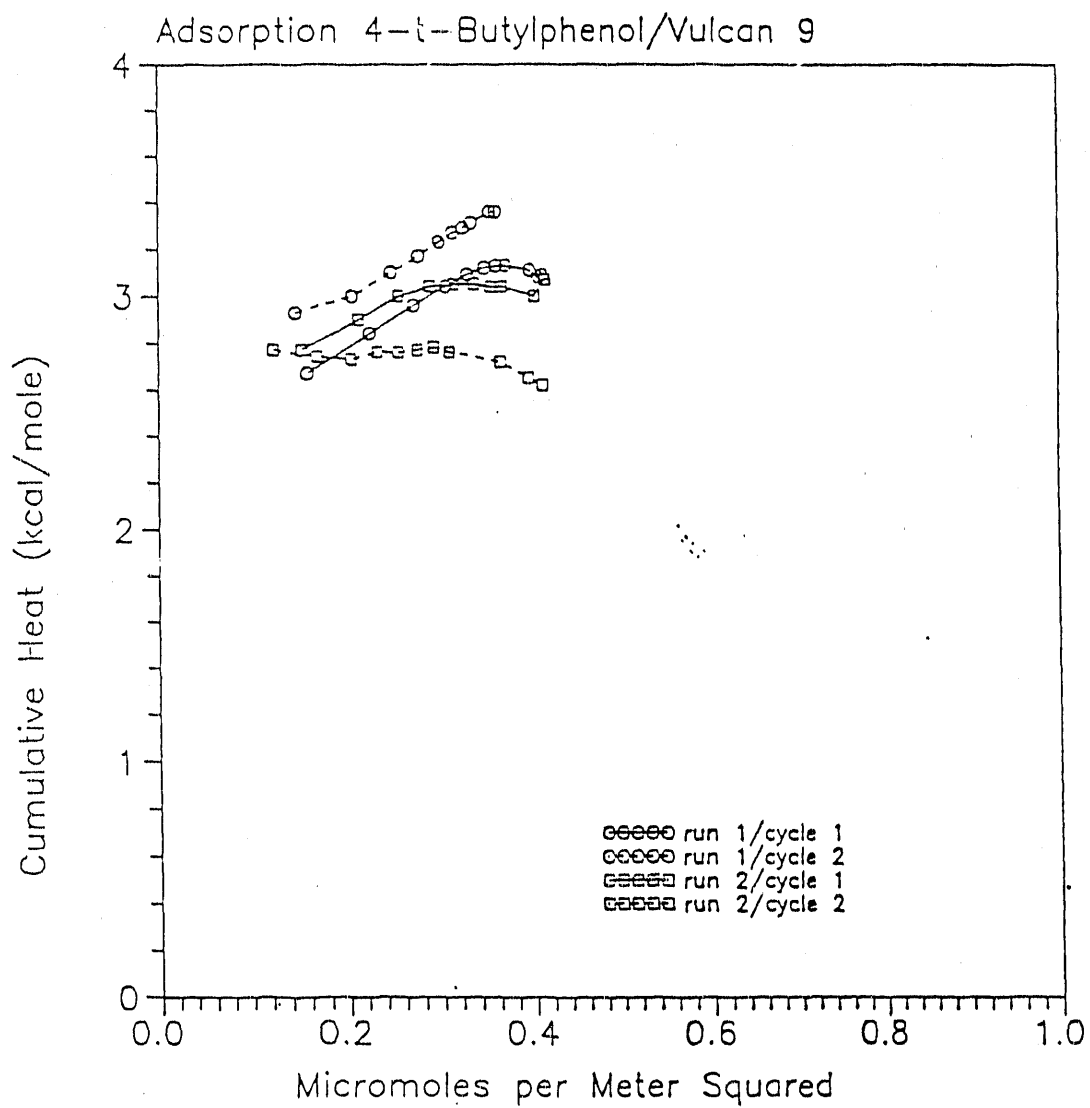


Figure 4.- Flow microcalorimetric titration of the basic surface sites of a carbon black (Vulcan 9) from Cabot, using a solution of t-butylphenol in cyclohexane at 30° C.

Table 1 Comparison of heats detected by the Microscal (flow) and the Tronac (batch) calorimeters to assess the thermal calibration techniques used in the Microscal studies. Average Ratio's of heat/unit area of Flow:Batch measurements are given.

System Compared	Heat ($\mu\text{cal}/\text{m}^2$)	
	Flow	Batch
19.8 mM pyridine in cyclohexane onto pigment Red 179	5839 6674	3938
<u>Average Ratio: 1.59</u>		
19.8 mM pyridine in cyclohexane onto pigment Violet 19	5165 6093	3733
<u>Average Ratio: 1.51</u>		
18.6 mM phenol in cyclohexane onto pigment Red 179	34800	21000
<u>Average Ratio: 1.66</u>		
19.5 mM phenol in cyclohexane onto pigment Violet 19	21540 22125	14080
<u>Average Ratio: 1.54</u>		
Average Ratio of the Systems: 1.57		

microcalorimeter, a powder with surface sites of uniform acidic or basic strength fully characterized by quantitative analytical techniques. Our first try has been with a silica powder, available in high purity, and with well-characterized surface acidity.⁷ Hi-Sil 233 silica from PPG, with a specific surface area of 127.1 m²/g was tried first, because this was the silica titrated in suspension in a decalin solution in a Tronac batch calorimeter for the first determination of its surface acidity.⁷ However, we have had difficulties. In eight separate runs, considerable irreproducibility in titration of the acidic sites was observed with pyridine solutions in decalin at 30° C.

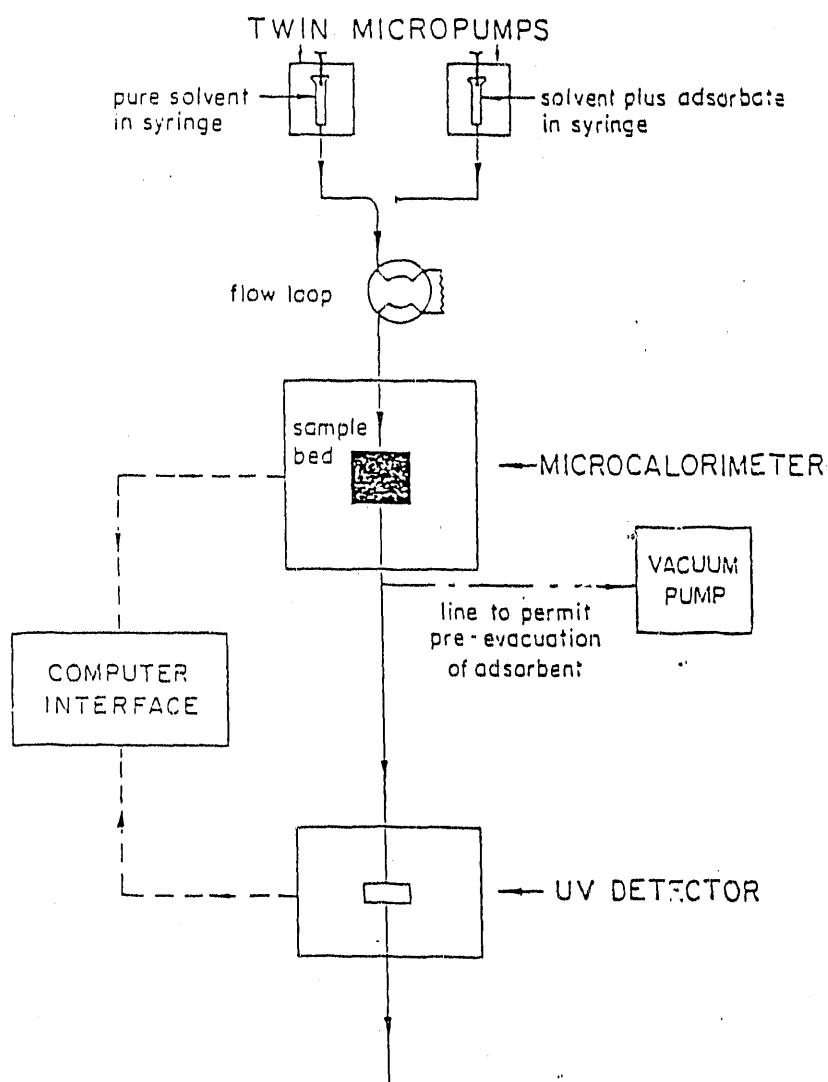


Figure 5. Flow diagram of flow microcalorimeter apparatus.⁸

Figure 6 and 7 show the differential and cumulative heats of adsorption of pyridine from solution in decalin adsorbing onto HiSil 233 at 30° C. These are the results of three of the eight runs made with this system, and they show much more scatter than we usually see. Run 8 is by far the best, with constant heats of adsorption over a wide coverage, but why such a scatter? Perhaps the combination of high surface area and high hydrophilicity provides particle agglomeration which leads to channelling and by-passing of portions of the bed. Details of these runs are shown in Figures 8 and 9, which point out that even after a one-hour run adsorption is far from complete, for the flux of the heat of adsorption is still about -5 mJ/minute after an hour of adsorption, and the concentration of pyridine in the eluent from the bed is still about 15% below the input concentration. It appears that the large adsorption capacity of this powder and the very slow rate of adsorption are giving us trouble. We have now a silica powder of about 35 m²/g for further tests; this should give a lower adsorption capacity. With decalin we could easily operate at higher temperatures, perhaps 50° C.; this should speed the rate of adsorption four-fold and allow completion of the titration in an hour or less.

Figure 6 shows the cumulative heat of adsorption of pyridine on silica measured with flow microcalorimetry, and compared with a batch titration in the Tronac calorimeter. Obviously, the Microscal heat is greater than that determined with accuracy in the Tronac. The Microscal calibration is done with heat input into the bed from a wire that is heated to produce a known amount of heat, but this heat is not generated throughout the bed in the same geometry as when a heat of adsorption generates heat. Obviously more of the heat from the hot wire bypasses the thermistors than with adsorption heat. The best run is #8, and its terminal value is about 82 kJ/mole, 1.57 times the

Tronac result, exactly the same ratio that was determined with the perylene pigment (Table 1).

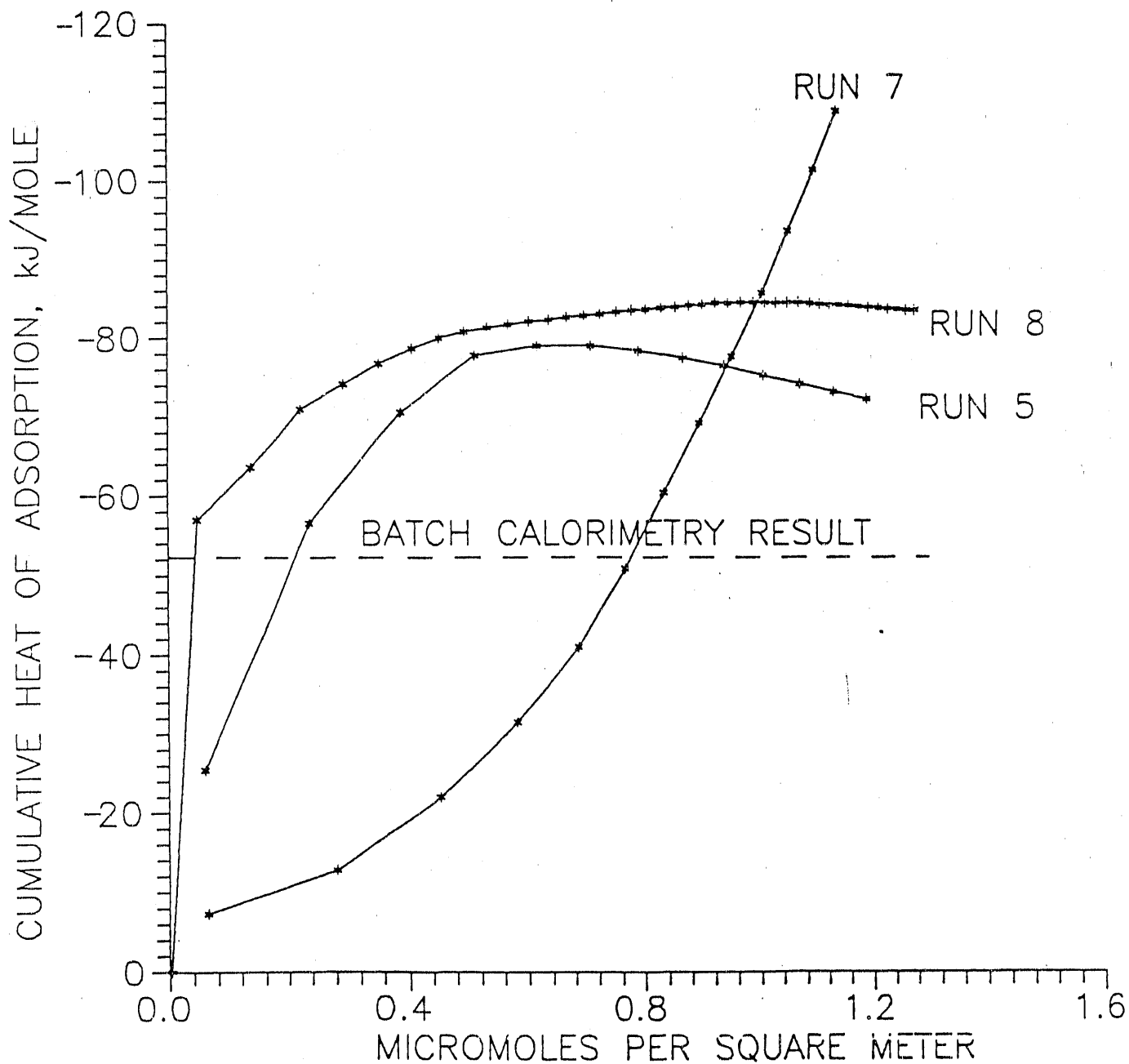


Figure 6. Cumulative heats of adsorption of pyridine from decalin at 30° C. versus surface coverage of HiSil 233 silica, from three presumably identical runs. Run #8 is what we expected to see, and what we expected to repeat.

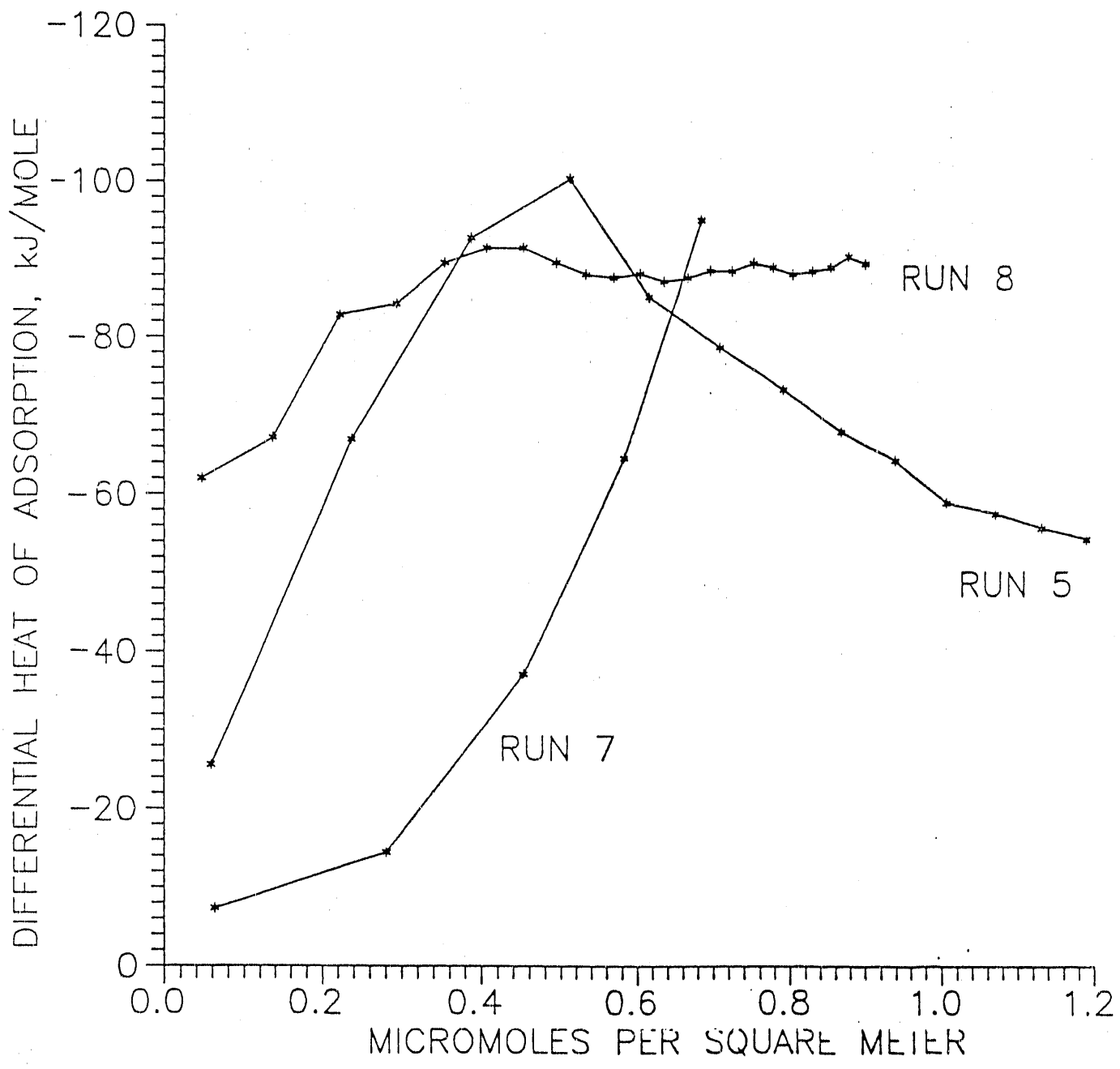


Figure 7.- Differential heat of adsorption of pyridine onto HiSil 233 silica from decalin at 30° C. Run #8 looks very good, but the others do not

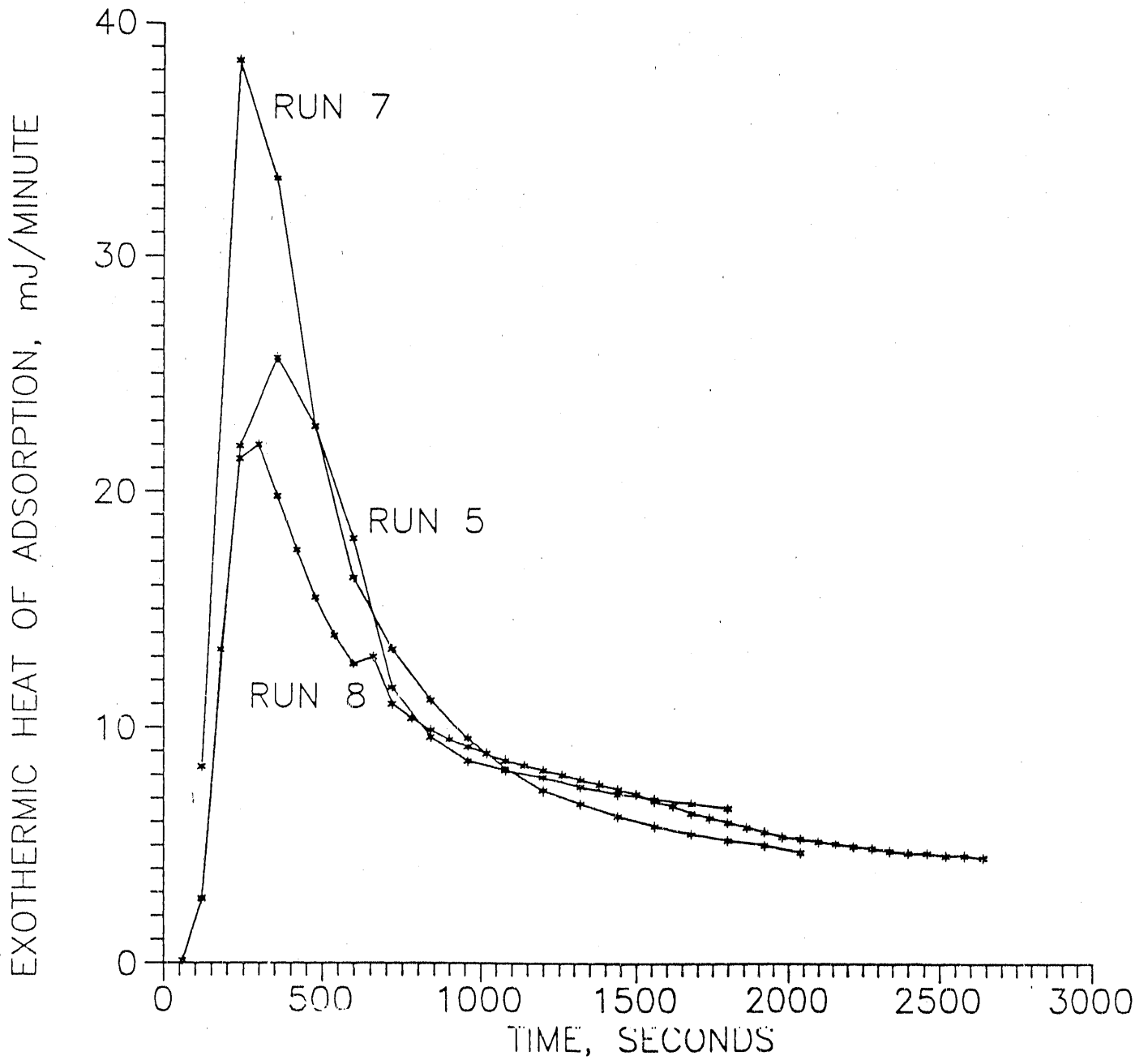


Figure 8.- Rate of heat generation in the calorimeter bed resulting from adsorption of pyridine from decalin at 30° C. onto HiSil 233 silica. The best run (#8) had the slowest climb in rate of heat generation.

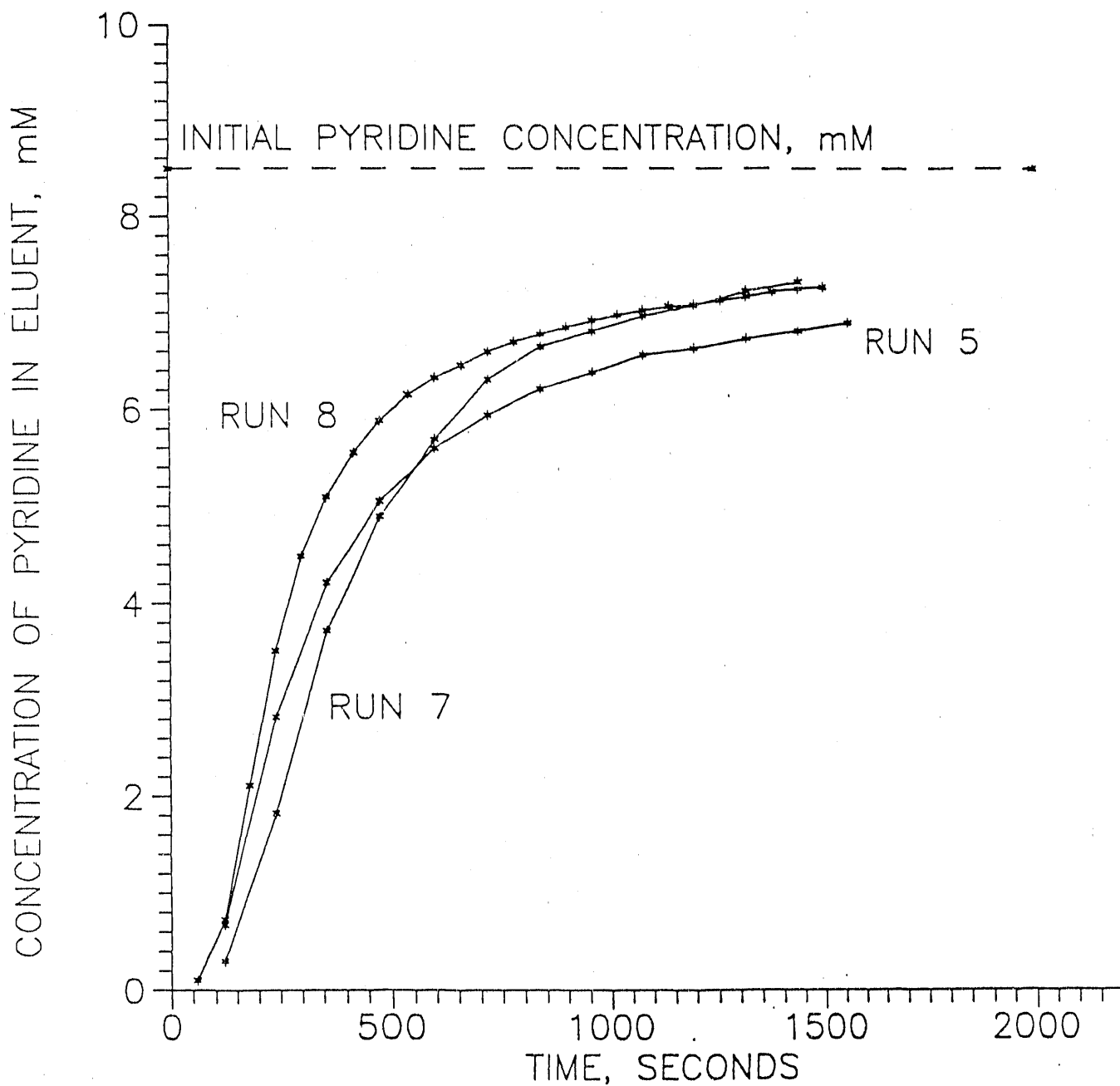


Figure 9. Concentration of pyridine in effluent from the adsorption bed during the surface titration by flow microcalorimetry. Note that even after 1500 seconds, the pyridine concentration remains about 15% below the input concentration.

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