USE OF REGULARIZATION FOR ESTIMATION OF PORE SIZE DISTRIBUTIONS

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Introduction

There has been considerable activity on the subject of estimation of pore size distributions from characterization data, and a variety of techniques have been developed for this purpose [1]. The principal characterization tool has traditionally been adsorption, though more recently various others also been utilized. In all of these cases the estimation of the pore size distribution involves inversion of an integral equation of the type

$$\Psi(\nu) = \int_0^\infty \psi(x,\nu) f(x) dx \qquad (1)$$

in which ν is an independent variable, $\psi(x,\nu)$ a theoretical response for a pore of size x, f(x) the pore volume distribution and $\psi(\nu)$ the overall observed response. For example for adsorption ν would represent the pressure (P) and $\psi(\nu,x)$ the local isotherm in a pore of size x. Given discrete data $\psi(x,\nu)$ the inversion of Eq. (1) is a classic ill-conditioned problem, prone to yielding unstable and oscillatory solutions. Such difficulties are well known to plague the traditional BJH and other techniques, often used with adsorption data [1], with results sensitive to choice of experimental pressure points. To obviate such difficulties the method of Tikhonov and Arsenin [2] suggests the use of regularization involving minimization of the objective

$$E_\alpha = \left\|\mathbf{Af} - \mathbf{C}_a\right\|_\rho^2 + \alpha\left[\left\|\mathbf{f}\right\|^2 + q\left\|\frac{d\mathbf{f}}{dx}\right\|^2\right] \qquad (2)$$

in which $\mathbf{C}_a$ is the measured isotherm, α a small filtering parameter and q a parameter of O(1).

We report here an application of the above Tikhonov method to adsorption, with the matrix operator **A** representing a finite element collocation discretization of the integral in Eq. (1). It is shown that the technique developed yields stable and converged non-negative solutions, while requiring very modest computational times.

Theory

Our algorithm for the solution of Eq. (1) permits different local response models in different pore size ranges. In the language of adsorption, for $0 \le x \le x_m$ micropore filling occurs, with capillary condensation in $x_m < x \le x_p(P)$ and multilayer adsorption for $x > x_p(P)$. However, the approach also accommodates a single isotherm, such as that from density functional theory. Consistent with this picture we rewrite Eq. (1), in the language of adsorption, as

$$C_a(P) = \int_{x_{min}}^{x_m} \rho(x,P) f(x) dx + \int_{x_m}^{x_p(P)} \rho_c(x,P) f(x) dx + \int_{x_p(P)}^{x_{max}} \rho_s(x,P) f(x) dx \qquad (3)$$

where $\rho(x,P)$ is the adsorbate density in a pore of size (half-width of a carbon slit-pore) x. After finite element collocation discretization of Eq. (3) we obtain the form

$$\mathbf{C}_a = \mathbf{Af} \qquad (4)$$

which is to be solved for the unknown vector **f** representing the pore size distribution values at the grid points. This is accomplished by minimizing the modified relative error-related objective

$$E_\alpha = (\mathbf{f}^*\mathbf{A}^* - \mathbf{C}_a^*)\mathbf{G}^{-1}\mathbf{G}^{-1}(\mathbf{Af} - \mathbf{C}_a) + \alpha\left[\mathbf{f}^*\mathbf{Wf} + q\mathbf{f}''^*\mathbf{Wf}''\right] + \mathbf{f}^*\Delta\lambda \qquad (5)$$

where λ is a vector of Lagrange multipliers. In Eq. (5) **W** and **G** are diagonal matrices of integration weights and measured amounts adsorbed respectively. Further, the vector **f''** represents the derivatives at the various collocation points, while Δ represents a constraint matrix following

$$\Delta^*\mathbf{f} = 0 \qquad (6)$$

Minimization of E_α provides the regularized solution for **f**. In case of an absolute error norm G becomes the identity matrix. For ensuring positivity of the solutions a Newton-Raphson method is used, and is much more efficient than the algorithm NNLS of Lawson and Hanson [3]. Further, the choice of α is made by matching the fitting error for the non-negative solution with the known measurement errors. More details of the finite element collocation discretization and regularization procedure are available elsewhere [4].

Results and Discussion

The above approach has been validated against several simulated isotherms for assumed pore size distributions. Initially CO_2 adsorption on a bimodial slit-pore activated

carbon at 195K was considered, with a Dubinin-Radushkevich isotherm over $0 \le x < \infty$ and a normally distributed random relative error having standard deviation of 1%. Figure 1 depicts the true and inversion pore size distributions from a 100 point overall isotherm, demonstrating convergence and good agreement. Here N_s is the number of elements and N the number of collocation points in each element. The agreement for the second mode was considerably improved when an additional 50 points were used in the high pressure region, indicating the importance of appropriately choosing the data points. Figure 2 depicts the variation of standard deviation of fitting error for the 100 and 150 point isotherms, with α, indicating the oscillations at small values of α with subsequent stabilization to the 1% level (the data error) over a wide range of values of α. On the other hand if the inversion used an absolute error norm the error was significantly larger and a much higher value of α was needed before stabilization occurred, and the result was much less satisfactory, as discussed elsewhere [4]. These observations also indicate the importance of appropriate choice of the fitting error norm.

Although we have outlined here the results for a single isotherm for all sizes, the algorithm has also been successfully applied [4] with different isotherm models in different pore size ranges. In addition the technique has been found to be more efficient than one involving nonlinear regression, while yielding consistent results for NORIT activated carbon with experimental CO_2 adsorption data [5].

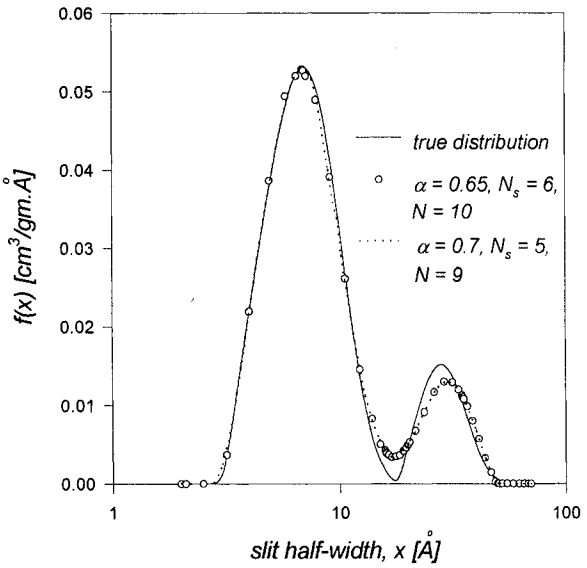

Figure 1. Estimated and true pore size distributions, using simulated isotherm for adsorption of CO_2.

Conclusions

Regularization with collocation over finite elements offers an attractive and efficient means for inverting characterization data.

The algorithm is general enough to be used with any combination of isotherm or characterization technique-specific models, and should have wide applicability.

References

1. Gregg, S.G. and Sing, K.S.W., *Adsorption, Surface Area and Porosity*, Academic Press. New York, 1982.
2. Tikhonov, A.N. and Arsenin, V.Y., *Solution of Ill-Posed Problems*, Winston. Washington D.C., 1977.
3. Lawson, C.L. and Hanson, R.J., *Solving Least Squares Problems*, Prentice Hall. Englewood Cliffs, N.J., 1974.
4. Bhatia, S.K., *Langmuir*, submitted, 1997.
5. Bhatia, S.K. and Shethna, H.K., *Langmuir*, **10**, 3230 (1994).

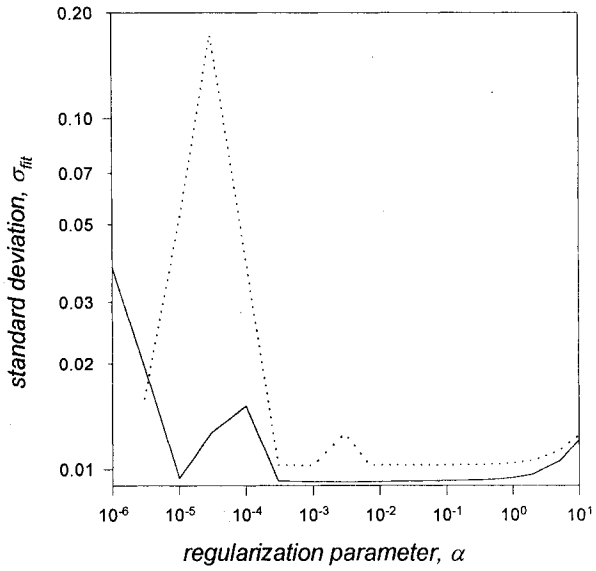

Figure 2. Variation of standard deviation of fitting error with regularization parameter α, for 100 point (solid line) and 150 point (dashed line) isotherms.