Optimal designs for estimating dielectric constants of polymers

Yiliang Zhu and Donald G. Watts
Department of Mathematics and Statistics, Queen's University, Kingston, Ontario, Canada K7L 3N6
(Received 6 May 1987; accepted 13 June 1987)

A statistical design criterion is applied to the problem of estimating dielectric constants in the model proposed by Havriliak and Negami. Under this criterion, the volume of the joint inference region of the parameter estimates is minimized. Because a computer program must be used to determine the optimal design points, simple approximating equations are presented for more practical use.

(Keywords: dielectric constant; statistical experimental design; D-optimal design; multiresponse estimation)

INTRODUCTION

Havriliak and Negami[1] proposed a model for the dielectric behaviour of polymers in the form

$$\varepsilon^*(f)=\varepsilon_\infty+(\varepsilon_0-\varepsilon_\infty)\left[1+\left(i\frac{2\pi}{f_0}f\right)^\alpha\right]^{-\beta} \quad (1)$$

where $\varepsilon^*(f)$ is the complex dielectric constant measured at oscillator frequency f (Hz), ε_∞ and ε_0 are the instantaneous and equilibrium dielectric constants, respectively, $i=(-1)^{1/2}$, and f_0 is the relaxation frequency. For different values of α and β, the model (1) includes other dispersion models. For example, when $\beta=1$ the Cole–Cole[2] expression is obtained, and when $\alpha=1$, the Cole–Davidson[3] expression is obtained.

Graphical[4] methods have been used to estimate the unknown parameters in (1), but more recently, multiresponse statistical methods have been applied by Havriliak and Watts[5] to obtain objective parameter estimates and to provide measures of precision for the estimates. To generate data which provide parameter estimates with the best precision, optimal statistical designs should be used.

D-OPTIMAL DESIGNS

An important measure of the precision of parameter estimates is the volume of the joint inference region for the parameters. If the experiment is designed so that this volume is minimized when generating the data, then the experimental design is called D-optimal. Draper and Hunter[6–8] formulated a general D-optimal criterion for the situation where there are multiple responses and the responses are nonlinear in the parameters.

Suppose there are M responses measured at N experimental settings, with P parameters and K variables involved in the model. Using a first-order Taylor series expansion with respect to the parameters, the volume of the approximate joint inference region is proportional to the square root of the reciprocal of $\det(\mathbf{X}^T(\Sigma^{-1}\otimes\mathbf{I})\mathbf{X})$, where $\mathbf{X}^T=(\mathbf{X}_1^T,\ldots,\mathbf{X}_M^T)$ and the element of the nth row and the pth column of $\mathbf{X}_m$, $(\mathbf{X}_m)_{np}$, is the derivative of the mth response with respect to the pth parameter evaluated at the nth case. $\mathbf{I}$ is an $N\times N$ identity matrix and $\otimes$ is the direct product operator. The variance–covariance matrix, Σ, of the distrubances infecting the responses on a particular case is assumed known. Note that the design depends on the unknown parameters through the derivative matrices, $\mathbf{X}_m$, and on the terms in the variance–covariance matrix, Σ, so that preliminary estimates for the parameters and the covariance terms must be supplied. If the model is conditionally linear in some parameters, then it can be shown that the D-optimal criterion is independent of these conditionally linear parameters[9].

For the dielectric model, there are $M=2$ responses (the real and imaginary parts), $P=5$ parameters (ε_0, ε_∞, α, β and f_0) and $K=1$ design variable (the frequency f). Also, the parameters ε_0 and ε_∞ are conditionally linear. Because there are only two responses, the criterion reduces to maximizing

$$D(f)=\det(\mathbf{X}^T\mathbf{X}) \quad (2)$$

with respect to $f=(f_1,f_2,\ldots,f_N)^T$. In (2),

$$\mathbf{X}=\begin{bmatrix}\mathbf{X}_r-\dfrac{\rho}{\lambda}\mathbf{X}_i\\[2ex]\dfrac{(1-\rho)^{1/2}}{\lambda}\mathbf{X}_i\end{bmatrix}$$

λ is the ratio of the standard deviation of the imaginary part to that of the real part, ρ is the correlation between the noises infecting the two responses, and $\mathbf{X}_r$ and $\mathbf{X}_i$ are, respectively, the derivative matrices with respect to the parameters of the real and the imaginary parts. Thus the design depends on the parameters α, β and f_0, and on the covariance terms λ and ρ. Havriliak and Watts[5] found that usually $\lambda\geqslant 3$ and ρ was small ($-0.2<\rho<0.2$), and that $0.5<\alpha<0.9$, $0.3<\beta<0.7$ and $80<f_0<15\,000$. The information about ρ and λ is particularly valuable for experimental design purposes.

0032-3861/88/020325-04$03.00

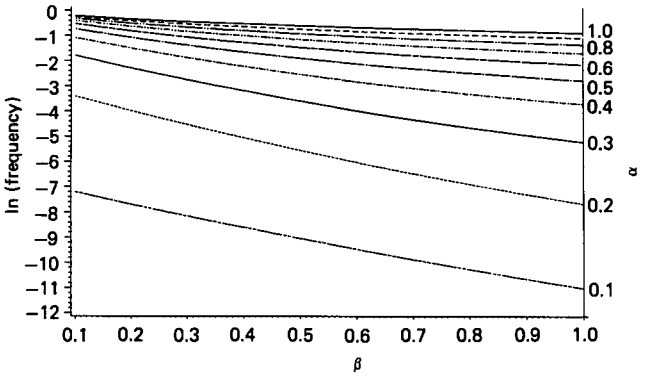

Figure 1 Plot of standardized optimum design frequency f_2^*. Curves are smoothed by spline

RESULTS

For the uniresponse case with P parameters, it has been shown[10] that optimal designs with N runs consist of replications of the optimal points required for a P-point design. Accordingly, we consider optimal designs with N equal to a multiple of five runs, where the five runs are determined using a generalized Gauss–Newton method[11]. Ideally, the oscillator frequency would extend from 0 to ∞, but in practice, $5 \leqslant f \leqslant 500\,000$ is a reasonable range[5]. In the following, we consider the ideal situation and the practical situation separately.

Ideal situation: $0 < f < \infty$

As might be expected, two of the design points should be at the lowest and the highest possible frequencies, so that if we denote the optimal design frequencies by $\hat{f} = (\hat{f}_1, \hat{f}_2, \hat{f}_3, \hat{f}_4, \hat{f}_5)^T$ with $\hat{f}_1 \leqslant \hat{f}_2 \leqslant f_3 \leqslant f_4 \leqslant f_5$, then $\hat{f}_1 = 0$ and $\hat{f}_5 = \infty$. Furthermore, given α, β, λ and ρ, the points in any two designs corresponding to different true relaxation frequencies f_0^1 and f_0^2 satisfy

$$\frac{\hat{f}_i^1}{f_0^1} = \frac{\hat{f}_i^2}{f_0^2} \qquad (i = 2, 3, 4) \tag{3}$$

where the superscripts refer to the two designs and the subscript refers to the ith design point. It is therefore convenient to determine the optimum design frequencies f_i^* for the standardized relaxation frequency $f_0^* = 2\pi$ and then compute the optimum design frequencies $\hat{f}_i$ at a different relaxation frequency, say f_0, as

$$\hat{f}_i = \left[\frac{f_0}{2\pi}\right] f_i^* \tag{4}$$

For conditions which occur in practice[5] ($-0.2 \leqslant \rho \leqslant 0.2$, and $3 \leqslant \lambda$), it was found that, for given α and β, all the designs can be well approximated by those with $\lambda = \infty$, which corresponds to the situation when only the real part of the response is measured. If, further, $|\rho| < 0.1$, the approximation is valid for $2 \leqslant \lambda$.

Plots of the standardized optimum design frequencies f_2^*, f_3^*, f_4^* for the range of α and β values used are given in *Figures 1–3*. The frequency curves are smooth and monotone, and could be used to obtain actual design frequencies using the relation (4). For $\lambda \leqslant 1$, the design frequencies are no longer monotone in α and β, and when $\lambda \leqslant 0.3$, it is impossible to estimate both ε_0 and ε_∞, and so the model cannot be fitted.

These results are informative, but they are not of practical use since they were derived under the assumption of ideal conditions, i.e. $0 < f < \infty$. To provide more useful designs, we incorporate bounds on the frequencies which can be applied.

Practical situation: $5 \leqslant f \leqslant 500\,000$

Under the practical restriction $5 \leqslant f \leqslant 500\,000$, the designs remain insensitive to λ and ρ when $\lambda \geqslant 3$, so we use designs with $\lambda = \infty$ to approximate those for finite λ. As before, f_1 should be as low as possible with f_5 as high as possible. We thus set $\hat{f}_1 = 5$ and $\hat{f}_5 = 500\,000$. However, the simple proportional relation (3) no longer pertains because of the frequency bounds, and so it is not possible to use the standard relaxation frequency $f_0^* = 2\pi$ and scale with the relation (4). Thus, for each specified set α, β and f_0, an optimization must be performed. This motivated us to search for a polynomial approximation to optimal designs suitable for $\lambda = \infty$ and $-0.2 < \rho < 0.2$.

Exact optimal design frequencies for $\lambda = \infty$, $\ln(f_0/2\pi) = 2.5, 3.0, \ldots, 7.5$, $\alpha = 0.1, 0.2, \ldots, 1.0$ and $\beta = 0.1, 0.2, \ldots, 1.0$ were obtained and polynomial models were fitted, by least squares, to each optimal frequency as a function of α, β and f_0. To a good approximation, the design frequencies are

$$\tilde{f}_1 = 5$$

$$\ln \tilde{f}_2 = \ln(f_0/2\pi) + 6.45 - 10.20\,\alpha - 0.64\,\beta - 1.68 \ln(f_0/2\pi) + 4.75\,\alpha^2 + 0.04\,[\ln(f_0/2\pi)]^2 + 2.11\,\alpha \ln(f_0/2\pi) - 0.86\,\alpha^2 \ln(f_0/2\pi)$$

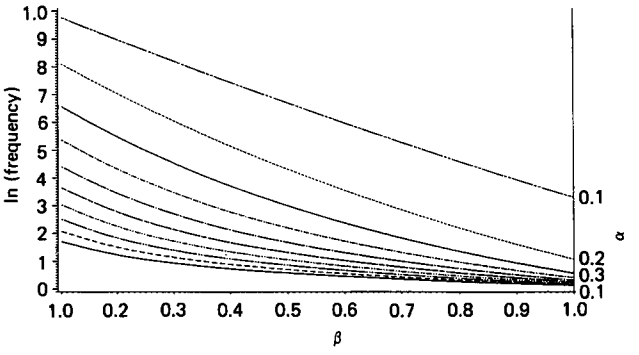

Figure 2 Plot of standardized optimum design frequency f_3^*. Curves are smoothed by spline

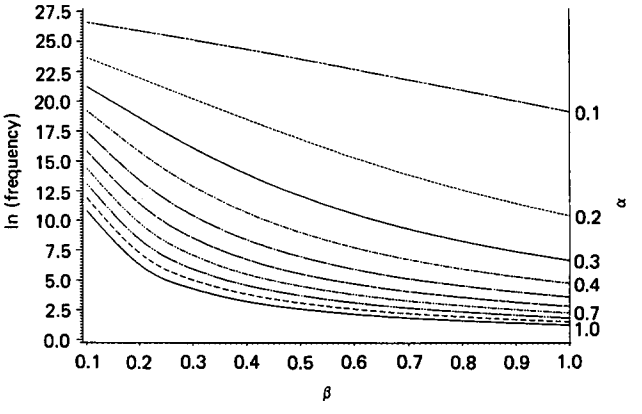

Figure 3 Plot of standardized optimum design frequency f_4^*. Curves are smoothed by spline

Table 1 Exact and approximate optimal designs

	Frequency					
	f_1	f_2	f_3	f_4	f_5	Determinant
Polycarbonate						
Optimal	5	76	515	10130	500000	5.44×10^{-3}
Approximate	5	74	515	10749	500000	5.43×10^{-3}
s-PMMA						
Optimal	5	95	1283	24556	500000	1.09×10^{-4}
Approximate	5	96	1260	23491	500000	1.09×10^{-4}

$$\ln \tilde{f}_3 = \ln(f_0/2\pi) + 10.71 - 14.00\,\alpha - 1.32\,\beta - 1.54\ln(f_0/2\pi) + 5.63\,\alpha^2 + 0.43\,\beta^2 + 0.02\,[\ln(f_0/2\pi)]^2 - 3.78\,\alpha\beta + 2.32\,\alpha\ln(f_0/2\pi) + 0.10\,\beta\ln(f_0/2\pi) + 3.16\,\beta\alpha^2 - 1.13\,\alpha^2\ln(f_0/2\pi)$$

$$\ln \tilde{f}_4 = \ln(f_0/2\pi) + 13.43 - 8.43\,\alpha + 2.94\,\beta - 1.57\ln(f_0/2\pi) + 1.46\,\alpha^2 - 2.05\,\beta^2 - 18.12\,\alpha\beta + 2.16\,\alpha\ln(f_0/2\pi) + 0.34\,\beta\ln(f_0/2\pi) + 7.30\,\alpha^2\beta - 0.91\,\alpha^2\ln(f_0/2\pi) + 4.60\,\alpha\beta^2$$

$$\tilde{f}_5 = 500000$$

The above expressions are not simple, but they are easy to compute, especially when compared to the calculations involved in maximizing a determinant. A typical relative error in a design frequency is less than 5%: as α, β and $\ln(f_0/2\pi)$ approach the ends of the ranges, the error increases, but even in the worst case, is less than 20%.

Examples

Havriliak and Watts[5] analysed dielectric data for polycarbonate and syndiotactic poly(methyl methacrylate) (s-PMMA), and found $\alpha=0.77$, $\beta=0.29$, $f_0=944$ and $\alpha=0.53$, $\beta=0.55$, $f_0=2864$, respectively. Using this information, we determined the exact and polynomial approximate optimal five-point designs as shown in *Table 1*. The approximate design points are seen to be very close to the optimum design points and the determinants are essentially equal.

COMPARISON OF DESIGNS

In this section, we compare the efficiency of designs based on the polynomial approximations, and designs typically used in practice, with optimal designs. The efficiency of a design, say $\tilde{f}$, relative to the optimal design, $\hat{f}$, can be defined as the square root of the ratio of the design determinant, $D(\tilde{f})$, to the optimal design determinant, $D(\hat{f})$. Then $\{D(\tilde{f})/D(\hat{f})\}^{1/2}$ gives the relative volume of the inference region for the optimal design to that of the design $\tilde{f}$. If the ratio is small, the design $\tilde{f}$ is poor because the parameters will be estimated with less precision; if the ratio is large, then the design $\tilde{f}$ is good because the parameters will be estimated with high precision.

In a typical experimental study of dielectrics, frequencies are selected by specifying a series of values, say 2, 3, 5, 7, 10, 15, on a unit dial and then applying power to the bridge at multiples of 10 times these frequencies. To allow comparison of a typical experimental design with a design consisting of replicated optimal points, we need to ensure that the typical design consists of a multiple of five runs. *Table 2* gives such a design by letting a design of $5L$ runs consist of the first L columns. For the optimal designs and the polynomial approximation designs, we replicate L times at each of the five optimal design frequencies. In this case, the determinant of the $5L$-run optimal (or polynomial approximation) design is L^5D, where D is the determinant of the five-point design. Because the optimal and polynomial approximation designs are determined with $\lambda=\infty$, to allow comparability with the typical designs, we let $\lambda=5$ and $\rho=0$ when calculating the determinants for the optimal and polynomial approximation designs.

In *Table 3*, we show the percentage efficiencies of the polynomial approximate optimal designs and the typical designs. For 25 runs, efficiencies for the typical designs drop to about 50%, while those for the polynomial approximations stay at 100%. With more observations, the efficiency of the typical design will become even worse.

DISCUSSION

Statistically designed experiments can be much more efficient than those planned otherwise. For this phenomenon, we have shown that typical designs, in which data are taken at roughly uniform spacing of frequency (on a logarithmic scale), are much less efficient than experiments in which replications are taken at statistically designed points. Experiments in which there are replications also provide vital information concerning the variances and covariances of the disturbances infecting the measurements, and so the optimal designs can be even more informative. For example, with even a modest number of replications, say three or four, it is possible to detect non-constant variance of the data and, using well established methods[12], to determine appropriate variance-stabilizing transformations if necessary.

We have also found that there is surprisingly little extra information gained about the parameters by measuring the imaginary part of the dielectric response.

Table 2 A 'typical' design

1	2	3	4	5
5	10	15	20	30
50	100	150	200	300
500	1000	1500	2000	3000
5000	10000	15000	20000	30000
	100000	150000	200000	300000
500000				

Table 3 Relative design efficiency (%) for $\lambda=5$, $\rho=0$

	Polycarbonate		s-PMMA	
L	Approximate	Typical	Approximate	Typical
1	100	90	100	67
2	100	74	100	70
3	100	63	100	62
4	100	57	100	60
5	100	55	100	55

Experimenters interested solely in precise estimation of the parameters in the Havriliak–Negami model need therefore only measure the real component.

REFERENCES

1 Havriliak, S. Jr and Negami, S. *Polymer* 1967, **8**, 161
2 Cole, R. H. and Cole, K. S. *J. Chem. Phys.* 1941, **9**, 341
3 Cole, R. H. and Davidson, D. J. *J. Chem. Phys.* 1950, **19**, 1484
4 Havriliak, S. Jr and Negami, S. *J. Polym. Sci. (C)* 1966, **14**, 99
5 Havriliak, S. Jr and Watts, D. G. *Polymer* 1986, **27**, 1509
6 Draper, N. R. and Hunter, W. G. *Biometrika* 1966, **53**, 525
7 Draper, N. R. and Hunter, W. G. *Biometrika* 1967, **54**, 147
8 Draper, N. R. and Hunter, W. G. *Biometrika* 1967, **54**, 662
9 Zhu, Y. *Master's Thesis* Queen's University, Kingston, Ontario, 1986
10 Box, M. J. *J. R. Statist. Soc.* 1968, **B30**, 290
11 Bates, D. M. and Watts, D. G. *SIAM J. Scient. Statist. Comput.* 1987, **8**, 49
12 Draper, N. R. and Smith, H. 'Applied Regression Analysis', 2nd Edn., Wiley, New York, 1981