FAST DETERMINATION OF OPTICAL CONSTANTS AND SAMPLE THICKNESS OF THIN LIQUID SAMPLES IN TERAHERTZ TIME-DOMAIN SPECTROSCOPY

F. Yang [1*], L.-P. Liu [2], M.-J. Song [1], F. Zhang [3]

[1] Guizhou Institute of Metrology,
Haimachong Road 111, Touqiao, Guiyang, 550003, China; e-mail: yfl8610@mail.ustc.edu.cn
[2] School of Pharmacy Engineering, Guizhou Institute of Technology, Guiyang, 550003, China
[3] Guiyang Vocational and Technical College, Biochemical engineering Department, Guiyang 550081, China

The accuracy of the extracted optical constants by terahertz time domain spectroscopy critically depends on the accuracy of the sample thickness. However, due to the large number of optimization steps, it is time consuming to extract the optical constants over a broad frequency range and determine the sample thickness simultaneously using conventional algorithms. With particular emphasis on thin liquid samples, a three-dimensional optimization algorithm was used to obtain the optical constants and sample thickness simultaneously, significantly reducing the calculation time. In the experiments, the THz signals of 200-μm-thick water in a known cuvette were measured, and its accurate thickness and optical constants were determined by the algorithm, validating the effectiveness of the approach.

Keywords: *terahertz time domain spectroscopy, Fabry–Perot, optical constants.*

БЫСТРОЕ ОПРЕДЕЛЕНИЕ ОПТИЧЕСКИХ КОНСТАНТ И ТОЛЩИНЫ ТОНКИХ ЖИДКОСТНЫХ ОБРАЗЦОВ МЕТОДОМ ТЕРАГЕРЦОВОЙ СПЕКТРОСКОПИИ С ВРЕМЕННЫМ РАЗРЕШЕНИЕМ

F. Yang [1*], L.-P. Liu [2], M.-J. Song [1], F. Zhang [3]

УДК 543.42;543.3

[1] Гуйчжоуский институт метрологии, Гуйян, 550003, Китай; e-mail: yfl8610@mail.ustc.edu.cn
[2] Школа фармации, Технологический институт Гуйчжоу, Гуйян, 550003, Китай
[3] Гуйянский профессионально-технический колледж, Гуйян 550081, Китай

(Поступила 4 июля 2017)

С использованием терагерцовой спектроскопии с временным разрешением и особенностей тонких жидкостных образцов предложен трехмерный алгоритм оптимизации, позволяющий одновременно получать оптические константы и толщину образца при значительном сокращении времени вычислений. Измерены терагерцовые сигналы слоя воды толщиной 200 мкм в кювете с известными параметрами. С помощью разработанного алгоритма определены его толщина и оптические константы воды с высокой точностью, что подтвердило эффективность предложенного подхода.

Ключевые слова: *терагерцовая спектроскопия с временным разрешением, Фабри—Перо, оптические константы.*

Introduction. In the past decades, terahertz time-domain spectroscopy (THz-TDS) has become a powerful spectroscopic technique to measure the materials' optical constants by identifying their fingerprint spectrum. For nearly homogenous solid samples, several material parameter extraction algorithms were proposed to determine the complex refractive indexes with THz-TDS by various research groups [1–3]; however, they are not applicable to strong absorbing material, especially water or hydrate, which has attracted particular interest within the terahertz community, since it plays a key role in the protein function expression [4, 5]. Because of strong interaction of water with terahertz radiation caused by its collective dynamics, the accuracy of extracting its optical constants is challenging.

Up to now, one scheme is to conduct the experiment in reflection geometries [6–8]. However, these schemes require very high accuracy of the optics position and orientation [9]. Another way is using thin film sample, e.g., sub-100-μm [10]; yet it suffers from overlapped Fabry-Pérot (FP)-echo pulses [11], which cannot be time separated well within a temporal scan. To resolve this issue, a numerical optimization procedure [3, 12–14] was employed by fitting the calculated theoretical transfer function to the measurement transfer function based on a guessed thickness. Afterwards, the sample thickness is accurately determined by performing the optimization for a set of thicknesses and minimizing the FP oscillation. This procedure is time consuming, since its optimization number is the product of the frequency steps and investigated thickness steps. Therefore, this study presents a novel method to extract optical constants of thin liquid samples, i.e., 200-μm-thick water in a cuvette, employing a single more sophisticated optimization over a three-dimensional set of parameters, including the real part and the imaginary part of the broadband refractive index and the sample thickness. The method is much less time consuming and accurate and thus is suitable for THz imaging and real-time monitoring.

In this paper the THz spectroscopy system in the experiments is described, the algorithm of parameter extraction is discussed in detail, and the experimental verification of the approach by analyzing thin samples of water is presented.

THz spectrometer. Figure 1 shows a typical THz-TDS system. The ultrafast femtosecond laser pulses, produced by an ultrafast laser generator, are divided into a probe beam and a pump beam by a beam splitter. The pump beam, after passing through a set of guiding optics, stimulates the THz emitter made with a photoconductive antenna to radiate out T-ray. The produced THz radiation is collimated and focused onto the sample and then is re-collimated and focused onto the THz receiver by off-axis parabolic mirrors. The pulse trace of T-ray signal is detected by the receiver and sampled by adjusting the optical path difference between the pump beam and probe beam with a computer controlled mechanical stage.

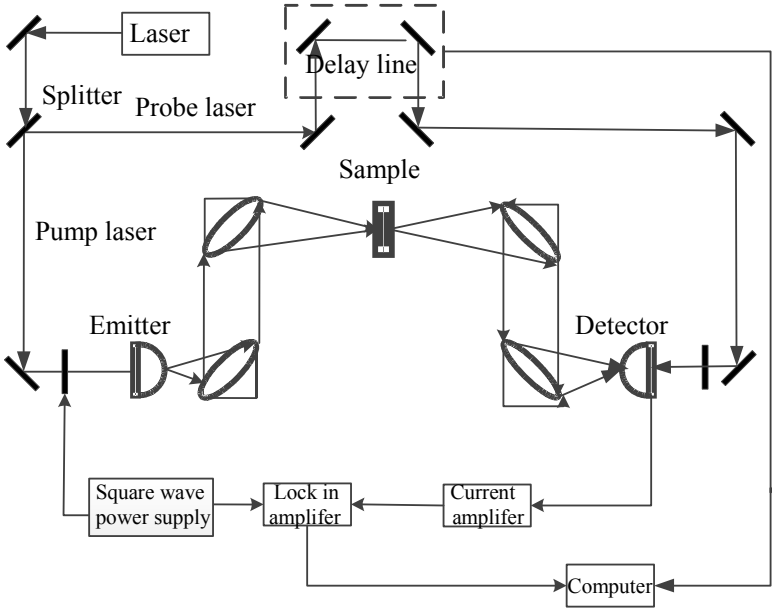

Fig. 1. THz-TDS system configured in transmission mode.

Algorithm. The optical constants of a liquid sample in a cuvette inserted in the THz spectrometer can be characterized by measuring the complex spectrum of the THz-wave propagating through the sample and through the empty cuvette, expressed as [15]

$$E_{\text{sam}} = E_0 T_{01} T_{12} P_1(l_1)^2 P_2(l_2) T_{21} T_{10} \left[1 + \sum_{i=1}^{M} \left(R_{21}^2 P_2(l_2)^2 \right)^i \right], \tag{1}$$

$$E_{\text{ref}} = E_0 T_{01} T_{10} P_1(l_1)^2 P_0(l_2) T_{01} T_{10} \left[1 + \sum_{i=1}^{M} \left(R_{01}^2 P_0(l_2)^2 \right)^i \right]. \tag{2}$$

Here, E_0 is the electric field of the terahertz wave emitted by the transmitting antenna, $T_{ab}(f) = 2\tilde{n}_a/(\tilde{n}_a + \tilde{n}_b)$ and $R_{ab}(f) = (\tilde{n}_b - \tilde{n}_a)/(\tilde{n}_a + \tilde{n}_b)$ are the transmission and reflection coefficients, respectively, from medium a to medium b, where f is the frequency, M is the maximal FP echo pulse that appears in the time window of the measurement. $P_a(f,d) = \exp[-2\pi\tilde{n}_a f d/c]$ is the propagation coefficient over a distance d with $\tilde{n}_a = n_a - j\kappa_a$ being the complex refractive index of medium a, where j is the imaginary unit, c is the speed of light in vacuum, and l_1 and l_2 represent the cuvette wall thickness and sample thickness, respectively.

The initial values of the complex refractive index should be derived first, where an experimentally determined transfer function $H_{\text{meas}}(f)$ is used, given by the ratio between these two complex spectra, i.e., $H_{\text{meas}}(f) = E_{\text{sam}}/E_{\text{ref}}$. Given an assumed sample thickness L_0, the initial values of the optical constants n_2 and κ_2 can be deduced as

$$n_{2,\text{init}}(f) = 1 - \frac{\arg\left[H_{\text{meas}}(f)\right]c}{2\pi f L_0}, \tag{3}$$

$$\kappa_{2,\text{init}}(f) = \frac{c}{2\pi f L_2}\left\{\ln\left[\frac{n_2(n_1+1)^2}{(n_1+n_2)^2}\right] - \ln\left[\left|H_{\text{meas}}(f)\right|\right]\right\}, \tag{4}$$

where the FP-oscillation is neglected. The phase of transfer function $\arg[H_{\text{meas}}(f)]$ is a continuous function by phase unwrapping [16]. The adapted phase unwrapping scheme discards the noisy phase at low frequencies (0 to ~0.2 THz) and carries out a normal unwrapping only with the reliable phase part. A missing phase profile at low frequencies down to DC is then extrapolated from the unwrapped phase at higher frequencies. If the unwrapping phase is not linear because of the signal noise, the phase is fitted to linear and is forced to start from 0 rad at DC.

Only if the correct sample thickness is used in the parameter extraction do the FP-oscillations of the optical constants disappear. Thus, by performing numeric optimizations to minimize the FP-oscillation amplitude over a set of assumed thicknesses, the correct thickness of the sample can be determined. The sample response for the THz waves can be described by the theoretically complex transfer function H_{theory} as

$$H_{\text{theory}}(n_2,\kappa_2,l_2) = \frac{(\tilde{n}_1+1)^2\tilde{n}_2}{(\tilde{n}_1+\tilde{n}_2)^2}\exp\left\{-j\left[\tilde{n}_2-1\right]\frac{2\pi f l_2}{c}\right\}\frac{\sum_{g=0}^{M}\exp(-j\frac{4g\pi f l_2\tilde{n}_2}{c})\left(\frac{\tilde{n}_1-\tilde{n}_2}{\tilde{n}_1+\tilde{n}_2}\right)^{2g}}{\sum_{g=0}^{M}\exp(-j\frac{4g\pi f l_2}{c})\left(\frac{\tilde{n}_1-1}{\tilde{n}_1+1}\right)^{2g}}. \tag{5}$$

Here, the parameter set to be optimized includes the real part n_2 and the imaginary part κ_2 of the refractive index together with the thickness l_2. For a thin sample, most FP echoes are overlapped in the time window (e.g., 2.1 ps delays between two echoes for 200 μm-thick water). In addition, the FP echo pulses after several reflections in the sample are very weak. Therefore, for the finite length of the experimental time window, infinitely many reflections can be treated in measuring thin sample. Thus, the transfer function when M tends to infinity can be represented as

$$H_{\text{theory}}(n_2,\kappa_2,l_2) = \tilde{n}_2\exp\left\{-j\left[\tilde{n}_2-1\right]\frac{2\pi f l_2}{c}\right\}\frac{(\tilde{n}_1+1)^2-(\tilde{n}_1-1)^2\exp(-j4\pi f l_2/c)}{(\tilde{n}_1+\tilde{n}_2)^2-(\tilde{n}_1-\tilde{n}_2)^2\exp(-j4\pi f l_2\tilde{n}_2/c)}. \tag{6}$$

In order to make the order of magnitude of parameters comparable in the numerical optimization, three scalar parameters ξ, ψ, and ζ are adopted

$$n_2(f) = \xi(n_{2,\text{init}}(f) - 1),\ \kappa_2(f) = \psi\kappa_{2,\text{init}}(f),\ l_2 = \zeta L_0. \tag{7}$$

Then, the resulting theoretical transfer function is given by

$$H(f) = H(f,\ \xi(n_{2,\text{init}}(f) - 1),\ \psi\kappa_{2,\text{init}}(f),\ \zeta L_0). \tag{8}$$

In the next step, a numerical optimization is performed to make the error function between the theoretical and the measured transfer functions as small as possible. In the optimization procedure, the Nelder-Mead simplex algorithm [17] is used with the initial values of all the three scalar parameters being 1, where the error function ΔH is defined as

$$\Delta H = \textstyle\sum_f |H_{\text{theory}}(f) - H_{\text{meas}}(f)|. \tag{9}$$

Equation (9) shows that the error function completely depends on the real and imaginary parts of the transfer function. Thus, the optical constants n_2, κ_2 and sample thickness l_2 significantly affect the error function.

Accordingly, after obtaining the optimal values of ξ_{opt}, ψ_{opt}, and ζ_{opt}, the thickness $l_{2,opt}$ is known, and the resulting material parameters can be calculated:

$$n_{2,opt}(f) = \xi_{opt}(n_{2,init}(f) - 1) + 1,\ \kappa_{2,opt}(f) = \psi_{opt}\kappa_{2,init}(f),\ l_{2,opt} = \zeta_{opt}L_0. \quad (10)$$

In the final step, in order to obtain precise material parameters, a single successive optimization is applied similar to [3] using the derived thickness $l_{2,opt}$. Here, $n_2(f_k)$ and $\kappa_2(f_k)$ are optimized at every frequency step f_k using the following error function:

$$\mathrm{Err}(f_k) = ||H_{theory}(f_k)| - |H_{meas}(f_k)|| + |\angle H_{theory}(f_k) - \angle H_{meas}(f_k)|. \quad (11)$$

Results and discussion. To demonstrate the functionality of the algorithm to extract the optical constants of thin liquid samples, the optical constants of pure liquid water are measured by THz-TDS. The THz-TDS system in use employs photoconductive antennas (PCA) at the transmitter and receiver. The bandwidth of the generated T-ray pulse is from 0.2 to 3 THz with a dynamical range of 60 dB. In order to remove the effects of water vapor, the THz optical path is purged with dry air to keep the relative humidity below 3%.

In the measurement, the pure water is transferred into a cuvette, with a nominal optical length of 0.2 mm, using a pipette, and the cuvette is then glued to the sample holder placed at the focal between the two parabolic mirrors. The reference and sample signals are measured alternately three times. The mean values of the three measured signals are shown in Fig. 2a, and the fitted and unfitted phases of the measured transfer function are calculated and shown in Fig. 2b.

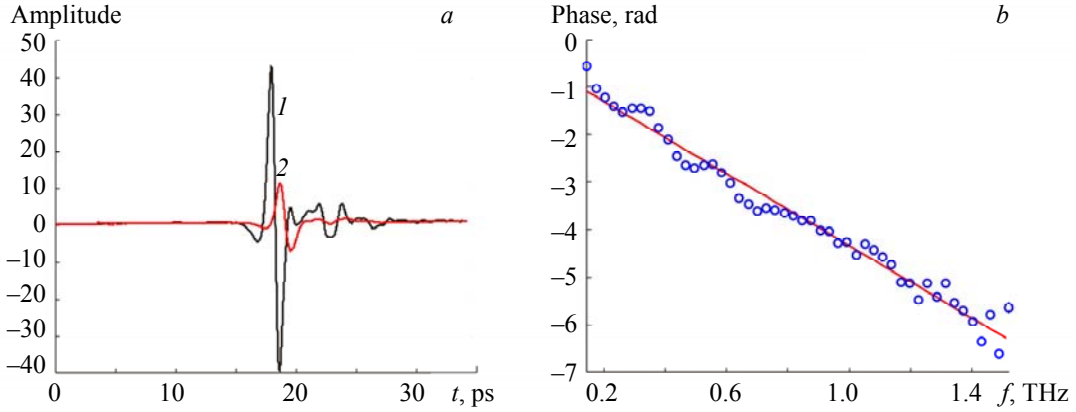

Fig. 2. THz waveforms of reference (1) and sample (2) signal (a), the fitted (line) and unfitted (○) phase of measured transfer function (b).

The corresponding initial values of refractive index and extinction coefficient of water are shown in Figs. 3, and are labeled as "initial raw values". The fitted initial data calculated with the fitted phase are also shown in Fig. 3, labeled as the "initial fitted values". The two groups of values are used as the initial values for the optimization procedure. The corresponding optimized data are also shown in Figs. 3, labeled as "extracted values" and "fitted extracted values". As shown in this figure, the optical constants exhibit FP oscillations, which almost disappears after the optimal sample thickness is determined in the optimization procedure. The optimization leads to a thickness of 185 μm, which agrees well with the optimum thickness (184.6 μm) using the conventional algorithm. Yet, the computation time is 26 ms using the three-dimensional optimization and is quite short versus that obtained by the conventional algorithm in [3] (approximately 1 min using the same computer). The extracted optical constants of water agree well with that reported in [9], where the optical constants are measured by THz attenuated total reflection spectroscopy.

In addition, the optimization was performed using the initial values of the thickness in the range from 100 to 300 μm with 1 μm step. As a result, for the initial values between 149 and 236 μm, the optimization stops at the correct thickness by the algorithm, and for other initial values, it converges to another local minimum (not shown). Yet, the global minimum can be distinguished from other minima by comparing the remaining value of the error function.

To give an insight into the search space of the parameters around the global minimum, the two-dimensional error function are calculated by setting the parameters ξ, ψ, and ζ constant, as shown in Fig. 4. The figure shows that the error values decrease along with the gradient direction in the close neighborhood of the minimum. The choice of ξ and ζ, which denote the thickness and the refractive index of the sample,

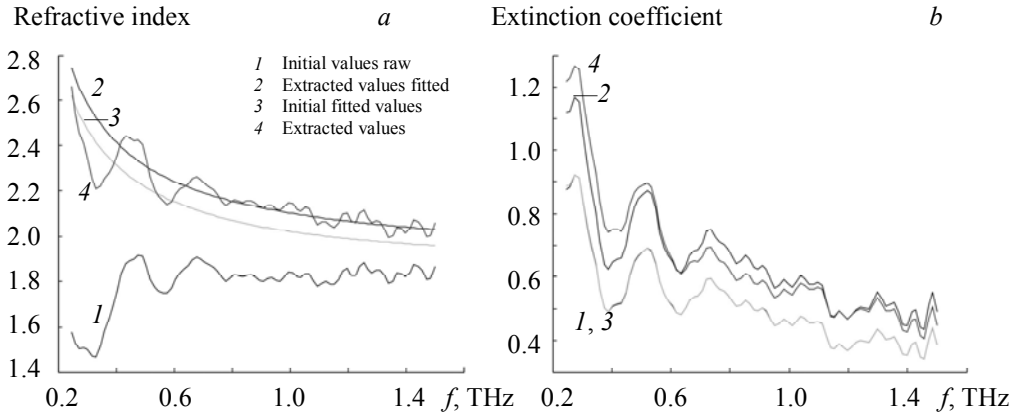

Fig. 3. Initial values and extracted optical parameters of water; (a) refractive index, (b) extinction coefficient.

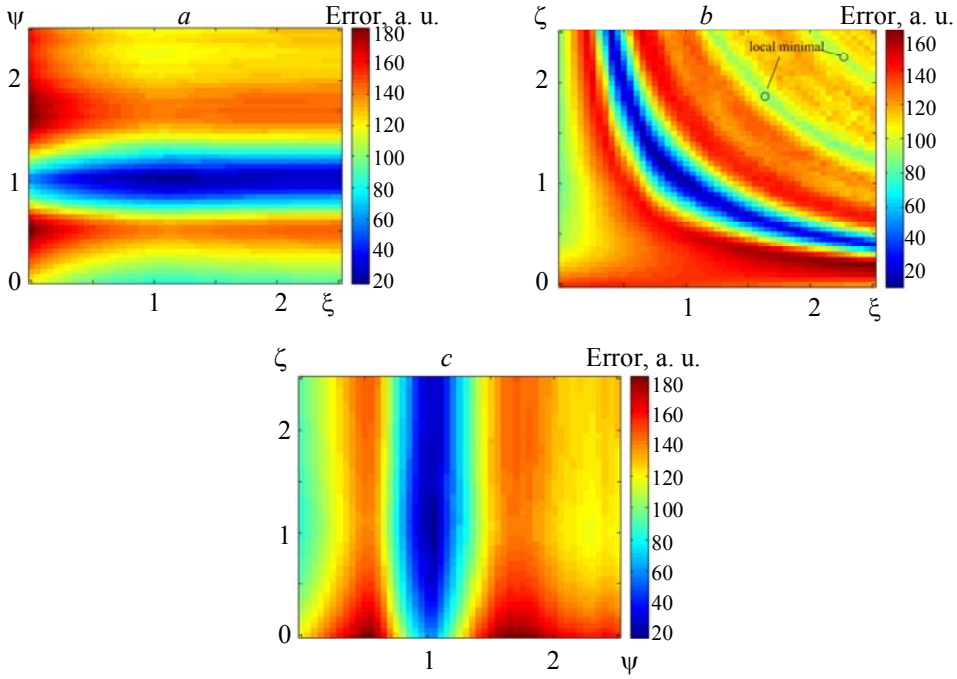

Fig. 4. Error values for constant ξ (a), constant ψ (b), and constant ζ (c) for the analysis of 200 μm water.

respectively, significantly affects the error function. Figure 4b shows the presence of circularly shaped sets of local minima in the ξ-ζ space. Namely, the algorithm is trapped into the local minimum if the initial values of ξ and ζ are around the area. Yet, the local minimum corresponds to a not real physical thickness and is significantly higher than the errors for the global minima. Figures 4a,c show that the imaginary part of the refractive index also affects the error because of the relatively high absorbance of water.

Conclusion. This study presents a new scheme to extract the optical constants of thin liquid samples by THz-TDS by performing the optimization on a three-dimensional space to minimize the difference between the measured and theoretical calculated transfer function. The scheme simultaneously determines the optical constants of the samples as well as their thickness in a short time compared to the conventional algorithms, and the optical constants of pure liquid water were measured by THz-TDS. The results showed that the scheme can highly accurately determine the optical constants and sample thickness simultaneously.

Acknowledgement. This research was financially supported by the National Natural Science Foundation of China (NSFC) (21503045) and the Guizhou Science and Technology Department (J20142107).

REFERENCES

1. J. L. Duvillaret, F. Garet, J.-L. Coutaz, *Appl. Opt*., **38**, 409–415 (1999).
2. T. Dorney, R. Baraniuk, D. Mittleman, *J. Opt. Soc. Am. A*, **18**, 1562–1571 (2001).
3. Ioachim Pupeza, Rafal Wilk, Martin Koch, *Opt. Express*, **15**, 4335–4350 (2007).
4. Benjamin Born, Martina Havenith, *J. Infrared Millim. Terahertz Waves*, **30**, 1245–1254 (2009).
5. Robert J. Falconer, Andrea G. Markelz, *J. Infrared Millim. Terahertz Waves*, **33**, 973–988 (2012).
6. C. Rønne, L. Thrane, P. O. Åstrand, A. Wallqvist, K. V. Mikkelsen, S. R. Keiding, *J. Chem. Phys*., **107**, 5319–5331(1997).
7. Peter Uhd Jepsen, Uffe Møller, Hannes Merbold, *Opt. Express*, **15**, 14717–14737 (2007).
8. Atsushi Nakanishi, Yoichi Kawada, Takashi Yasuda, Koichiro Akiyama, Hironori Takahashi, *Rev. Sci. Instrum*., **83**, 033103 (2012).
9. A. Soltani, T. Probst, S. F. Busch, M. Schwerdtfeger, E. Castro-Camus, M. Koch, *J. Infrared Millim. Terahertz Waves*, **35**, 5, 468–477 (2014).
10. Maik Scheller, Christian Jansen, Martin Koch, *Opt. Commun*., **282**, 1304–1306 (2009).
11. P. U. Jepsen, D. G. Cooke, M. Koch, *Laser Photon. Rev*., **5**, 1,124–166 (2011).
12. R. Wilk, I. Pupeza, R. Cernat, M. Koch, *IEEE J. Select. Top. Quantum Electron.*, **14**, 392–398 (2008).
13. M. Scheller, *Opt. Express*, **19**, 11, 10647–10655 (2011).
14. T. Wang, P. Klarskov, P. U. Jepsen, *IEEE Trans. Terahertz Sci. Technol.*, **4**, 425–431 (2014).
15. M. Scheller, *J. Infrared Millim. Terahertz Waves*, **35**, No. 8, 638–648 (2014).
16. Withayachumnankul, Withawat, M. Naftaly, *J. Infrared Millim. Terahertz Waves*, **35**, 610–637 (2014).
17. J. C. Lagarias, J. A. Reeds, M. H. Wright, P. E. Wright, *SIAM J. Optim*., **9**, 112–147 (1998).