

A BAYESIAN METHOD TO QUANTIFYING CHEMICAL COMPOSITION USING NMR: APPLICATION TO POROUS MEDIA SYSTEMS

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ABSTRACT

This paper describes a Bayesian approach for inferring the chemical composition of liquids in porous media obtained using nuclear magnetic resonance (NMR). The model analyzes NMR data automatically in the time domain, eliminating the operator dependence of a conventional spectroscopy approach. The technique is demonstrated and validated experimentally on both pure liquids and liquids imbibed in porous media systems, which are of significant interest in heterogeneous catalysis research. We discuss the challenges and practical solutions of parameter estimation in both systems. The proposed Bayesian NMR approach is shown to be more accurate and robust than a conventional spectroscopy approach, particularly for signals with a low signal-to-noise ratio (SNR) and a short life time.

Index Terms— NMR spectroscopy, Bayesian inference, porous media, chemical quantification

1. INTRODUCTION

Nuclear Magnetic Resonance (NMR) spectroscopy is commonly used to identify both the structure of unknown chemical species and the composition of mixtures. In NMR experiments, the system is excited using a radiofrequency pulse. As it returns to equilibrium, the nuclei produce an oscillating magnetic field which is recorded as a free induction decay (FID) dataset. Conventionally, the FID is Fourier transformed (FT) to extract the magnitude and frequency of the spectral components, which are related to the chemical composition and identification respectively. NMR is non-invasive, chemically-selective, and quantitative and thus it finds many uses in the study of petrophysics [1], biophysics [2] and reaction engineering [3]. However, these applications often require measurements from liquid in porous media; NMR of such samples is limited by a low signal-to-

noise ratio (SNR) and spectral line broadening. Therefore, advanced signal processing techniques that can provide chemical information from low quality data are desirable.

Many advanced NMR signal processing techniques have been developed in the last few decades [4]. Of these, black-box methods require minimal user input but are not well suited to incorporating prior information, whilst non-linear optimization can be computationally intensive. Bayesian approaches have also been proposed and shown to improve the sensitivity of relative to FT spectroscopy [5]–[9], but can be complex to implement. Therefore, the current standard method in quantitative NMR is still FT spectroscopy [10].

In this paper, we adapt our recently presented Bayesian NMR model [11] to characterize the chemical composition of liquid imbibed in porous materials. The model is an extension of Bretthorst’s Bayesian NMR model [5] that permits accurate estimation of species with multiple resonant frequencies. The proposed model is applied to ¹³C NMR, in which the sensitivity is approximately four orders of magnitude lower than ¹H NMR. In our earlier work, [11], we have shown the effectiveness of the proposed model in extracting quantitative measurements from pure liquid systems. Here we focus on its extension to porous media samples. Quantitative analysis of NMR data in porous materials is complicated by the low SNR and short signal lifetime, due to the rapid NMR relaxation decay arising from surface interaction between the liquid and solid surface [12]. Fig. 1 shows ¹³C NMR data for a mixture of octane and cyclooctane, comparing the FID and Fourier transform (FT) spectrum acquired from a pure liquid sample (Fig. 1 (a) and (b)) to data acquired from liquid within porous media (Fig. 1 (c) and (d)). It can be seen that the SNR from the measurements on the porous material is about four times lower and its signal lifetime is an order of magnitude shorter. The short signal lifetime means that conventional analysis using the FT spectrum is difficult as the spectral peaks that are used to identify different chemical species overlap. This characteristic of measurements within porous material adds new challenges to both conventional FT analysis and our proposed Bayesian model.

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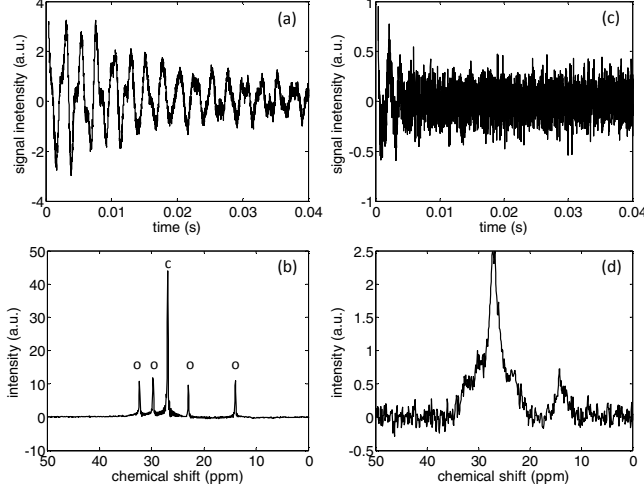


Fig. 1 Experimental NMR data from a 50% octane: 50% cyclooctane mixture. (a) FID from pure liquid. (b) FT spectrum of (a) where peaks arise from octane (labelled as “o”) and cyclooctane (labelled as “c”). (c) FID from such a mixture imbibed within the porous silica catalyst support. (d) FT spectrum of (c). Corresponding peaks are located at the same place as in (b). It is difficult to distinguish them due to the effect of line broadening. (a) and (c) are acquired at the same noise level.

2. BAYESIAN MODEL DEVELOPMENT

Our model follows the description given in [11] for pure liquids. However, for liquid on porous material, the estimation of the composition is more sensitive to the signal lifetime. Therefore, we extend our earlier model to include alternative descriptions of the signal lifetime.

2.1. NMR signal model specification

The model used closely follows that described in [11], the reader is referred there for a detailed description. Here the model is introduced briefly, and the features that are characteristic of porous materials are highlighted. In NMR spectroscopy, the time domain data $y(t_i)$ are acquired from real and imaginary channels that can be modeled as the sum of noise-free signal $f(t_i)$ and independent white Gaussian noise $\varepsilon(t_i) \sim N(0, \sigma_n^2)$.

The real and imaginary channels both follow a similar form (full details are given in [11]); for the real channel the noise-free signal $f_R(t_i)$ takes the form

$$f_R(t_i) = \sum_{r=1}^R A_r \sum_{k=1}^{m_r} B_{rk} \cos[(\omega_{rk} - \omega_0)t_i + \theta_0 + (\omega_{rk} - \omega_0)\tau] d_r(t_i), \quad (1)$$

where amplitude A_r represents the composition of the r th chemical, ω_{rk} is the k th resonant frequency for the r th chemical species, ω_0 is the offset reference frequency, θ_0 is the global phase shift, τ is the dead-time, B_{rk} is the known intensity of the k th chemical group for the r th species, and

$d_r(t_i)$ is a function describing the signal lifetime, typically $d_r(t_i) = e^{-\alpha t_i}$ and α parameterizes the decay.

The time series \mathbf{y} from both real (\mathbf{y}_R) and imaginary (\mathbf{y}_I) channels can be expressed as a multiplication of amplitudes $\mathbf{a} = [A_1, A_2, \dots, A_R]^T$ with sinusoidal basis function matrix $\Phi(\psi)$:

$$\mathbf{y}_{R \text{ or } I} = \Phi_{R \text{ or } I}(\psi)\mathbf{a} + \varepsilon \quad (2)$$

where $\psi = \{\omega_{rk}, \omega_0, \theta_0, \tau, \alpha\}$ represents all parameters that are non-linear in the function.

For ^{13}C NMR (not acquired on a high resolution NMR spectrometer) on pure liquids, $d_r(t_i)$ is dominated by magnet field inhomogeneity, and it is well established that $d_r(t_i) = e^{-\alpha_0 t_i}$, where α_0 is a global decay rate constant. However, in many applications the signal lifetime may not follow an exponential decay. Previous experimental measurements suggest that for liquids imbibed on macroscopically homogeneous porous supports, the single exponential model is a close approximation [13]. However, not all systems can be described as macroscopically homogeneous and therefore non-exponential models may be important. Furthermore, the interaction of the liquid and solid in porous materials introduces variations in the magnetic field and signal lifetime. These variations can be different for different chemical species, depending on the physical and chemical interaction of each species with the solid phase. Such differences were not included in our previous model for pure liquid samples, but are found to be significant here. We therefore extend the earlier model by characterising the signal lifetime using an individual decay model for each species, that is $d_r(t_i) = e^{-\alpha_r t_i}$.

Our primary goal is to infer a distribution over amplitudes \mathbf{a} , which represents chemical composition. It should be noted that ψ and σ_n are also unknown but one has prior knowledge about the approximate range for each parameter.

2.2. Bayesian inference

The posterior distribution of amplitudes \mathbf{a} , assuming \mathbf{y}_R and \mathbf{y}_I are independent measurements conditioned on nuisance parameters ψ and σ_n , is given from Bayes’s theorem:

$$\begin{aligned} p(\mathbf{a} | \mathbf{y}_R, \mathbf{y}_I, \psi, \sigma_n) \\ \propto p(\mathbf{y}_R | \mathbf{a}, \psi, \sigma_n) p(\mathbf{y}_I | \mathbf{a}, \psi, \sigma_n) p(\mathbf{a}) \\ = N(\mathbf{y}_R; \Phi_R \mathbf{a}, \sigma_n^2 \mathbf{I}) N(\mathbf{y}_I; \Phi_I \mathbf{a}, \sigma_n^2 \mathbf{I}) N(\mathbf{a}; \boldsymbol{\mu}_0, \sigma_a^2 \mathbf{I}) \\ \propto N(\mathbf{a}; \boldsymbol{\mu}, \boldsymbol{\Sigma}) \end{aligned} \quad (3)$$

where the posterior mean $\boldsymbol{\mu}$ and covariance matrix $\boldsymbol{\Sigma}$ are given by,

$$\boldsymbol{\Sigma} = \left(\frac{\Phi_R^T \Phi_R}{\sigma_n^2} + \frac{\Phi_I^T \Phi_I}{\sigma_n^2} + \frac{\mathbf{I}}{\sigma_a^2} \right)^{-1} \quad (4)$$

$$\boldsymbol{\mu} = \boldsymbol{\Sigma} \left(\frac{\Phi_R^T \mathbf{y}_R}{\sigma_n^2} + \frac{\Phi_I^T \mathbf{y}_I}{\sigma_n^2} + \frac{\boldsymbol{\mu}_0 \mathbf{I}}{\sigma_a^2} \right) \quad (5)$$

Note that a Gaussian prior $p(\mathbf{a}) = N(\mathbf{a}; \boldsymbol{\mu}_0, \sigma_a^2 \mathbf{I})$ has enabled a fully analytic inference procedure. σ_a is set to be $\gg \boldsymbol{\mu}_0$ so that it is a vague uninformative prior on amplitudes \mathbf{a} , reflecting that we have no prior information about the

relative chemical concentrations before taking measurements.

Before the posterior can be used to predict the chemical composition in mixtures, the nuisance variables ψ and σ_n need to be quantified. We calculate the marginal likelihood $p(\mathbf{y}_R, \mathbf{y}_I | \psi, \sigma_n)$ to approximate the joint distribution of all the nuisances $p(\psi, \sigma_n | \mathbf{y}_R, \mathbf{y}_I)$:

$$p(\mathbf{y}_R, \mathbf{y}_I | \psi, \sigma_n) = \int p(\mathbf{y}_R, \mathbf{y}_I | \mathbf{a}, \psi, \sigma_n) p(\mathbf{a}) d\mathbf{a} \quad (6)$$

The log marginal likelihood is therefore,

$$\begin{aligned} \log p(\mathbf{y}_R, \mathbf{y}_I | \psi, \sigma_n) &= -\frac{1}{2\sigma_n^2} (\mathbf{y}_R - \Phi_R \boldsymbol{\mu}_R)^T (\mathbf{y}_R - \Phi_R \boldsymbol{\mu}_R) \\ &\quad -\frac{1}{2\sigma_n^2} (\mathbf{y}_I - \Phi_I \boldsymbol{\mu})^T (\mathbf{y}_I - \Phi_I \boldsymbol{\mu}) \\ &\quad - (N + M) \log(\sigma_n) - R \log(\sigma_a) \\ &\quad -\frac{1}{2\sigma_a^2} (\boldsymbol{\mu}_R - \boldsymbol{\mu}_0)^T (\boldsymbol{\mu}_R - \boldsymbol{\mu}_0) \\ &\quad -\frac{1}{2} (\boldsymbol{\mu} - \boldsymbol{\mu}_R)^T \boldsymbol{\Sigma}_R^{-1} (\boldsymbol{\mu} - \boldsymbol{\mu}_R) - \frac{r}{2} \log(2\pi) \\ &\quad -\frac{1}{2} \log \left| \frac{\Phi_R^T \Phi_R}{\sigma_n^2} + \frac{\Phi_I^T \Phi_I}{\sigma_n^2} + \frac{\mathbf{I}}{\sigma_a^2} \right| \end{aligned} \quad (7)$$

where

$$\boldsymbol{\Sigma}_R = \left(\frac{\Phi_R^T \Phi_R}{\sigma_n^2} + \frac{\mathbf{I}}{\sigma_a^2} \right)^{-1} \quad (8)$$

$$\boldsymbol{\mu}_R = \boldsymbol{\Sigma}_R \left(\frac{\Phi_R^T \mathbf{y}_R}{\sigma_n^2} + \frac{\boldsymbol{\mu}_0 \mathbf{I}}{\sigma_a^2} \right) \quad (9)$$

R is the number of species in mixtures and N and M are the number of data points in the real and imaginary channels, respectively. The first two terms in Eq. (7) are called *model fit* as $\Phi_R \boldsymbol{\mu}_R$ and $\Phi_I \boldsymbol{\mu}$ represent estimates of the noise-free signal. The remaining terms are referred to as *model complexity* [14]. To deal with the nuisances, one can get point estimations by optimizing the log marginal likelihood Eq. (7), or integrate away these variables.

2.3. Calculation of chemical composition

The chemical quantification in mixtures using the proposed Bayesian NMR method follows a three step procedure:

- 1, Obtain point estimates of ψ_{est} and $\sigma_{n_{\text{est}}}$ by maximizing the log marginal likelihood Eq. (7) using an explicit simulated annealing simplex algorithm (SIMPSA) [15]. For analysis on porous material, point estimates of α are unreliable as amplitudes \mathbf{a} are sensitive to the value of α . Therefore, we adapt our earlier approach by numerically integrating each individual α_r over its approximate range.

- 2, Calculate the posterior distribution of amplitudes $p(\mathbf{a} | \mathbf{y}_R, \mathbf{y}_I, \psi, \sigma_n)$ as in Eq. (3), conditioned on the estimates of the nuisance parameters.

- 3, Sample from the distribution over amplitudes \mathbf{a} and calculate the composition distribution for chemical r from $C_r^{(i)} = A_r^{(i)} / \sum_{r=1}^R A_r^{(i)}$.

3. EXPERIMENTAL

We compare the performance of the proposed model with conventional FT spectra on various liquid mixtures of 2-butanone/cyclohexane and octane/cyclooctane. The porous media samples were silica catalyst support pellets and were prepared by wetting the pellets with the liquid mixtures.

NMR experiments were performed using Bruker DMX 300 and AV 400 spectrometers operating at a ^{13}C resonant frequency of 75.47 MHz and 100.64 MHz respectively. The time domain FID data were acquired using a single 90° excitation pulse with ^1H decoupling.

FT calculation follows a typical NMR spectroscopy procedure [10]. Peak intensities are obtained by integrating peak areas between selected frequency limits. In porous media systems, peaks may overlap. One might use small frequency windows to separate them, but this introduces significant bias. We illustrate this is true even for well resolved peaks using measurements of pure liquids. The second approach is to integrate over the area that contains multiple overlapping peaks, and subtract the contribution from other peaks that can be isolated. Here we use the second approach for all the FT calculations on porous media, as it does not introduce bias and is feasible on such systems that only contain a small number of species.

4. RESULTS

In this section, we describe a series of synthetic and experimental NMR measurements that were conducted to assess the performance of the proposed Bayesian model. In order to illustrate the difference between measurements of pure liquids and those imbibed on porous materials, we begin by presenting an analysis of pure liquids. The study is then extended to porous media systems, where the short signal lifetime and low SNR add extra challenges.

4.1. Pure liquids

As described in section 2.3, we can estimate the nuisance parameters ψ and σ_n through optimization or sampling. The behaviour of the log marginal likelihood in pure liquid measurements is simulated as a function of all nuisances. The behaviour of the likelihood as a function of some representative variables is shown in Fig. 2, with the ground truth indicated by dashed red lines. The likelihood surface is unimodal for most nuisances as shown in Fig.2(b), but severely multimodal as a function of frequencies ω_{rk} . This multi-modal, multi-variable likelihood surface must be navigated to estimate the nuisance parameters ψ and σ_n . The presence of multiple local optima in Fig. 2 (a) leads most greedy optimizers to converge to undesirable local optima, resulting in inappropriate interpretation of the data. Popular sampling techniques also have limited application here, as the global optimum is sharply peaked in the frequency space. Here we adopt the SIMPSA algorithm [6],

which was designed for continuous, bounded, global optimization, and is suitable for this Bayesian NMR model.

It has been observed from simulations that out of all the nuisance parameters, the final composition estimation is most sensitive to the frequency estimates. As the SNR decreases, frequency estimation becomes increasingly challenging. As in [11], we define the SNR in the frequency domain using the peak with the lowest intensity. We find that SIMPSA obtains robust, accurate estimates of all nuisance parameters ψ and σ_n when the SNR is above about 4 or 5. Based on such accurate point estimation, the proposed Bayesian NMR model is able to robustly estimate the final chemical concentration within its 95% credible interval.

Fig. 3 shows some representative experimental results from the Bayesian and FT approaches, acquired on various binary mixtures of octane/cyclooctane (Fig. 3 (a)) and 2-butanone/cyclohexane (Fig. 3 (b)). For chemical concentrations exceeding 10%, Bayesian NMR is more accurate and robust, resulting in predictions with increased accuracy and confidence. When analyzing dilute mixtures (<10%), the conventional FT approach is strongly influenced by the overlap of low intensity and high intensity peaks, causing a systematic bias in the final prediction of concentrations. However, the proposed Bayesian method removes such bias and is able to estimate dilute concentrations accurately.

4.2. Porous media

Compared with data acquired from pure liquid, those arising from liquid imbedded on porous material not only suffer from lower SNR, but also a much shorter signal life time, due to magnetic susceptibility variations. This does not significantly change the behavior of the log marginal likelihood as a function of most nuisance variables, but causes the shape for frequencies to be much broader. Similar effects can also be observed in the FT spectra. Here line broadening leads to severe peak overlap, which makes peak assignment and calculation almost impossible, as illustrated in Fig. 4 (a) and (b). However, the proposed Bayesian NMR model can still unambiguously resolve the nearby peaks (Fig. 4 (c) and (d)), which in turn makes the estimation of the composition more accurate.

Whilst in pure liquid systems the final composition estimation is dominated by the accuracy of frequency predictions, for porous media systems composition prediction is also sensitive to the relaxation decay modelling and estimation. Therefore, the inference procedure used for pure liquid samples, which uses a single exponential decay model $d_r(t_i) = e^{-\alpha_0 t_i}$ and a point estimate of α_0 , does not work.

To apply the Bayesian NMR spectroscopy model [11] to liquids imbedded on porous material we make two adjustments. Firstly, the exponential decay rate is estimated independently for each species. Secondly, the contribution from the decay parameters is numerically integrated away. Ideally, the decay model would be further extended to allow for non-exponential decay, for example through the use of the

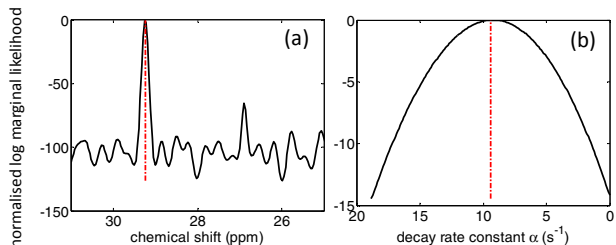


Fig. 2 Log marginal likelihood plot as a function of (a) resonant frequency (b) decay rate constant in a pure liquid of octane/cyclooctane mixture, with the other nuisances set to be the true value. The red dash lines indicate the ground truth. SNR is 7.9.

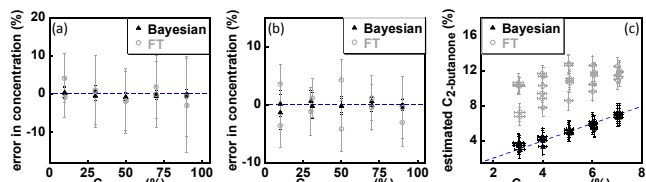


Fig. 3 Experimental results from the Bayesian and FT approaches on high concentration pure liquid (a) octane and cyclooctane, (b) 2-butanone and cyclohexane, with similar noise level. The lowest SNR are about 5 (for 10%). (c) Experimental results from dilute liquid mixtures (2-butanone and cyclohexane). Two mixture samples were prepared at each concentration.

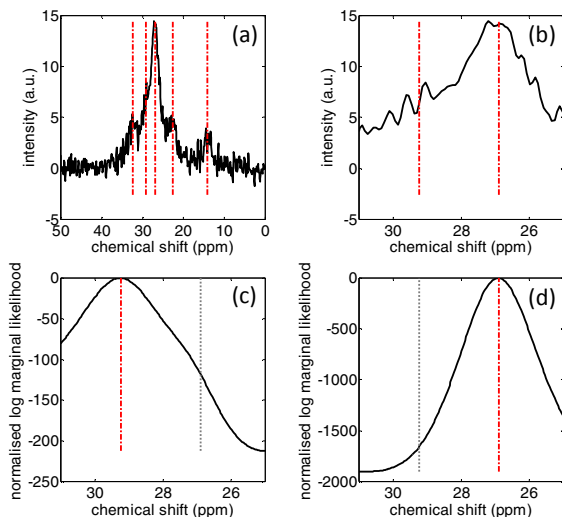


Fig. 4 (a) Simulated ^{13}C FT spectrum on silica support saturated with octane/cyclooctane mixture. The five resonant peaks overlap with each other with true positions indicated by the red lines. (b) zoomed region for the two peaks in (a) that almost merge into a single peak in FT spectrum. (c) shows that the Bayesian NMR model resolves the frequency of the 29.24 ppm peak (---) from the overlapping peak at 26.90 ppm (⋯) clearly. (d) Shows the reverse of (c), whereby the 26.90 ppm peak (---) is well resolved from the 29.24 ppm peak (⋯).

so-called Voigt model [16]. However, this significantly increases the complexity of the model fit, particularly at the low SNR typical of liquids imbedded on porous material. In practice, we found that the independent exponential decay model works efficiently and with acceptable error, and therefore the additional complication of non-exponential

decay is not required. This approach was used for all subsequent analysis of porous media systems.

Fig. 5 shows the experimental concentrations estimated using the Bayesian and FT methods for mixtures of 2-butanone/cyclohexane and octane/cyclooctane imbedded on porous material. FT analysis of these data results in a large uncertainty owing to the low SNR of the data. Further, the measured concentration does not always agree with the known concentration of the mixture, even within the uncertainty. Conventional analysis of the FT spectrum also requires human input for the post-processing procedures, and to perform the integration of the spectrum. Variations in the approach of different people can lead to large variations in the measured concentration, in some cases even exceeding the error arising from noise [10]. The concentrations estimated using the Bayesian approach agree well with the ground truth. In a small number of cases, the estimated 95% credible interval is too small, owing to the lack of uncertainty estimation of the nuisance parameters. As the marginal likelihood surface for the frequencies is not as sharply peaked as in the pure liquid case, it is possible that a sampling approach may help address this issue. However, even allowing for this error, the Bayesian NMR spectroscopy approach estimates the chemical composition with an uncertainty of better than 2%, which is up to an order of magnitude better than the conventional FT approach.

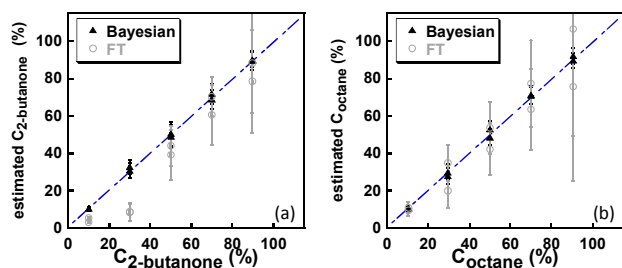


Fig. 5 Experimental comparison of Bayesian and FT methods on chemical quantification in porous media (silica catalyst support) from (a) 2-butanone/cyclohexane mixtures with 3–5 SNR and (b) octane/cyclooctane mixtures with 5–8 SNR.

5. CONCLUSION

This paper presents a Bayesian NMR approach for quantifying chemical composition for liquids in porous material. The approach is based on analyzing NMR data in the measurement (time) domain. The model overcomes many of the uncertainties associated with the post-processing required in a conventional FT spectroscopy method. The new approach was validated numerically and experimentally on various chemical mixtures, and is shown to be more accurate and robust than the conventional FT method.

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