Kramers–Kronig transforms calculation with a fast convolution algorithm

P. Bruzzoni a, R.M. Carranza a,*, J.R. Collet Lacoste a, E.A. Crespo b

a Unidad de Actividad Materiales, Comisión Nacional de Energía Atómica (CNEA), Av. GHral. Paz 1499, 1650 San Martín, Buenos Aires, Argentina
b Depto. de Física, Fac. Ingeniería, Univ. Nac. Comahue, Buenos Aires 1400, 8300 Neuquén, Argentina

Received 10 July 2002; received in revised form 3 October 2002

Abstract

Kramers–Kronig transforms (KKT) constitute a powerful tool to validate experimental impedance data. A new algorithm, containing a Fast Fourier Transform (FFT) sub-routine, for the numerical calculus of the KKT has been developed. This algorithm is based in the convolution theorem and it uses only two FFT calculi. It was finally tested in the validation of an experimental transfer function for hydrogen permeation into an iron membrane. Unlike common algorithms for numerical integration, this algorithm allows the calculation of all frequencies at the same time at a high speed using a regular frequency interval for the whole calculation with the same or even higher precision. The FFT sub-routine is accessible in all languages so that the use of this code is very simple.

© 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Kramers–Kronig; FFT; EIS; Transfer function; Hydrogen permeation

1. Introduction

The impedance technique is being increasingly used in the study of a wide variety of electrochemical systems: measurement of corrosion rates, study of reaction mechanisms, characterization of porous electrodes, etc. [1]. More recently, modulation of non-electrical quantities have incorporated new transfer functions to the universe of impedance, deepening the knowledge of those systems [2,3] which are often non-linear and unstable. These experimental results can be validated, before fitting any theoretical model on them, by performing Kramers–Kronig Transforms (KKT) [4–9].

A transfer function $H(\omega)$ is by definition the Fourier Transform (FT) of the Green function of the system $h(t)$, which is the system response to an impulsive perturbation. Since $h(t)$ is a real function, $H(\omega)$ is a complex function whose real and imaginary parts are even and odd functions of the frequency, respectively. Real and imaginary components are not independent. They are related by the KKT:

$$\text{Re}H(\omega) = \frac{1}{\pi} P \int_{-\infty}^{+\infty} \frac{\text{Im}H(\omega')}{\omega' - \omega} \, d\omega'$$
$$\text{Im}H(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{+\infty} \frac{\text{Re}H(\omega')}{\omega' - \omega} \, d\omega'$$

(1)

where $P$ is the principal part of the integral.

Multiplying both numerator and denominator of the above integrals by $(\omega' + \omega)$, and taking into account that:

i) the integral over the whole frequency domain of an odd function is equal to zero and;

ii) the integral over the whole frequency domain of even functions is equal to twice the integral from zero to infinity;

* Corresponding author. Fax: +54-11-6772-7362
E-mail address: carranza@cnea.gov.ar (R.M. Carranza).

0013-4686/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0013-4686(02)00677-1
then, eq. (1) can be expressed using positive frequencies only:

\[ \text{Re} H(\omega) = \frac{2}{\pi} \int_{0}^{+\infty} \frac{\omega' \text{Im} H(\omega')}{\omega^2 - \omega'^2} \, d\omega' \]

\[ \text{Im} H(\omega) = -\frac{2\omega}{\pi} \int_{0}^{+\infty} \frac{\text{Re} H(\omega')}{\omega^2 - \omega'^2} \, d\omega' \]  

(2)

The following conditions must be fulfilled for these relationships to be valid:

i) Causality. The response of the system is only due to the applied perturbation \( h(t - \tau) = 0 \forall \tau > t \) and contains no significantly spurious sources (noise).

ii) Linearity. The operator relating input and output signals must be linear. This condition implies that \( H(\omega) \) must be independent of the perturbation magnitude.

iii) Stability. The system must be stable. Once the perturbation is eliminated the system must return to its original state (invariance of the physical properties of the system with time).

iv) Finiteness. Real and imaginary parts of \( H(\omega) \) must be finite both at \( \omega = 0 \) and \( \omega = \infty \). They must be also continuous and single-valued in \( \omega \).

Relationships of eq. (1) and (2) are independent of the physical properties of the system. Moreover, the assumption of any theoretical model for the calculation is not needed. This means that KKT are a convenient and powerful method to evaluate the validity of experimental results, which are not correctly transformed if one of the above conditions is not fulfilled.

2. Numerical solution of the Kramers–Kronig transforms

Calculus of the KKT is generally numerically performed by converting eq. (2) to its finite difference form:

\[ \text{Re} H(\omega) = \left( \frac{2\omega}{\pi} \right) \sum \frac{\omega' \text{Im} H(\omega')}{\omega^2 - \omega'^2} \Delta \omega' \]

\[ \text{Im} H(\omega) = -\left( \frac{2\omega}{\pi} \right) \sum \frac{\text{Re} H(\omega')}{\omega^2 - \omega'^2} \Delta \omega' \]  

(3)

A huge amount of experimental data is needed in order to solve these integrals. Besides, these data must be uniformly distributed along the whole frequency range. A method consisting in a non-uniform frequency distribution by means of a geometrical progression of \( \Delta \omega \) has just been developed [10], which required a modification of the Newton method. Unfortunately, the amount of experimental data usually available are not enough for these calculations. In addition, they are not uniformly distributed in the frequency range. Then, new data must be created from the experimental ones by using interpolation techniques like the cubic spline method or the polynomials fitting. On the other hand, the finite differences method requires that integrals in eq. (3) be calculated for each desired data. Consequently, the computational time required to calculate \( M \) data will be proportional to \( MN \), being \( N \) the total number of data obtained by interpolation. A numerical method using fast Fourier transform (FFT) routines [11–13] can be developed allowing KKT to be calculated for half of the frequencies and all frequencies at the same time. This method reduces computational time considerably. If the number of data is \( N \), obtained by interpolation, the computational time to calculate \( N/2 \) data becomes proportional to \( N \log_2 N \), while using the finite differences method the time needed to calculate the same number of \( N/2 \) data is proportional to \( N^2/2 \). Nevertheless, it must be emphasized that this method does not alleviate the ‘tails’ problem, which arises because data can be measured only over a finite bandwidth.

The FFT method is based on the fact that both real and imaginary parts of the KKT integrals, eq. (1), are proportional to the convolution product between the real or imaginary components and the function \( 1/\omega \). With this and the time-convolution theorem in mind, FT can be applied to both members of eq. (1), with the following results:

\[ \text{FT}[\text{Re} H(\omega)] = \frac{1}{\pi} \text{FT}[\text{Im} H(\omega)] \text{FT}[1/\omega] \]

\[ \text{FT}[\text{Im} H(\omega)] = -\frac{1}{\pi} \text{FT}[\text{Re} H(\omega)] \text{FT}[1/\omega] \]  

(4)

The FT for real and imaginary parts can be calculated numerically, while that of \( 1/\omega \) is already known analytically:

\[ \text{FT} \left[ \frac{1}{\omega} \right] = -j \quad \text{for} \quad \tau > 0 \]

\[ \text{FT} \left[ \frac{1}{\omega} \right] = j \quad \text{for} \quad \tau < 0 \]  

(5)

being \( \tau \) the conjugated variable of \( \omega \) and \( j = \sqrt{-1} \).

Real and imaginary parts for all the frequencies is then obtained by applying the inverse FT to the product of these two functions.

The numerical calculus of the convolutions of eq. (1) can be performed using FFT routines. Numerical FFT calculus by digital machine computation has some constraints. The original function is approximated by
$N$ samples. Sampling in the variable domain (frequency in this case) results in a periodic function in its conjugate variable. Sampling in this conjugate variable results in a periodic function in its variable domain. Hence, numerical FFT calculus requires that both the original and transformed functions be modified such that they become periodic functions. The choice of the number of samples $N$ and the sample interval is relevant to diminish aliasing and truncation [11]. Numerical FFT calculus can only be easily implemented for positive real functions. Eq. (1) must then be reorganized in order to fulfill the requirements of this calculus. Due to the parity of the functions, integrals in eq. (1) are completely solved by splitting them into two integrals and calculating just the positive frequency domain:

$$\text{Re}H(\omega) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\text{Im}H(\omega')}{\omega - \omega'} d\omega' = \frac{1}{\pi} \int_{-\infty}^{0} \frac{\text{Im}H(\omega')}{\omega - \omega'} d\omega' + \frac{1}{\pi} \int_{0}^{+\infty} \frac{\text{Im}H(\omega')}{\omega - \omega'} d\omega'$$

(6)

The limits of the first integral can be swapped changing its sign. Swapping $\omega'$ to $-\omega'$ and taking into account that $\text{Im}H(\omega') = -\text{Im}H(-\omega')$, it then results:

$$\text{Re}H(\omega) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\text{Im}H(\omega')}{\omega - \omega'} d\omega' = \frac{1}{\pi} \int_{-\infty}^{0} \frac{\text{Im}H(\omega')}{\omega - \omega'} d\omega' - \frac{1}{\pi} \int_{0}^{+\infty} \frac{\text{Im}H(\omega')}{\omega + \omega'} d\omega'$$

(7)

Thus, the real part can be obtained subtracting this two integrals: Applying FT to both members of eq. (7):

$$\text{FT}[\text{Re}H(\omega)] = \frac{1}{\pi} \text{FT}[1/\omega]\text{FT}[\text{Im}H(\omega)] - \frac{1}{\pi} \text{FT}[1/\omega]\text{FT}[\text{Im}H(\omega)]^*$$

(8)

where * denotes the conjugate and Im[FT[ImH(\omega)]] is now a real and odd function.

Taking into account eq. (5) it is obtained:

$$\text{FT}[\text{Re}H(\omega)] = \frac{2}{\pi} \text{Im}[\text{FT}[\text{Im}H(\omega)]] \quad \text{for } \tau > 0$$

$$= -\frac{2}{\pi} \text{Im}[\text{FT}[\text{Im}H(\omega)]] \quad \text{for } \tau < 0$$

(9)

where $\tau$ is the conjugate variable of $\omega$.

Finally, applying the inverse FT to eq. (9), $\text{Re}H(\omega)$ as a function of $\omega$ is obtained. Eq. (9) is a real and even function so, its inverse transform is also a real and even function.

In the same way with the imaginary integral eq. (1) it results:

$$\text{FT}[\text{Im}H(\omega)] = \frac{2j}{\pi} \text{Re}\{\text{FT}[\text{Re}H(\omega)]\} \quad \text{for } \tau > 0$$

$$= -\frac{2j}{\pi} \text{Re}\{\text{FT}[\text{Re}H(\omega)]\} \quad \text{for } \tau < 0$$

(10)

Eq. (10) is an imaginary and odd function so, its inverse transform is a real and odd function.

The detailed numerical procedure used for the calculation of eq. (9) and (10) is as follows:

i) FFT calculus requires that the number of data $N$ be equal to any power of two ($N = 2^j$, where $j$ is an integer) and they must be equally spaced. The interval between frequencies is $\Delta \omega = \omega_{\text{max}}/N$, being $\omega_{\text{max}}$ the highest experimental frequency. Thus, $N$ values separated by $\Delta \omega$ are generated by cubic spline starting from the experimental data, either for its real or imaginary parts.

ii) FFT is applied to this set of $N$ values obtaining a new set of $N$ pair of data (real and imaginary parts for each data). Due to the structure of the FFT calculus, the first half of the results correspond to the new positive $\tau$ and the second half to the negative $\tau$. These new data are equally spaced by a new conjugated variable $\tau = n\tau_0$ (with $n = 1, \ldots, N/2$) and $\tau_0 = 1/\omega_{\text{max}}$.

iii) Then the convolution product between these data and $\text{FT}[1/\omega]$ is performed. Taking into account eq. (9), (10) and (5), this procedure can be simplified as:

- Real from imaginary: multiply the imaginary part by $2\pi$ for positive values of $\tau$ and by $-2\pi$ for negative values of $\tau$. Swap real and imaginary parts and set the imaginary part equal to zero.
- Imaginary from the real: multiply the real part by $2\pi$ for positive values of $\tau$ and by $-2\pi$ for negative values of $\tau$. Swap real and imaginary parts and set the real part equal to zero.

iv) The final result is obtained by performing the inverse FT with the same FFT routine used in "ii". Imaginary parts must be previously multiplied by $-1$ [11]. Convolution results must be scaled both by the sample interval $\omega$ and the numbers of points $N/2$, to obtain results equivalent to continuous convolution. In order to do this, it is necessary to multiply each inverse FT by $2\pi N/2$.

Since the first half of these results correspond to the positive frequencies while the second half to the negative
ones, results for the highest $N/2$ frequencies are lost. Nevertheless, this is not a problem for most experimental results because they are normally obtained using a logarithmic frequency sweep, so that obtaining the first $N/2$ results of a linear subdivision means that only the first three to five higher frequencies of the impedance diagram are missed.

When the direct integration method is used, the first high frequency points are obtained with a high degree of uncertainty due to the fact that the main contribution to the KK integrals belongs to the surroundings of the desired value. Since the KK integrand is a function of $1/(\omega^2 - \omega_0^2)$, extrapolated and interpolated values introduce a higher error in the low and high frequency limits.

### 3. Accuracy of the transformation

The algorithm developed in this work for KKT calculation is compared in this section to the common algorithm of numerical integration described by Macdonald et al. [15], where synthetic data for an RC parallel circuit were generated. Since this circuit satisfy all the conditions previously described, it must correctly transform. Real and imaginary parts for this circuit where calculated for each frequency value using the following equations:

\[
\begin{align*}
\text{Re}(\omega) &= R/(1 + \omega^2R^2C^2) \\
\text{Im}(\omega) &= \omega R^2C/(1 + \omega^2R^2C^2)
\end{align*}
\]  

Using eq. (11) a set of data was generated ranged from 1 to $10^6$ Hz with ten points per frequency decade, taking $R$ and $C$ as 100 $\Omega$ and 100 $\mu$F, respectively (these values are the same as those chosen by Macdonald et al. [14,15]). The cubic spline method was applied to these data to obtain a new data set consisting of $2^{14}$ points equally spaced with $\Delta f = 6.1$ Hz, from which KKT were calculated. Table 1 shows the circuit parameters obtained by applying complex nonlinear least square (CNLS) fitting to both real and imaginary parts of eq. (11). The fitting was carried out on both the cubic spline and the KKT results. It can be seen that the interpolation produces a maximum error of 0.03% in $R$ and of 0.08% in $C$, and that the error becomes higher for the calculus of the real from the imaginary parts. This effect is mainly due to a truncation error that can be improved increasing the number of points, keeping the same frequency interval. On the contrary, for the calculus of the imaginary from the real parts, no changes were observed on the value of $R$ and the value of $C$ was closed to the actual one. The values of $\chi^2/N$ showed that the calculation on the KKT results produces a dispersion four orders of magnitude higher than one obtained for the cubic spline.

The average error (AE) was also calculated with the formula used by Macdonald et al. [15]:

\[
AE = \frac{100}{mW_{\text{max}}/(\omega_{\text{ex}})} \sum_{i=1}^{m} |W_i(\omega)_{\text{ex}} - W_i(\omega)_{\text{KK}}|	ag{12}
\]

where $W_i(\omega)_{\text{ex}}$ and $W_i(\omega)_{\text{KK}}$ are the values for real or imaginary part observed experimentally and calculated by the appropriate KKT, respectively. $W_{\text{max}}/(\omega_{\text{ex}})$ is the maximum value of the real or imaginary part in the experimental data set, and $m$ is the total number of real–imaginary pairs. In order to compare different data set, which may differ by orders of magnitude in their impedance values, the average error was normalized to the maximum value in the data set. The results obtained were the same as those calculated for Macdonald et al. [15]: $AE = 0.5\%$ both for real and imaginary parts.

| Table 1 |
|---|---|
| Fitting parameters of the CNLS fitting applied to both real and imaginary parts coming from: a) cubic spline of the data generated with eq. (11), ranging from 1 to $10^3$ Hz with 10 points per frequency decade, and b) KKT calculus after cubic spline |
| | Real | | Imaginary | |
| | $R$ (\Omega) | $C$ (\muF) | $R$ (\Omega) | $C$ (\muF) |
| (a) Cubic Spline | 99.98 | 99.91 | 99.97 | 99.92 |
| $\chi^2/N = 1.1 \times 10^{-11}$ | $\chi^2/N = 8.2 \times 10^{-12}$ |
| (b) KKT | 99.89 | 100.41 | 99.97 | 99.99 |
| $\chi^2/N = 3.9 \times 10^{-7}$ | $\chi^2/N = 4.3 \times 10^{-8}$ |

### 4. Application to the permeation transfer function

Recently, a few papers related to the application of the EIS technique to study hydrogen permeation, have appeared [16–19]. The existence of noise and non-linearity are the most common problems that can be found in these systems. Fluctuations, that are not related to hydrogen diffusion processes (i.e. due to corrosion processes), can take place at the input side of a permeation membrane. Also, nonlinear processes like surface adsorption before hydrogen ingress to the metal, can exist, especially in non-ideal systems containing exponential interaction terms (i.e. Frumkin isotherm [20]). To our knowledge, the only non-purely electrochemical impedance function that has been evaluated by the KKT is the photoelectrochemical impedance function introduced by Song and Macdonald [21].

In order to evaluate the application of KKT to these systems, synthetic data were generated with the mathematical expression for the permeation transfer function [16], which relates hydrogen flow and concentration at the output and input side of the permeation membrane, respectively:
\[ H_{J,c_0}(\omega) = \frac{J(L, \omega)}{c(0, \omega)} \]  

which is linear and whose exact solution is:

\[ H_{J,c_0}(\omega) = \frac{kD\alpha}{\sinh(\alpha L)} , \quad \alpha = \sqrt{\frac{j\omega}{D}} \]  

Its real and imaginary parts being:

\[ \text{Re}H_{J,c_0}(\omega) = \frac{kD\theta[\sinh(\theta L)\cos(\theta L) + \cosh(\theta L)\sin(\theta L)]}{[\cosh(\theta L)\sin(\theta L)]^2 + [\sinh(\theta L)\cos(\theta L)]^2}, \]

\[ \text{Im}H_{J,c_0}(\omega) = \frac{kD\theta[\sinh(\theta L)\cos(\theta L) - \cosh(\theta L)\sin(\theta L)]}{[\cosh(\theta L)\sin(\theta L)]^2 + [\sinh(\theta L)\cos(\theta L)]^2}, \]

where \( J \) and \( c \) stand for fluxes and concentrations of hydrogen, respectively, and the suffixes 0 and \( L \) for the input and the output side of the metallic membrane, respectively. \( L \) is the membrane thickness, \( D \) is the diffusion coefficient of hydrogen in the metallic phase and \( k \) is a constant.

Using \( D = 9 \times 10^{-9} \text{m}^2 \text{s}^{-1}, k = 1 \text{cm}^{-1} \) and \( L = 0.05 \text{cm} \), a set of data were generated between \( 10^{-5} \) and 10 Hz with 5–50 points per decade. The cubic spline method was applied to these data sets for different \( \gamma \) values (2\(^\gamma \) points).

Fig. 1 shows the AE, eq. (12), as a function of the number of points per decade for real and imaginary parts. The KKT were performed on data obtained from a cubic spline of 2\(^{14} \) equally spaced points with \( \Delta f = 6.1 \times 10^{-4} \) Hz. Three are the components of AE: one due to interpolation, i.e. cubic spline in this case, while the others due to the KKT calculus known as aliasing and truncation errors in the FFT calculus. Aliasing will occur if samples of the function are not taken sufficiently close together. As a result the function folds, or overlaps, on itself. Truncation occurs when the total number of samples chosen to characterize the function truncates the original waveform. Truncation can produce considerable rippling in the FFT results.

Since the same set of points was used for all the KKT calculations, the aliasing and truncation errors are constants. In consequence, the relative variation of the AE value is due to interpolation errors (cubic spline). In the range between 5 and 10 points per decade a significant variation of AE is observed, being equal to 0.05\% for 10 points per decade, a small value compared with the experimental error of these systems. For 20 points per decade or higher values the error is lower than 0.015\% with aliasing and truncation errors smaller than 0.002\%. This shows the goodness of the FFT integration method, the highest error being due to interpolation.

Fig. 2 shows the aliasing error for different values of \( 2^\gamma \), for values of \( \gamma \) higher than 11 the error is lower than 0.06\%. Then, both cubic spline and aliasing errors can be lowered by increasing the number of points per decade of the source data in one case, and lowering \( \Delta f(\text{increasing } N) \) in the other, respectively. On the other hand, the truncation error, which is the most critical one at high frequencies, can only be lowered by improving the experimental design. This is due to the fact that the amplitude of the signals at high frequencies is comparable in magnitude to the system noise.

Fig. 3 shows real and imaginary parts as a function of frequency for synthetic data from eq. (15). Fig. 4 shows the corresponding Nyquist diagram. Finally, Figs. 5 and 6 shows the experimental results and KKT calculus obtained for the permeation transfer function of an iron membrane with a Pd electrodeposit [16].

![Fig. 1. AE, calculated using eq. (12), as a function of the number of points per decade for real and imaginary parts.](image1)

![Fig. 2. AE, calculated using eq. (12), for different values of \( \gamma \).](image2)
5. Conclusions

- It was demonstrated that the algorithm presented here is as effective as the classical algorithm of numerical integration.
- Its advantage is that it allows the calculation of all frequencies at the same time and at a great speed with the same or even better precision than the integration.
method. In addition, no especial subdivision in frequencies is needed.

This new algorithm is based on the convolution theorem and use only two FFT calculi. Its code is easy to implement due to the fact that the FFT routine is available in all languages.

References