

# **ZSimpWin Version 3.00**

**For Windows 98/2000/XP**

**Electrochemical Impedance Spectroscopy  
Data Analysis Software**

**Technical Note 1:  
Extrapolation using Kramers-Kronig relations**

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**Technical Note 1:**  
**Extrapolation using Kramers-Kronig relations**

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When ZSimpWin Version 2.00 was released in March, 2001, this feature was not fully developed. The updates in this Note are applicable to V 2.10 and V 3.00.

**1. Background**

Theoretically,  $Z''$  can be determined from  $Z'$  using Eq. 1, if the data were available in the full frequency range. Conversely,  $Z'$  can be determined from  $Z''$  using Eq. 2.

$$Z''(\omega_i) = -\frac{2\omega_i}{\pi} \int_0^{\infty} \frac{[Z'(x) - Z'(\omega_i)]}{(x^2 - \omega_i^2)} dx \quad (1)$$

$$Z'(\omega_i) = Z'_{\infty} + \frac{2}{\pi} \int_0^{\infty} \frac{[xZ''(x) - \omega_i Z''(\omega_i)]}{(x^2 - \omega_i^2)} dx \quad (2)$$

- Experimental difficulties in acquiring data in the low frequency region.
- The contributions to the integrals of the K-K relations are very large in the region near the frequency being evaluated. Without sufficient data in the low frequency region, it may not be possible to calculate the data in the region with a reasonable accuracy.

**2. Assumptions**

1. No change of electrochemical system during measurement, i.e., the values of the electrical components are constant.
2. Experimental data satisfy the K-K relations.

**3. Conditions to be satisfied**

1. Continuities in  $Z'$  and  $Z''$
2. K-K relations.

**4. Extrapolate Menu**

**Apply Kramers-Kronig:** the work horse of this routine. Other menus are integrated into this routine.

**Add points:** Adds the extrapolated points to measured data.

**Remove points:** Removes the extrapolated points.

**Calculate Impedance :** After opening a file, calculate  $Z'$  and  $Z''$  using the K-K relations.

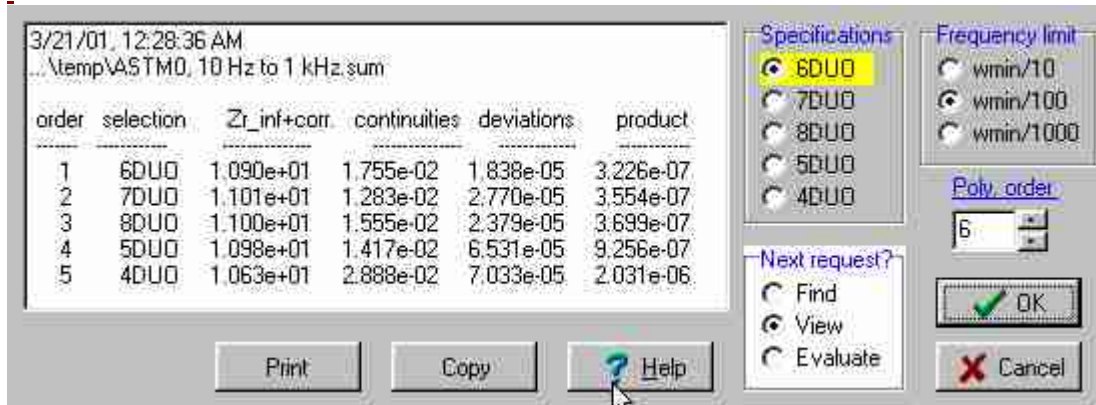
**Save Extrapolated:** Adds an extrapolated segment and then saves as a file.

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Page Break

## 5. Apply Kramers-Kronig Dialog Box

This routine was developed using the algorithm described in the Reference. Extrapolate  $Z'$  and  $Z''$  below the lowest measured frequency using polynomials of the same order.



**Find:** finds the order of the polynomials providing the least deviations of the extrapolated curves from the calculated curves. Computations are performed for polynomials of different orders (4 to 8). Select this request and click on the [OK] button.

**View:** displays the extrapolated curve associated with the order of the polynomials, and the lower bound of the extrapolation frequency. The order is selected by clicking the Up or Down button in the **Poly. order**. The lower bound is selected by clicking the radio button in the **Frequency limit**. It is also possible to select a radio button in the **Specifications** representing a combination of the **Poly. order** and the **Frequency limit**. Select this request and click on the [OK] button.

**Evaluate:** adds the extrapolated segment to the measured data, and then calculates  $Z'$  and  $Z''$  using the K-K relations. Select this request and click on the [OK] button.

**Print:** Prints the results and displayed plot.

**Copy:** Copies the results to Windows clipboard.

## 6. Test Run Results

The order of the polynomials providing the best extrapolations were selected based on the value of the (continuities) x (deviations).

| Test File Name         | Order of Polynomials | Capacitive term At cut-off freq. | Effect of Extrapolations on Deviations |
|------------------------|----------------------|----------------------------------|--|
| ASTM0, 10 Hz to 1 kHz  | 6                    | Large                            | Significant                            |
| ASTM0, 1 Hz to 1 kHz   | 6                    | Small                            | Moderate                               |
| ASTM0, 0.1 Hz to 1 kHz | 5                    | Very small                       | Insignificant                          |
| ASTM0                  | -                    | Negligible                       |  |
| Coated steel, 72h      | 7                    | Small                            | Insignificant                          |
| Cylinder in NaCl       | 6                    | Large                            | Significant                            |
| Steel, 72h             | 5                    | Moderate                         | Moderate                               |

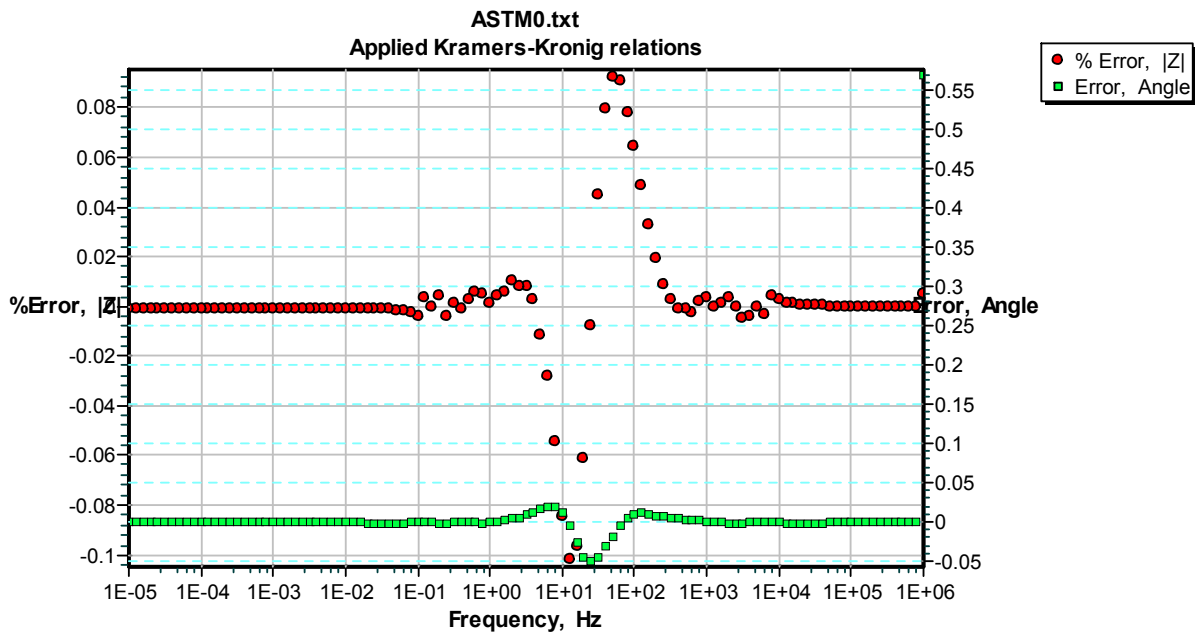
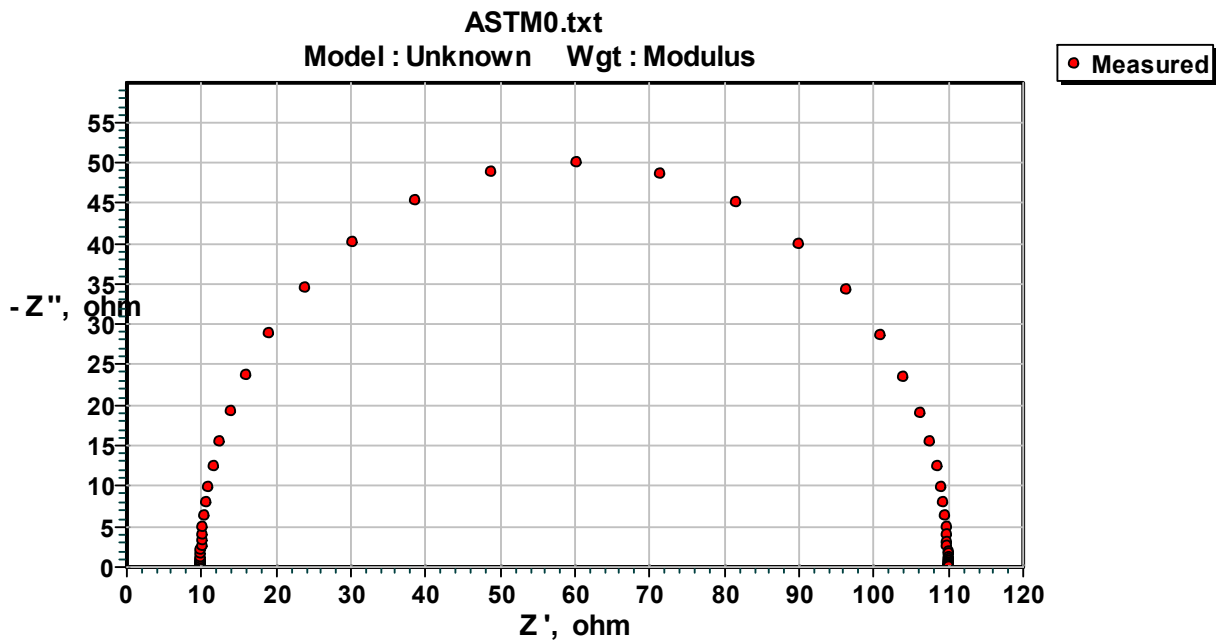
- Without extrapolations: Calculate impedance ( $Z'$  and  $Z''$ ) using measured data → Compare the calculated curve with the measured data → Determine the deviations.

- With extrapolations: Extrapolate and append to measured data → Calculate impedance ( $Z'$  and  $Z''$ ) using the extrapolated data → Compare the extrapolated curve with calculated curve → Determine the deviations.
- The best extrapolations = the order of the polynomials providing the minimum of the product, (continuities) x (deviations).
- When the capacitive term ( $Z''$ ) is large at the low cut-off frequency, extrapolations have significant effects on reducing the deviations.

### 6.1. Impedance Calculation Routine

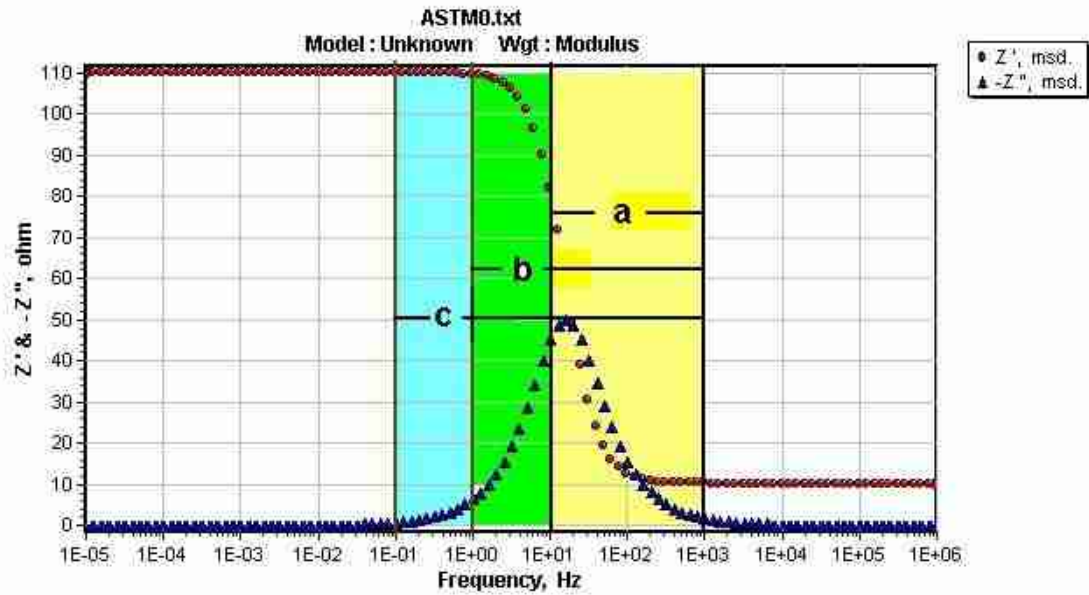
#### ASTM0

Theoretical data for Randles circuit. Evaluated the performance of the routine to compute  $Z'$  and  $Z''$  using the K-K relations. After opening this file, selected “Calculate Impedance” in the Extrapolate Menu.



The maximum error is about 0.1%. This indicates that impedance calculation routine is working properly.

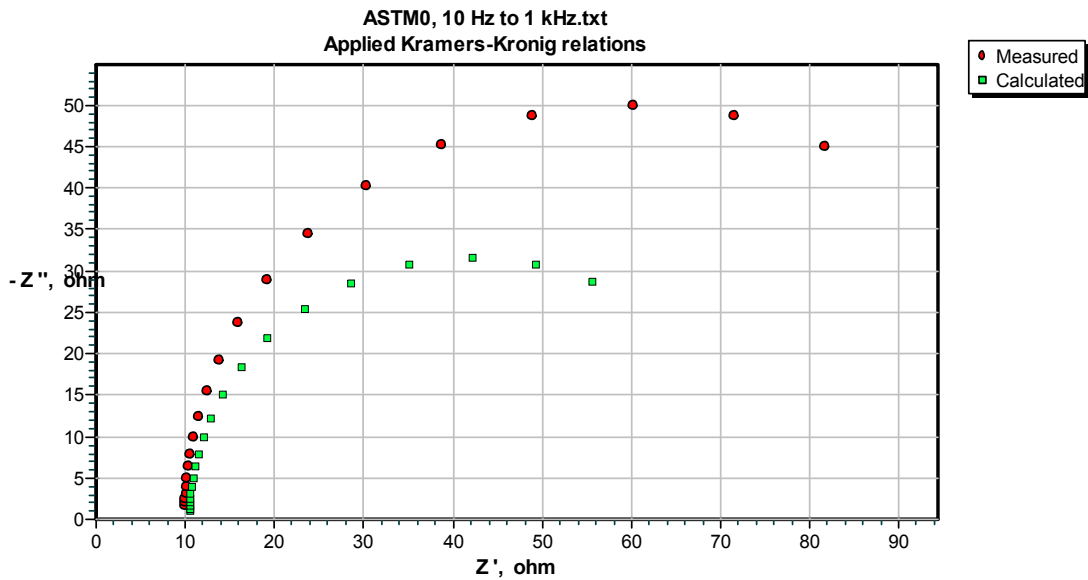
For further testing, the data points were taken in the three frequency ranges a, b, and c and then extrapolated using the routine.

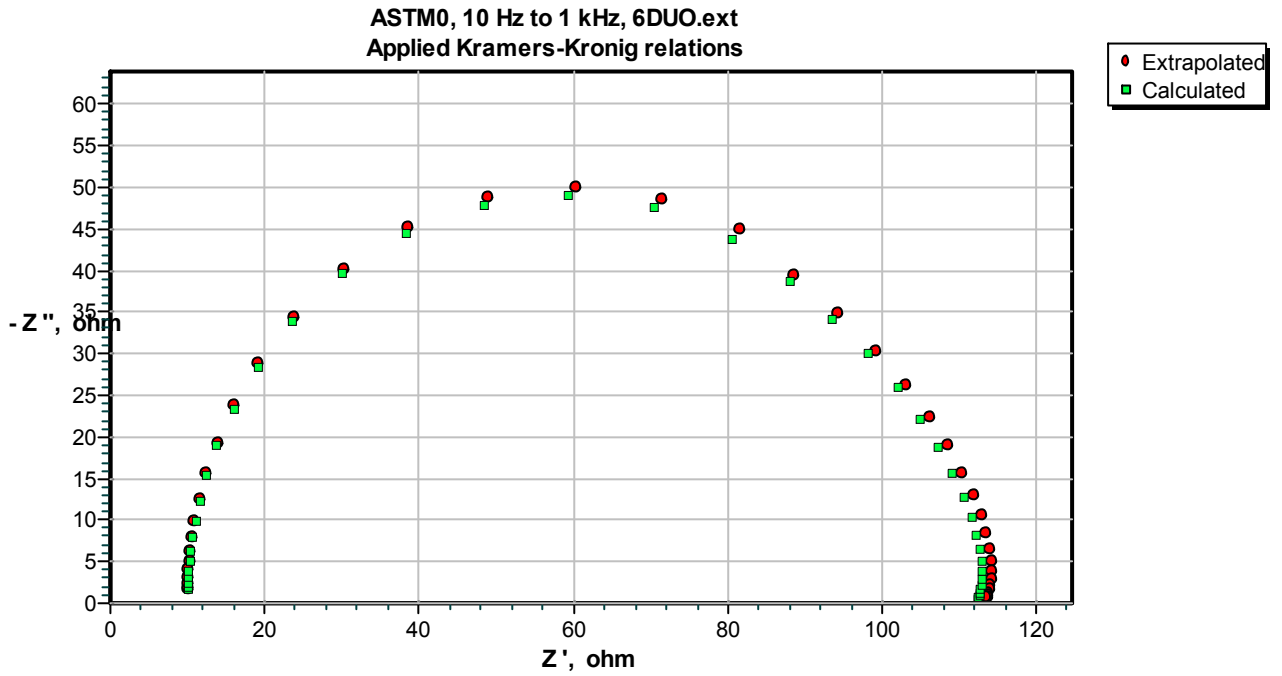
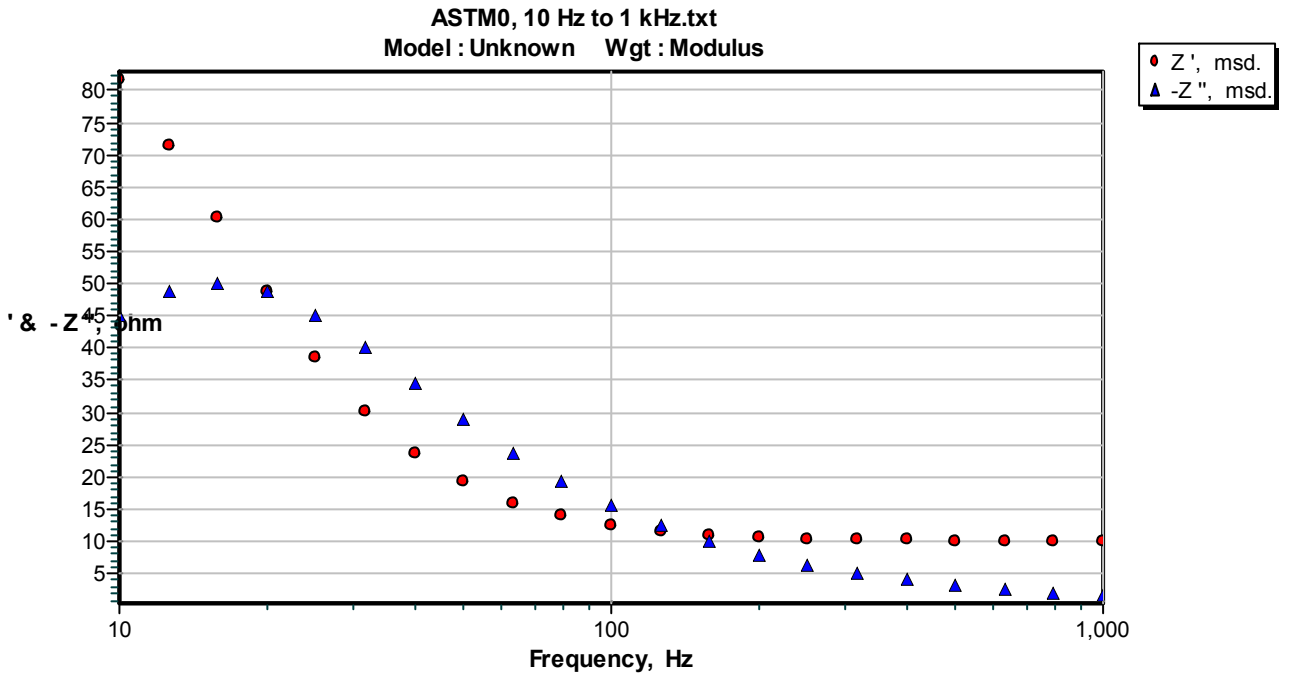


## 6.2. Data with a large capacitive term at cut-off frequency

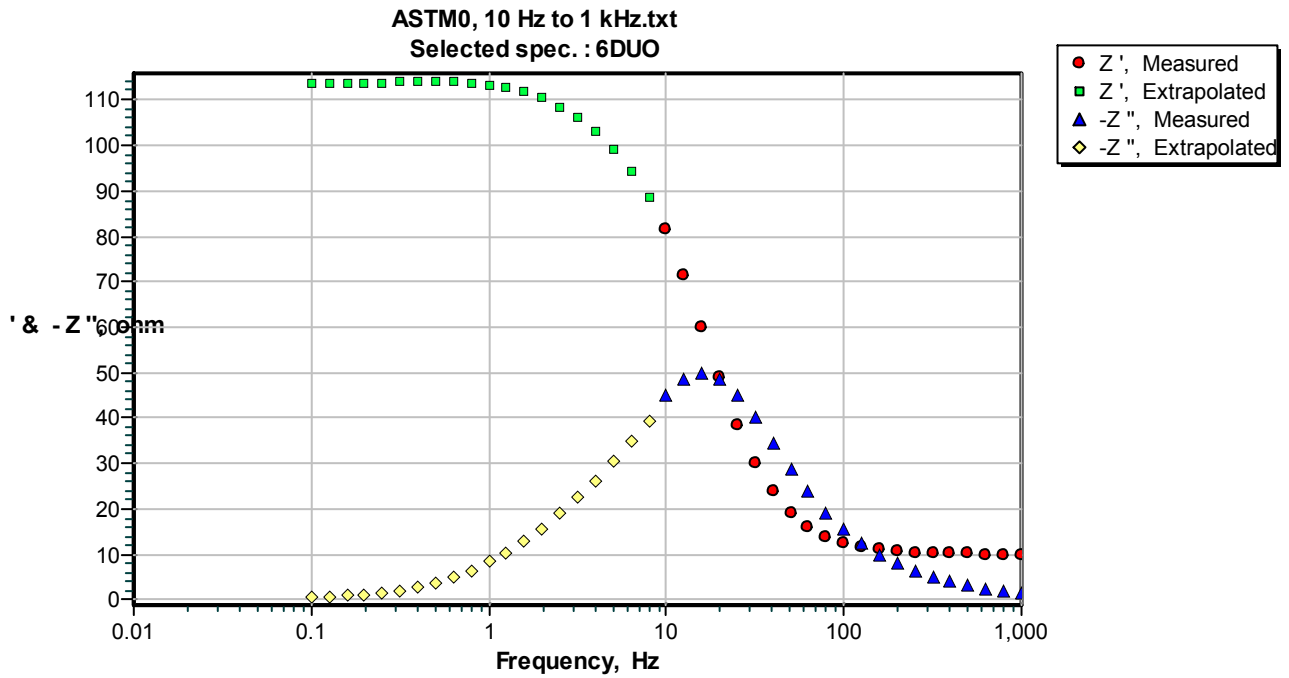
### ASTM0, 10 Hz to 1 kHz

Because of the very large capacitive term, the calculated curve is much different from the data. The deviation increases with decreasing the frequency.





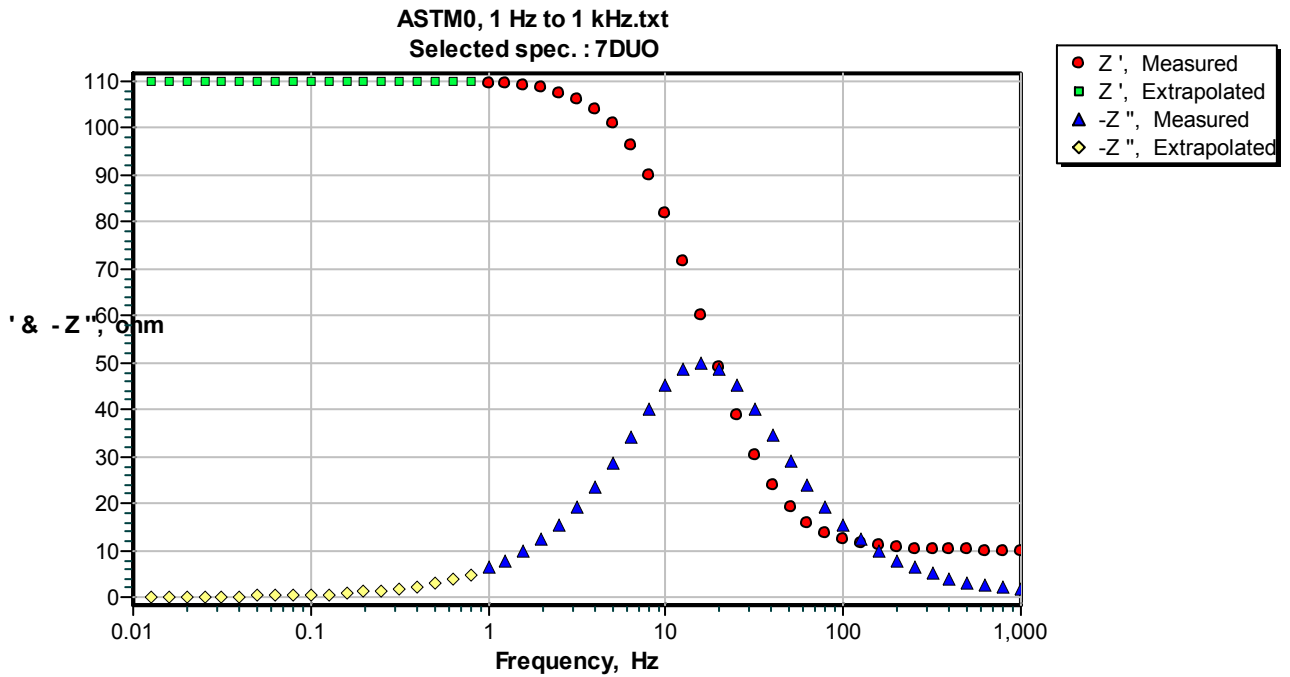
These data were extrapolated by two decades below the cut-off frequency. Extrapolated curves provided much smaller deviations.



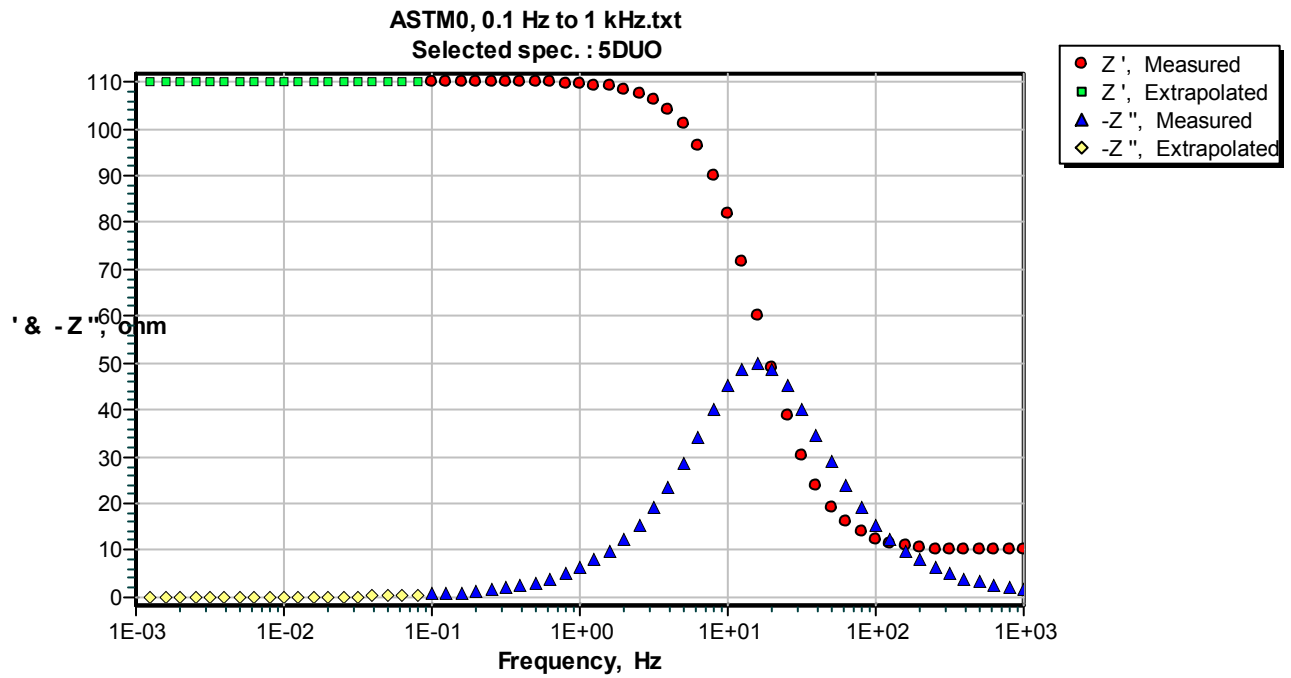
The extrapolated segments are very close to the corresponding truncated segments.

### 6.3. Data with small capacitive term at cut-off frequency

#### ASTM0, 1 Hz to 1 kHz



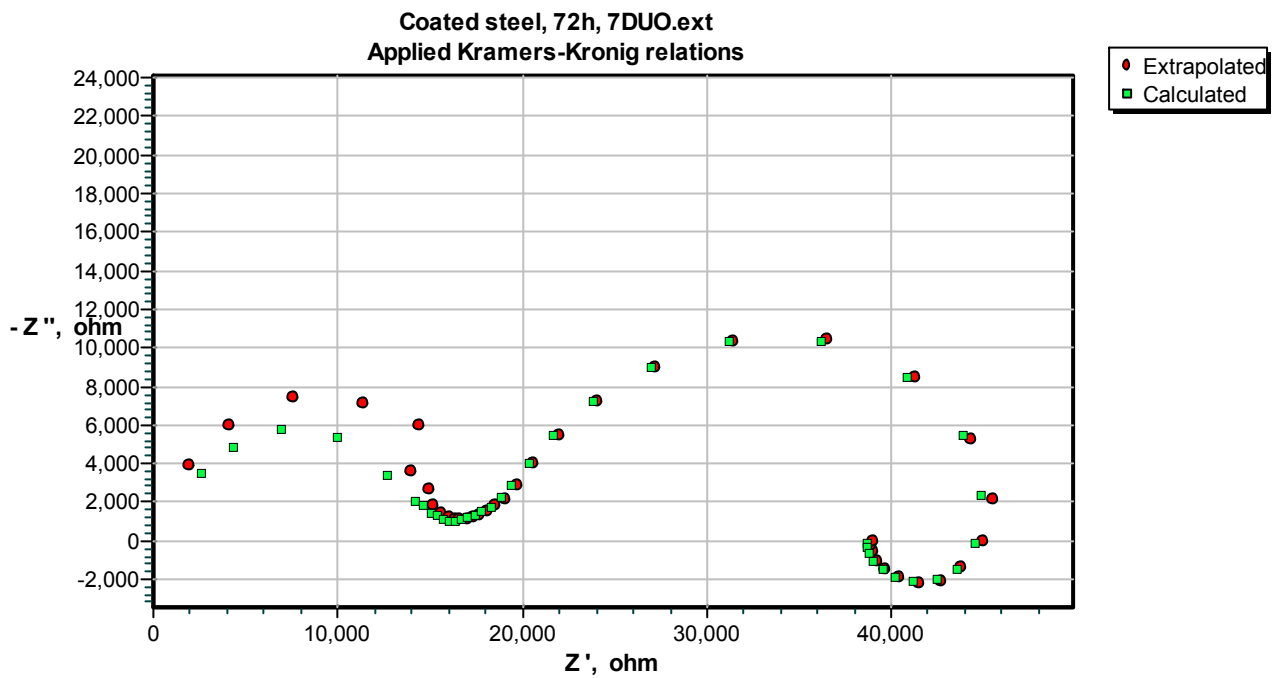
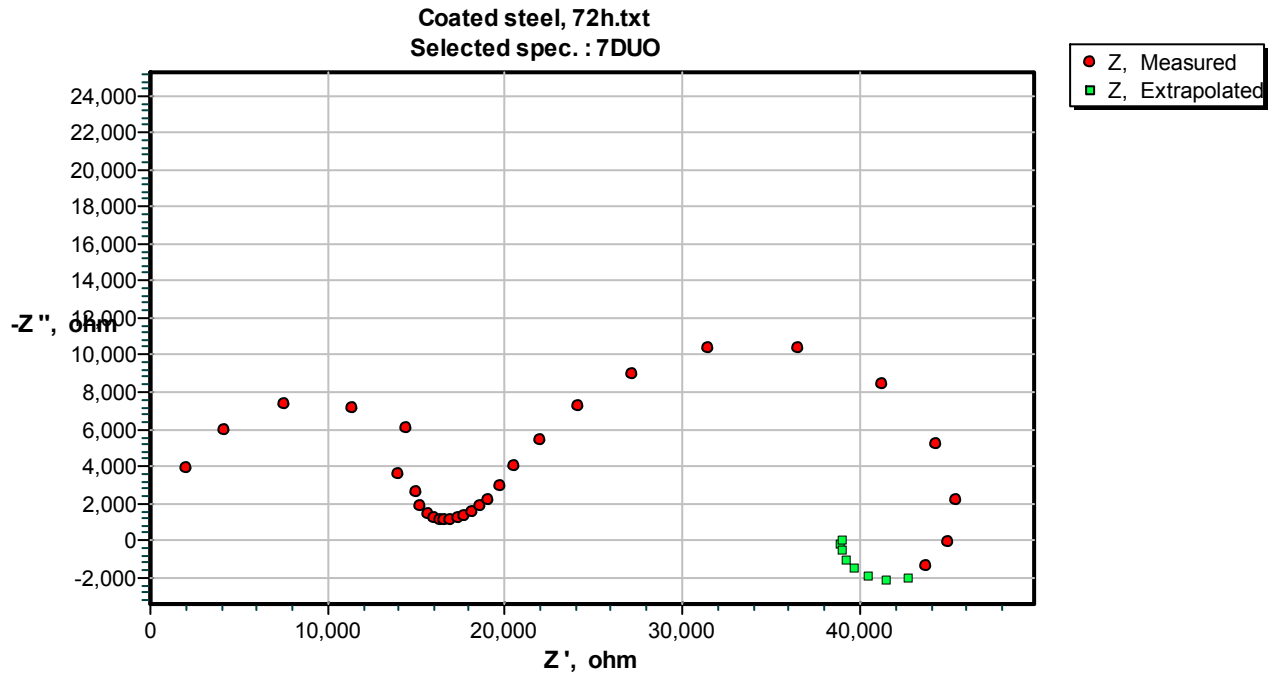
ASTM0, 0.1 Hz to 1 kHz



Capacitive term is very small at the truncation frequency. Extrapolations have insignificant effect in reducing the deviations.

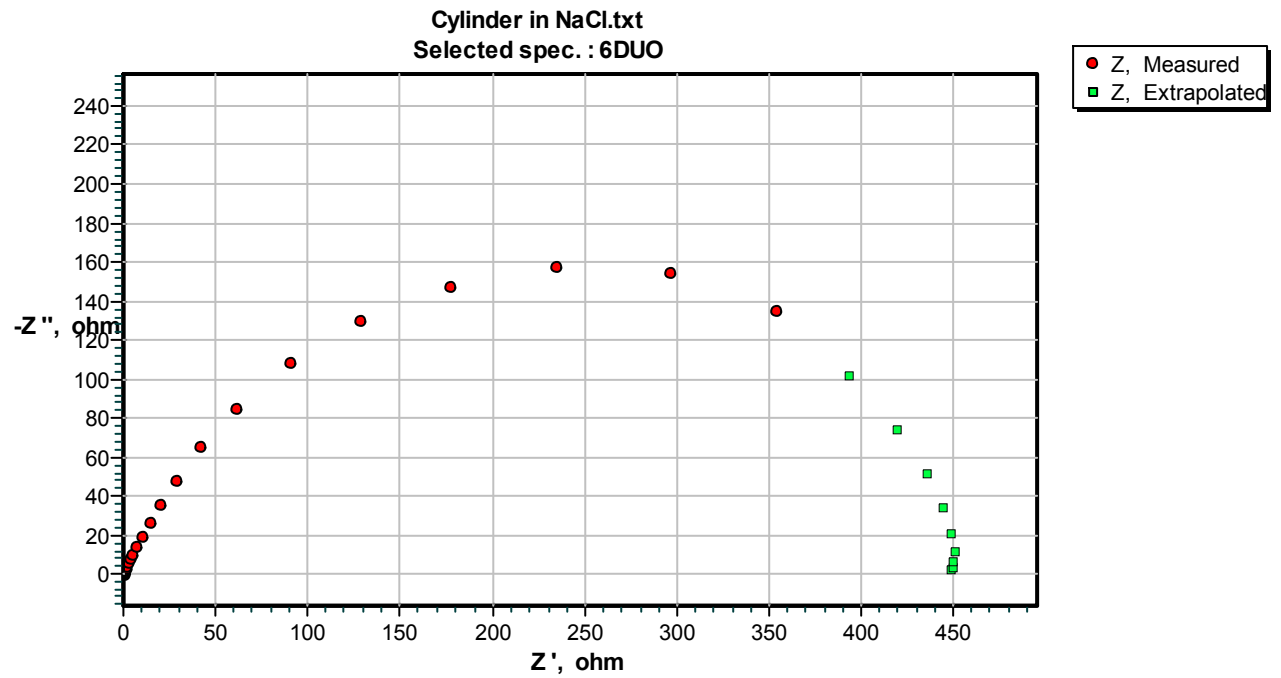
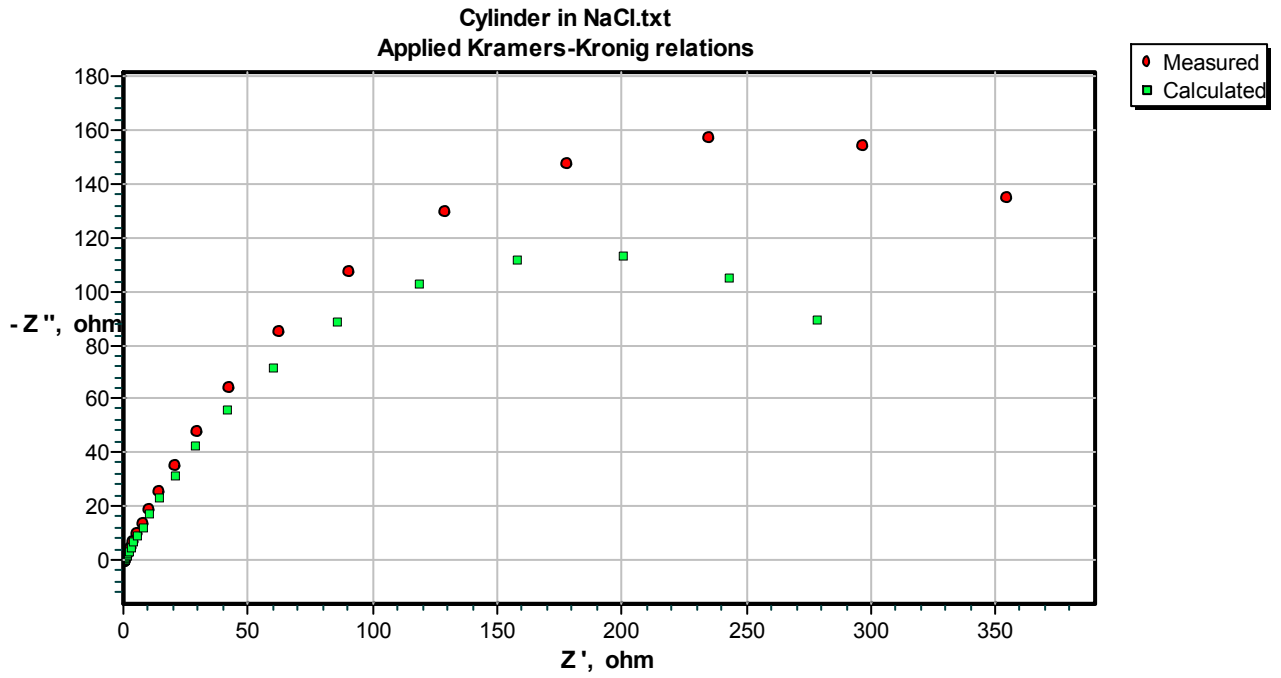
## 6.4. Extrapolation and Impedance Computation

### Coated Steel, 72h

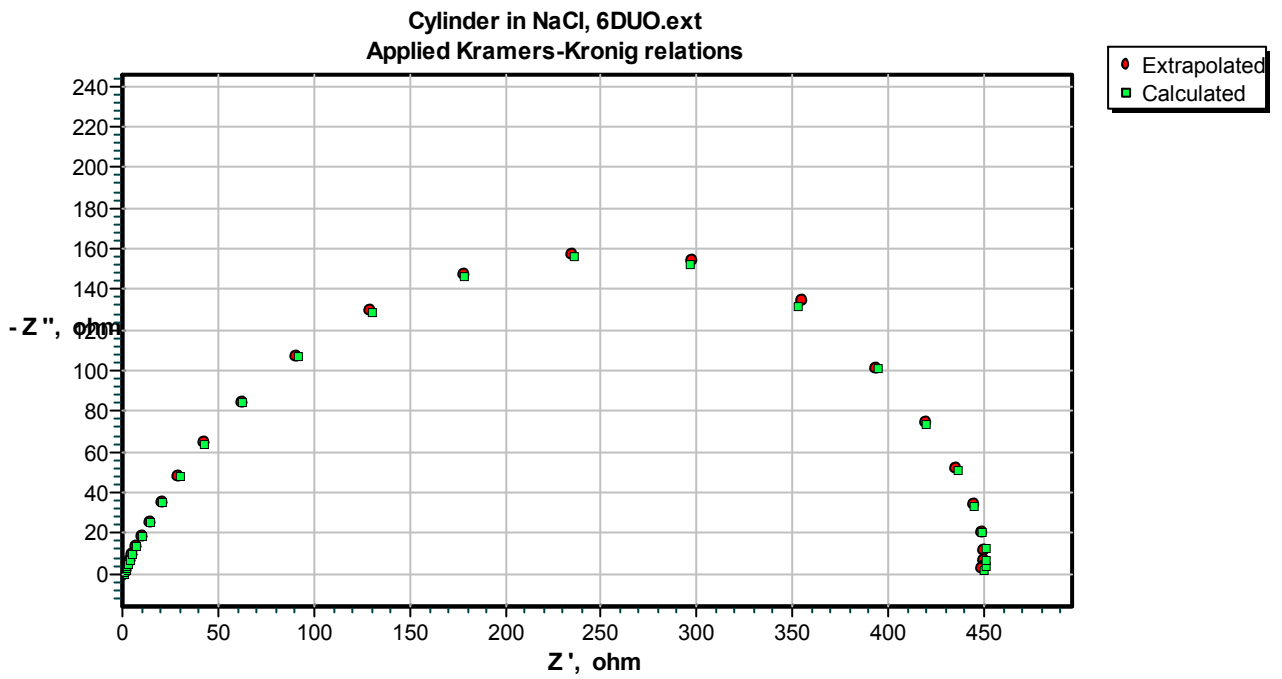
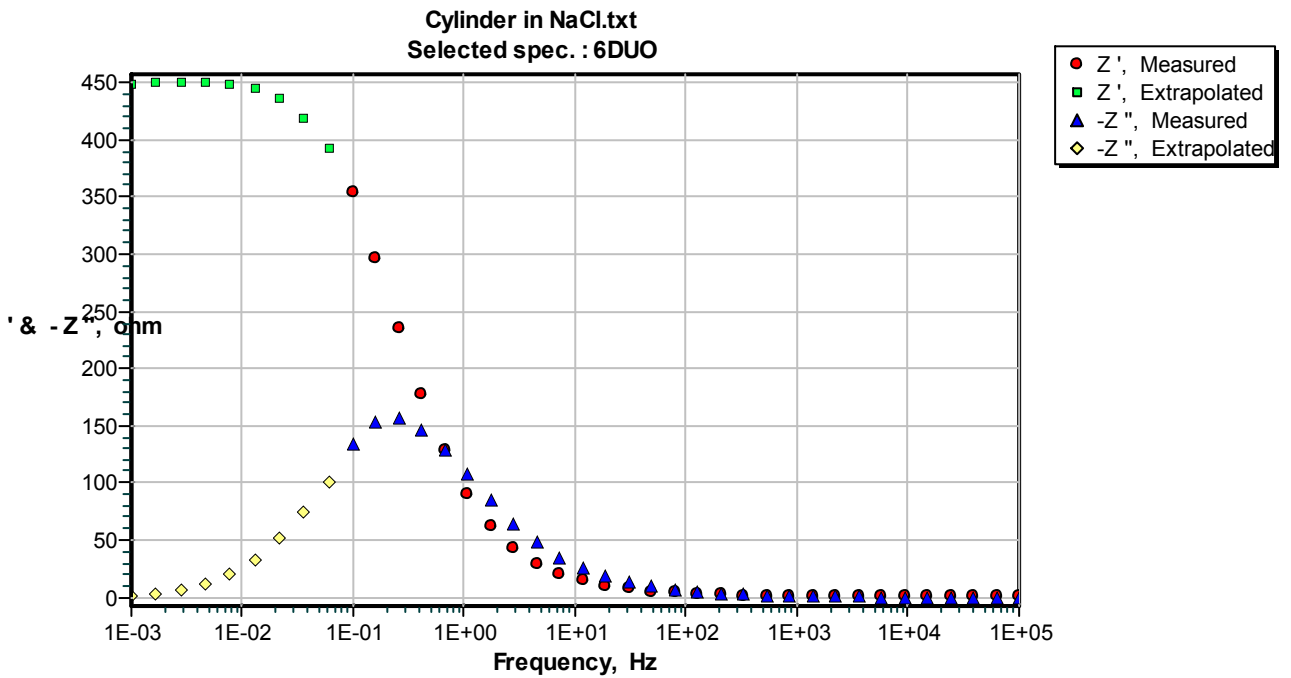


## Cylinder in NaCl

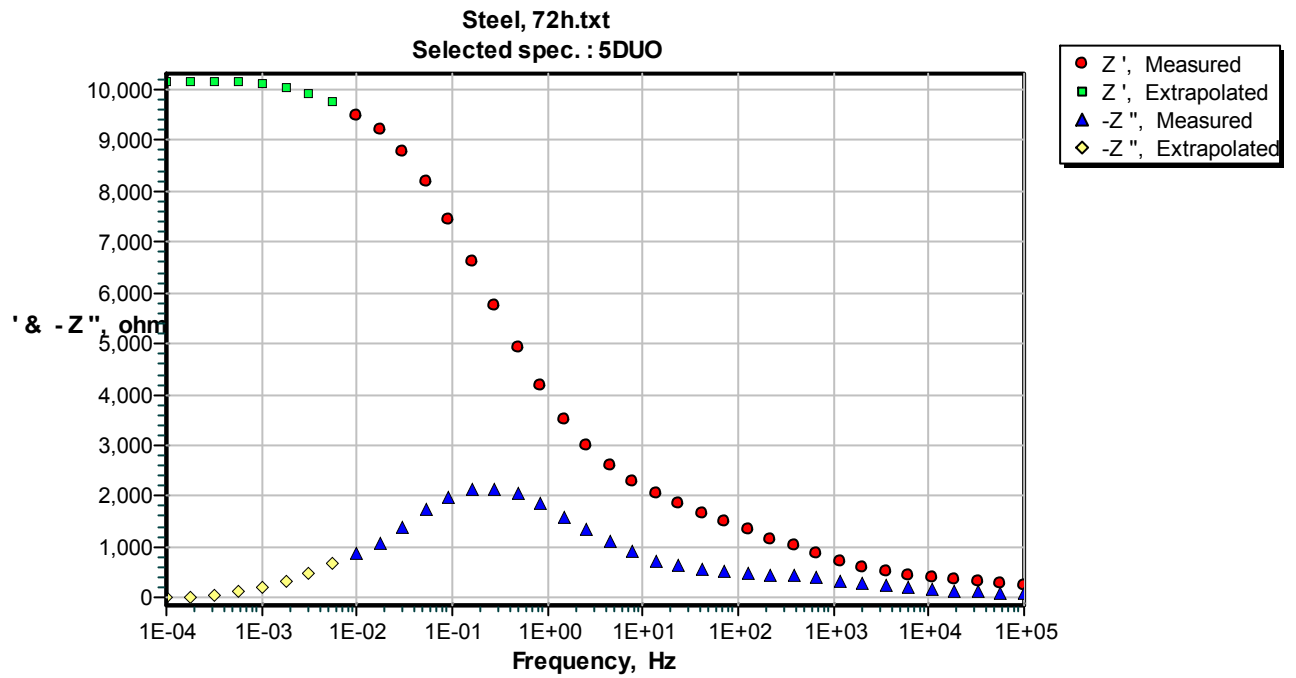
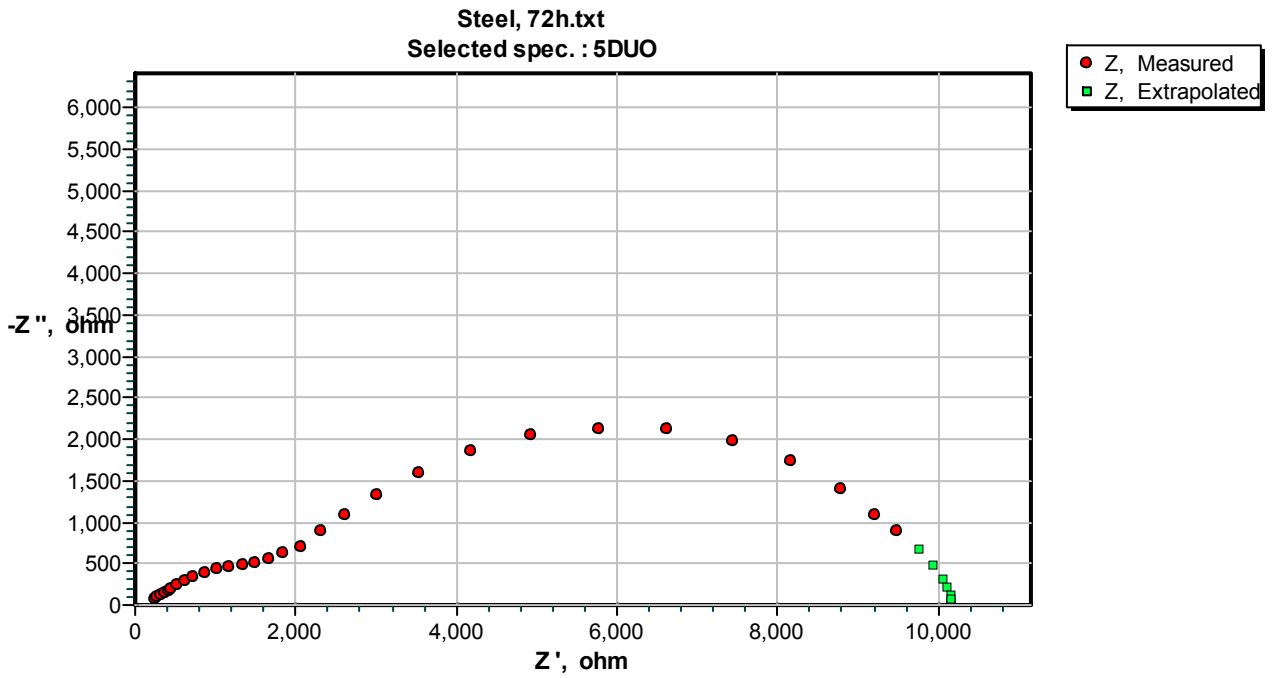
Because of the significant capacitive term at the low cut-off frequency, the impedance calculated using the K-K relations is quite different from the data.



The 6<sup>th</sup> order polynomial provided the best results. Extrapolations substantially reduced the deviations. The calculated curve is very close to the extrapolated curve.



Steel, 72h



## 7. Additional Tests

The equivalent electrical circuits were taken from the Reference for testing. Simulation run results were obtained, and then the test data were created by truncating data points for low and high frequencies. The test data file name indicates the frequency below which data points were truncated. Data points in the high frequency range were also truncated for some data. The order of the polynomials which provided good results are indicated in the parentheses.

| Simulation run | Circuit Description Code | Parameters  | Test data file (order of poly.)  |
|----------------|--------------------------|---|--|
| TestA          | R1(C2R3)                 | R1 = 10 ohms<br>C2 = 100 uF<br>R3 = 1e5 ohms  | TestA, 1 mHz to 100 Hz (4)<br>TestA, 10 mHz to 100 Hz (7)                          |
| TestB          | R1(C2(R3O4))             | R1=10 ohms<br>C2 = 10 uF<br>R2 = 100 ohms<br>O4-Yo = 0.00612 S-sec <sup>0.5</sup><br>O4 -B = 1.22 sec <sup>0.5</sup>                                  | TestB, wmin = 1 Hz (7)   |
| TestC          | R1(Q2R3)                 | R1 = 1.87 ohms<br>Q2-Yo = 1100 uF<br>Q2-n = 0.71<br>R3 = 5.80 ohms  | TestC, wmin = 1Hz (4)<br>TestC, wmin = 10 Hz (5)<br>TestC, wmin = 50 Hz (5)        |
| TestD          | R1(C2(R3O4(C5R6)))       | R1 = 23 ohms<br>C2 = 19 uF<br>R3 = 418 ohms<br>O4-Yo = 9.96e-4 S-sec <sup>0.5</sup><br>O4-B = 0.843 sec <sup>0.5</sup><br>C5 = 95 uF<br>R6 = 695 ohms | TestD, 0.1 Hz to 1 kHz (7)<br>TestD, 1 Hz to 1 kHz (7)<br>TestD, 5 Hz to 1 kHz (8) |

These data files are also located in the ...\**data\kktest data** folder. Find extrapolations and compare with the simulation run results.

### Summary

1. When the impedance below the lowest measured frequency seem to have a dominant effect on the measured data, you may consider extrapolating the measured data and using the extrapolated data for analysis.
2. It is not pertinent to test the validity of the measured data using the K-K relations without extrapolations when capacitive term is significant at the low cut-off frequency (no data below this frequency).
3. Standard procedure: (a) determine the extrapolations of the  $Z'$  and  $Z''$  satisfying the K-K relations, (b) compare the extrapolated curves with corresponding calculated curves, and (c) determine the deviations. If the deviations are very large, we may question the validity of the measured data.

### Reference

J.M. Esteban and M.E. Orazem: "On the Application of the Kramers-Kronig Relations to Evaluate the Consistency of Electrochemical Impedance Data," J. Electrochem. Soc., Vol. 138, No. 1, 1991, pp. 67-76.