

# **VAJA IZ IMPEDANČNE SPEKTROSKOPIJE**

**Predmet: Vaje iz Materialov**

**Vodja vaje: Miran Gaberšček**

**Fakulteta za kemijo in kemijsko tehnologijo**

# SOME BASIC ASPECTS OF THE IMPEDANCE SPECTROSCOPY

*M. Gaberšček*

## 1. INTRODUCTION

Impedance spectroscopy is a relatively new and powerful method of characterising many of the electrical properties of materials and their interfaces with electronically conducting electrodes. It may be used to investigate the dynamics of bound or mobile charge in the bulk or interfacial regions of any kind of solid or liquid material: ionic, semiconducting, mixed electronic-ionic, and even insulators (dielectrics). Recently, a revolution in the automation of an otherwise difficult measuring technique has moved impedance spectroscopy out of the academic laboratory and has begun to make it a technique of significant importance in the areas of industrial quality control of paints, emulsions, electroplating, thin-film technology, materials fabrication, mechanical performance of engines, corrosion, and so on. The parameters derived from impedance spectroscopy fall generally into two categories:

- a) those pertinent only to the material itself, such as conductivity, dielectric constant, mobilities of charges, equilibrium concentrations of the charged species, and bulk generation-recombination rates,
- b) those pertinent to an electrode-material interface, such as adsorption-reaction rate constants, capacitance of the interface region, and diffusion coefficient of neutral species in the electrode itself.

Today, commercial instruments are available which measure the impedance as a function of frequency automatically in the frequency ranges of about 1mHz to 1MHz. In this range impedance values from about 0.1  $\Omega$  up to 100 M $\Omega$  can be measured. A major advantage of the impedance spectroscopy over other techniques for electrical characterisation of materials (pulse methods, white noise techniques, classical electrochemical dc and ac techniques) is its high accuracy - usually the relative error of measurements does not exceed 1%. On the other hand, the complexity of many impedance spectra and, consequently, the difficulties in their interpretation, still represent one of the major obstacles for this technique to become a standard spectroscopic method.

## 2. DEFINITIONS AND EXAMPLES

If a potential (voltage) is applied across a given material (batteries, corroding material, ceramics, polymers etc.) a current is caused to flow through it, with a value determined by the mechanisms of the electrical transport taking place. Let the applied voltage  $U$  have a sinusoidal shape:

$$U = U_o e^{j\omega t} = U_o [\cos(\omega t) + j\sin(\omega t)] \quad (1)$$

where  $U_o$  is the amplitude of the voltage excitation signal,  $\omega$  is its angular frequency,  $t$  is time and  $j = \sqrt{-1}$ . The subsequent current will also be sinusoidal, with a value of:

$$I = I_o e^{j(\omega t + \phi)} = I_o [\cos(\omega t + \phi) + j \sin(\omega t + \phi)] \quad (2)$$

where  $I_o$  is the amplitude of the current response and  $\phi$  is the phase shift between the voltage excitation and current response.

The relationship between the applied potential and the current flow is known as the impedance,  $Z$ , which is analogous to the resistance-current-potential relationship of a dc circuit:

$$Z = \frac{U}{I} = \frac{U_o}{I_o} e^{-j\phi} = \frac{U_o}{I_o} [\cos(\phi) - j \sin(\phi)] \quad (3)$$

Now, if a sinusoidal potential is applied across a pure resistance, the amplitude equals  $U_o/I_o = R$  and the phase shift  $\phi = 0$  for all frequencies. This gives for the impedance:

$$Z = R e^{-j0} = R [\cos(0) - j \sin(0)] = R \quad (4)$$

This is shown on a plot of the real (a) and imaginary (jb) components of the real axis (Fig.1,a).

If the sinusoidal voltage is applied across a dielectric with capacitance  $C$ , the amplitude of the impedance is now dependent on the frequency, namely,  $U_o/I_o = 1/\omega C$  and the phase angle equals  $90^\circ$ . The impedance becomes:

$$Z = \frac{1}{\omega C} e^{-j(\pi/2)} = \frac{1}{\omega C} [\cos(\pi/2) - j \sin(\pi/2)] = \frac{-j}{\omega C} = \frac{1}{j\omega C} \quad (5)$$

Here the rule  $-j = j^{-1}$  was taken into account. As the frequency increases the magnitude of the impedance decreases, as shown in the plot (Fig.1,b).

The result of combining these two basic circuit components, in series or parallel, can be easily deduced, with 2 simple examples shown in Fig.1,c and in Fig.1,d, for a series resistance and capacitance and a parallel resistance and capacitance. A measuring material represented by a network of resistors and capacitors is generally known as an equivalent circuit. From an impedance spectrum plotted in the real/imaginary plane it is possible to deduce the equivalent circuit and determine the significance of the different components.

## 2.1 Distribution of electrical properties

If the material under investigation is not electrically homogeneous (porosity, polycrystallinity, rough electrode surfaces, fractal structure of interfaces, etc.) anomalies in the impedance plots may be observed, such as declination from  $90^\circ$  (Fig.2,a) or depression of the semicircle (Fig.2,b). The anomalies are usually described by introducing a parameter  $\alpha$  which is related to a distribution of the resistive and/or the capacitive properties within the material. In such cases, the values of  $R$  and/or  $C$  obtained from the impedance spectra represent a sort of "average" values of the resistive and/or capacitive properties of the material studied.

## 2.2 Evaluation of the impedance parameters of a bulk material

By choosing appropriate electrodes it is possible to avoid transport complications at the material/electrode interfaces so that only the bulk properties of the material under investigation are measured within a certain frequency range. If so, then the interpretation of the resistance  $R$  and the capacitance  $C$  is rather straightforward:

- a) The measured resistance  $R$  is related to its specific resistivity  $\rho$  according to:  $R = \rho(l/A)$ , where  $l$  is the distance between the electrodes and  $A$  is the electrode surface area,
- b) The measured capacitance  $C$  is related to the geometry of the measured sample and to its dielectric constant  $K$  according to:  $C = K\varepsilon_0(A/l)$  where  $A$  and  $l$  have the same meaning as above and  $\varepsilon_0$  is the permittivity of vacuum.

## 3. REFERENCES

1. *Impedance spectroscopy emphasising solid materials and systems*, J.Ross Macdonald, Ed., J. Wiley & Sons, Inc., New York, 1987.
2. N.D.Cogger, *An introduction to electrochemical impedance measurement*, Solartron Instruments, Technical report number 006/83, Hampshire 1983.

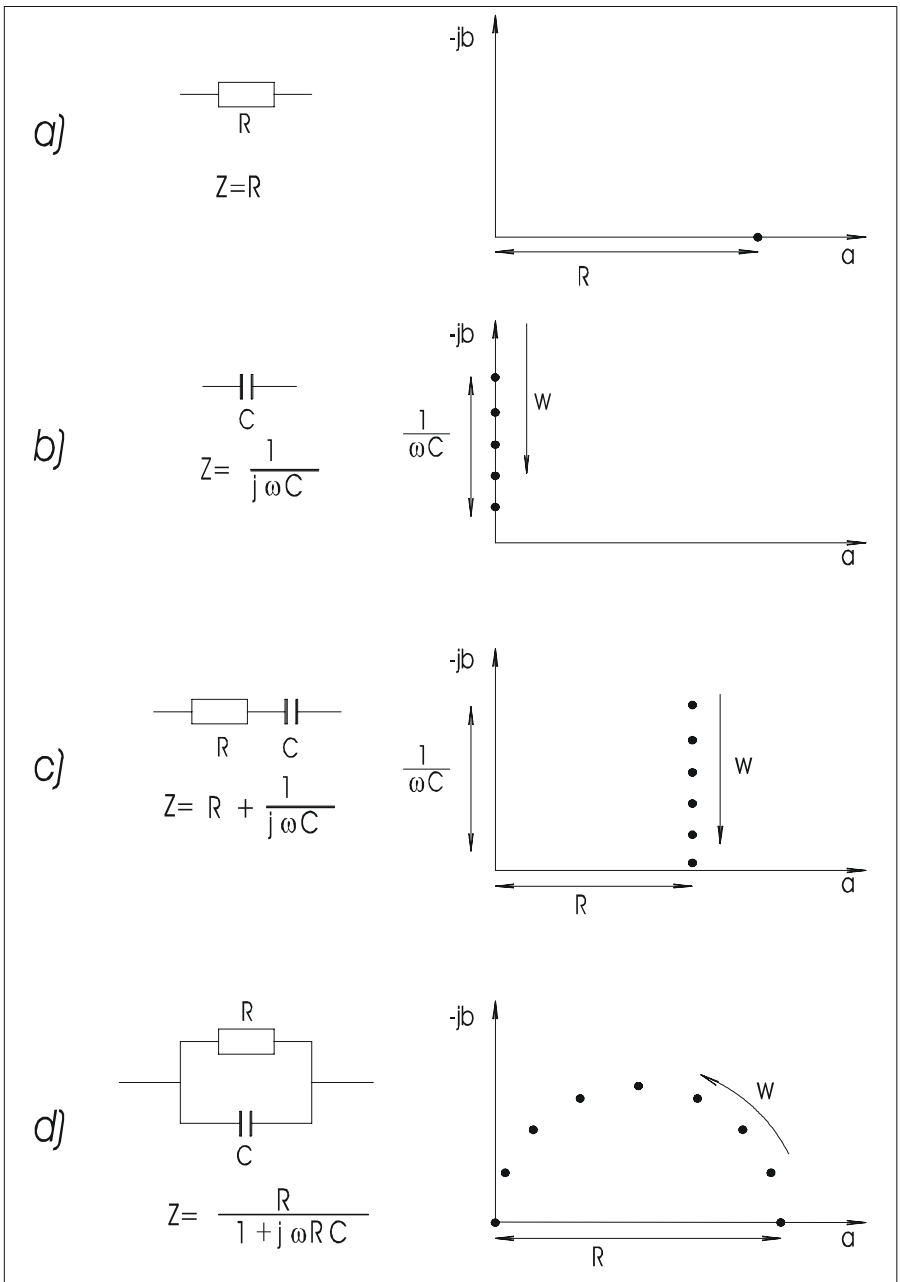
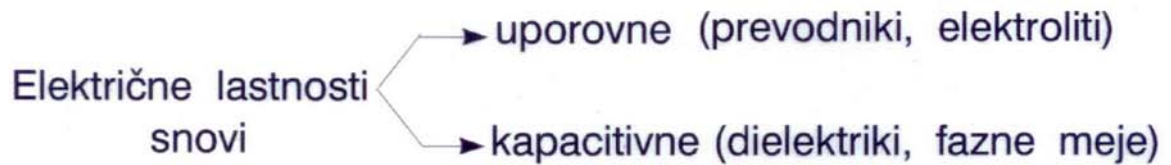


Fig. 1: Impedance of simple equivalent circuits.

## IMPEDANČNA SPEKTROSKOPIJA



### Impedančna spektroskopija (IS)

- najbolj natančna metoda za merjenje električnih lastnosti
- loči med uporovnimi in kapacitivnimi lastnostmi
- loči med transportom po volumnu snovi in transportom preko faznih mej.

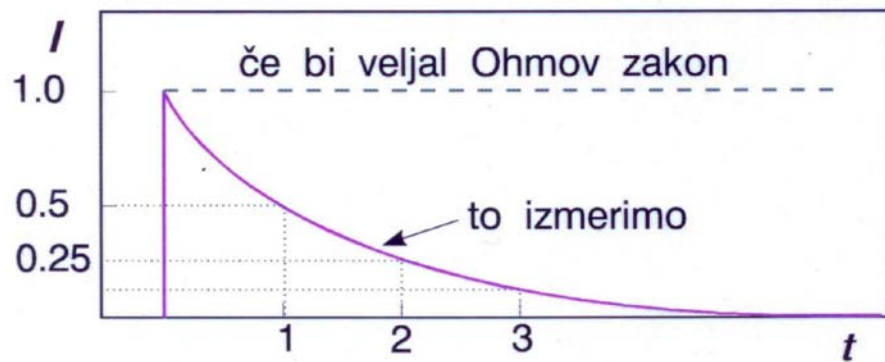
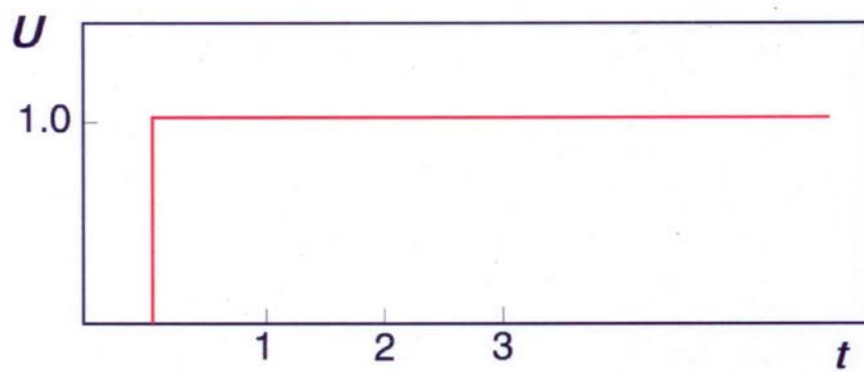
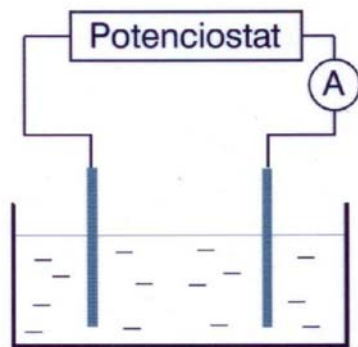
### DEFINICIJA IMPEDANCE

Zelo posplošeno:

Impedanca ( $Z$ ) je razmerje med *napetostnim* in *tokovnim* signalom pri vzburjanju merjenca.

Vprašanje: Kakšna je pravzaprav razlika med Ohmovim zakonom in impedanco?

Napravimo miselni poskus.



t	U	I	R
0	1	1	1
1	1	0.5	2
2	1	0.25	4
3	1	0.125	8

Rezultat poskusa:  $\frac{U}{I} = f(t)$

V splošnem  $\frac{U(t)}{I(t)}$  ne moremo izraziti eksplicitno, ker:

$$U(t) = \int_0^{\infty} f(\tau) \cdot I(t - \tau) d\tau ; f(\tau) \text{-lastnost sistema}$$

Zapleteni konvolucijski integral pretvorimo v frekvenčni prostor s Fourierovo transformacijo, za katero velja:

$$X(\omega) = \int_0^{\infty} x(t) \cdot \exp(-j\omega t) dt ; \begin{array}{l} j = \sqrt{-1} \\ \omega \text{ - krožna frekv.} \end{array}$$

Če Fourierovo transformacijo uporabimo na konvol. integralu, dobimo:

$$U(\omega) = Z(\omega) \cdot I(\omega)$$

Za razliko od  $f(\tau)$ , impedanco  $Z(\omega)$  torej lahko izrazimo eksplicitno.

Posebno ugodna lastnost impedance:

- pri določenih tipih vzbujanja je lahko merljiva količina.

Primer: vzbujamo z napetostnim sinusnim signalom določene frekvence in izmerimo ustrežni sinusni tokovni odziv. Podelimo vzbujanje in odziv in dobimo impedanco sistema pri dani frekvenci.

Postopek ponovimo pri različnih frekvencah in dobimo impedanco kot funkcijo frekvence (frekvenčni odziv).

$$U = U_o \cdot \exp(j\omega t)$$

$$I = I_o \cdot \exp[j(\omega t + \phi)]$$

$$Z = \frac{U_o}{I_o} \exp(-j\phi)$$

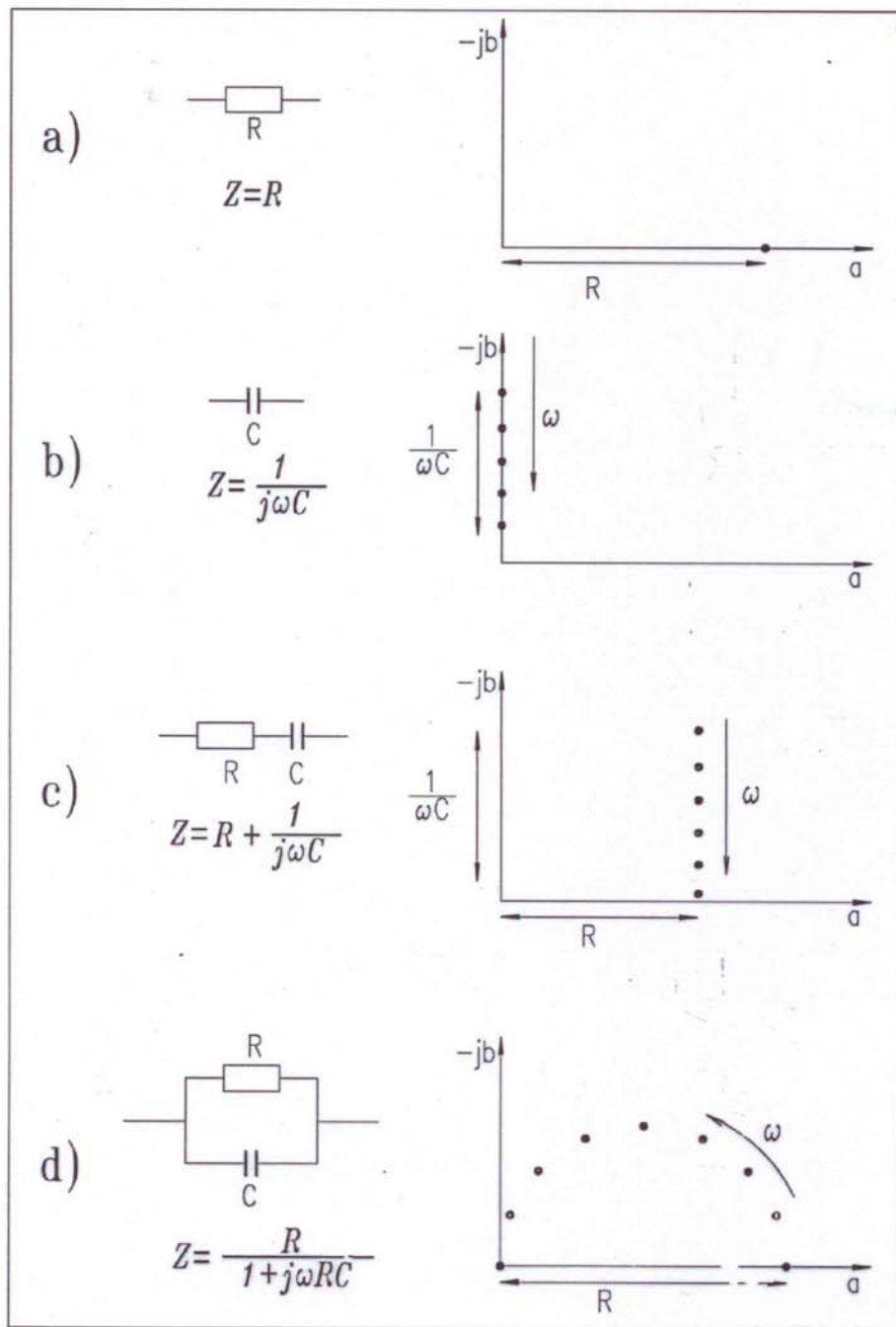
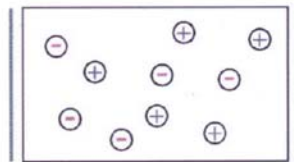
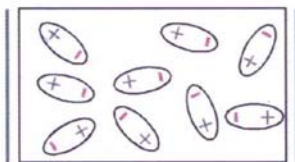


Fig.1: Impedance of simple equivalent circuits.

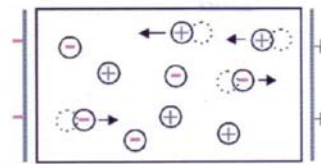
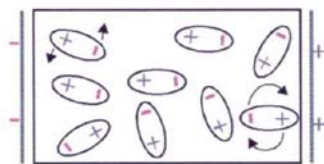
### *Dielektriki*

### *Prevodniki*

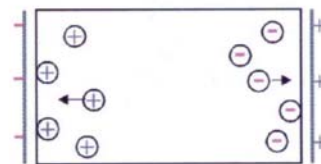
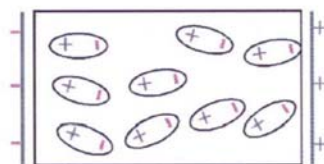
$t=0$   
 $\omega = \infty$



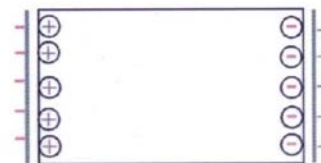
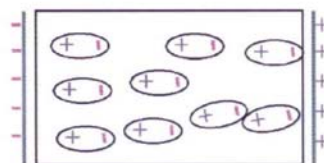
$t=1$   
 $\omega=100$



$t=100$   
 $\omega=1$



$t=\infty$   
 $\omega=0$



Dipoli lahko v električnem polju samo rotirajo. Kapacitivnost je odvisna od razdalje med + in - in od števila dipolov.

Prosti naboji se v el. polju premikajo. Pri tem pride do 'trenja', ki določa upornost sistema.

## OPIS IZVEDBE VAJE IZ IMPEDANČNE SPEKTROSKOPIJE

Vaja iz impedančne spektroskopije sestoji iz treh delov: priprave elektrod na danem vzorcu, meritve in analize izmerjenega spektra.

### 1. Priprava elektrod

Postopek priprave elektrod je odvisen od tega ali je merjenec tekoč (npr. elektrolit) ali trden (tanek film, polimer itd.) in od geometrije vzorca:

#### a) tekoči vzorci

- v tem primeru najprej pripravi vzorec, ki ga boš meril, in sicer okoli  $10^{-5}$  M raztopino bakrovega acetata,
- v raztopino namesti dve enaki bakrovi (ali platinovi) elektrodi,
- eno od elektrod poveži z vhodom WE in RE2, drugo pa z vhodom CE in RE1 na elektrokemijskem vmesniku instrumenta Solartron.

#### b) baterije

- prispajkaj eno bakreno žico na negativni, drugo pa na pozitivni pol baterije. Žici naj bosta dolgi okoli 2-3 cm.
- eno od žic poveži z vhodom WE in RE2, drugo pa z vhodom CE in RE1 na elektrokemijskem vmesniku instrumenta Solartron.

#### c) trdni ploščati vzorci

- iz priloženega koluta izreži dve 3cm dolgi grafitni nitki,
- eno od grafitnih nitk položi na eno od površin ploščatega vzorca in na to površino nanesi srebrno ali ogljikovo pasto, ki se uporabljata pri elektronski mikroskopiji (pomembno je, da naneseš dovolj paste, da se bo nitka sprijela s srebrno elektrodo),
- počakaj, da se pasta posuši,
- postopek ponovi na drugi strani ploščatega vzorca,
- preveri, da nista srebrni elektrodi v kratkem stiku,
- eno od grafitnih nitk poveži z vhodom WE in RE2, drugo pa z vhodom CE in RE1 na elektrokemijskem vmesniku instrumenta Solartron.

#### d) tanki filmi, nanešeni na steklo ali drug izolator

- ob robu takih vzorcev sta že pripravljene kovinski elektrodi,
- na vsako od obstoječih kovinskih elektrod prilepi grafitno nitko po enakem postopku kot pod točko c),
- eno od grafitnih nitk poveži z vhodom WE in RE2, drugo pa z vhodom CE in RE1 na elektrokemijskem vmesniku instrumenta Solartron.

## 2. Meritev

- a) Na računalniku, ki je povezan z elektrokemijskim vmesnikom in frekvenčnim analizatorjem odtipkaj ukaz **meri**.
- b) Pojavi se anketa z nastavitvenimi parametri za meritev.
- c) Za začetek nastavitvenih parametrov ne spreminjaj, le pri postavki **Ime datoteke**: odtipkaj poljubno ime, pod katero boš shranil meritev.
- d) Poženi meritev s pritiskom na tipko **Enter**. Na spodnjem delu ekrana se pojavi napis *Run*.
- e) Počakaj, da se na ekranu v spodnji vrstici pojavi napis *completed*.
- f) Če merske točke sipajo, enkrat pritisni na tipko **Esc**, s čimer se vrneš v anketo. Spremeni vrednost amplitude z 1 na 10 in spet poženi meritev.
- g) Če opaziš, da je skala grafa premajhna ali prevelika, da bi lahko opazoval potek meritve, se prav tako vrni v anketo in ustrezno popravi skalo pod postavko **Maksimum skale**: ter ponovno poženi meritev.
- h) Če ima impedančni spekter podobno obliko kot grafi v preglednem tekstu o impedanci, si na list papirja skiciraj približen potek izmerjenega spektra.
- i) Z dvakratnim pritiskom na tipko **Esc** se vrni v operacijski sistem DOS.

## 3. Analiza izmerjenega spektra

- a) Če ima spekter, ki si ga izmeril, obliko, podobno grafu 1a), odtipkaj na računalniku ukaz **Upor**. Nato:
  - odtipkaj ime, pod katerega si shranil svojo meritev
  - iz grafa, ki ga dobiš na ekranu, odčitaj upornost svojega vzorca
  - izmeri dimenzije vzorca (razdaljo med elektrodama in njuno površino),
  - izračunaj specifično upornost svojega vzorca.
- b) Če ima spekter, ki si ga izmeril, obliko, podobno grafu 1b), odtipkaj na računalniku ukaz **Kapac**. Nato:
  - odtipkaj ime, pod katerega si shranil svojo meritev,
  - poženi prilagajanje, tako da odtipkaš številko 3 in tipko **Enter**,
  - pritisnjaj tipko **Enter** toliko časa, da računalnik začne izvajati prilagajanje,
  - po končanem prilagajanju si zapiši vrednosti parametrov C in alfa,
  - izmeri dimenzije vzorca (razdaljo med elektrodama in njuno površino),
  - Izračunaj dielektrično konstanto svojega vzorca.
- c) Če ima spekter, ki si ga izmeril, obliko, podobno grafu 1d), odtipkaj na računalniku ukaz **RC**. Nato:
  - odtipkaj ime, pod katerega si shranil svojo meritev
  - poženi prilagajanje, tako da odtipkaš številko 3 in tipko **Enter**,
  - pritisnjaj tipko **Enter** toliko časa, da računalnik začne izvajati prilagajanje,
  - po končanem prilagajanju si zapiši vrednosti parametrov C, R in alfa

## Impedančna spektroskopija - naloge

1. Nariši graf impedančnega odziva za vzorec, ki ima:
  - a) samo uporovne lastnosti
  - b) samo kapacitivne lastnosti.
2. Nariši graf impedančnega odziva za vzorec, ki ima uporovne in hkrati (vzporedno s tem) kapacitivne lastnosti. Na grafu podaj količine na oseh in smer naraščanja frekvence vzbujanja.
3. Izračunaj debelino in specifično upornost izbranega vzorca, če si pri meritvi ugotovil, da znaša upor  $106 \Omega$ , kapacitivnost  $10^{-11} \text{ F}$ , iz literaturnih podatkov pa veš, da je dielektrična konstanta vzorca enaka 5. Absolutna dielektrična konstanta  $\epsilon_0 = 8.85 \cdot 10^{-12} \text{ As/Vm}$ , površina elektrod pa je bila  $1 \text{ cm}^2$ .
4. Upornost ionskega prevodnika pri  $100^{\circ} \text{ C}$  znaša  $10^6 \Omega$ , pri  $1000^{\circ} \text{ C}$  pa  $1 \Omega$ . Izračunaj aktivacijsko energijo za ionsko prevajanje v danem vzorcu!