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Split-Ring Resonator as Detector for Liquid Chromatography

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Introduction

Liquid Chromatography (LC) is an important method of physical separation of compounds in liquids. The fields of application are wide-ranging such as food, drug and environmental analysis, process monitoring in chemical industry and bioreactors [1-3]. Therefore, LC detectors require a broad range of compounds that can be detected when eluting from the LC column. Common universal detectors use different detection principles and therefore, different characteristics of the compounds, and can be categorized in light based detectors (fluorescence, absorption, refraction and scattering) and resistive detectors [4]. However, the sample preparation process for some of these detectors is time consuming and elaborate to make the compounds detectable, e.g. by optical detectors [5]. Other detectors such as mass spectrometers imply high instrumental effort with high purchasing and operating costs. Nevertheless, mass spectrometry adds a second dimension of separation for better compound identification [4]. These examples show that universal and inexpensive detectors without elaborate sample preparation would ease LC.

Following our last presentation at the Dresdner Sensor Symposium in 2019 "*Split-ring resonator: A new detector in liquid chromatography*" [6], we now present two new different split-ring resonator (SRR) topologies with different fluidic setups that are both compared to the SRR used in [6]. For calibrating the system, we use a vector network analyzer (VNA) and mixtures of isopropanol and deionized water.

A split-ring resonator (SRR) is a LCR resonant circuit that is built with a split microstrip line formed to a ring that is coupled to a microstrip transmission line. The split in the microstrip line acts as a capacitor and affects the resonance frequency. At resonance frequency, the wave couples into the ring and forms a standing wave with a wavelength depending on the circumference of the ring and the capacitance of the split. When the input signal frequency is matching the resonance frequency of the SRR, an intense electric field localized in the split is formed [7]. Thus, the amplitude of the transmitted signal through the microstrip line reaches a minimum in case of resonance. This means that the resonance frequency of the SRR can be used to measure the electromagnetic properties of liquids located at the split capacitor by changing R and C of the LCR resonant circuit. In particular, the liquid changes the capacitance of the split capacitor due to permittivity changes, especially changes in the real part of the permittivity. In recent works, SRRs are used for measuring liquids in different applications, especially with biological analytes [8-10]. This shows the general usability of split-ring resonators for liquid sensing. Here, this principle is transferred to develop a new universal detector for liquid chromatography.

The standard measuring principle for the determination of the resonance frequency of SRRs is a broadband frequency sweep using a vector network analyzer (VNA). The VNA has the advantage of analyzing the SRR by measuring the transmitted and the reflected signal at the inputs and outputs of the SRR. These measurements are performed at multiple discrete frequencies in the frequency range of the SRR. For illustration, such a broadband frequency sweep is simulated, see Fig. 1, using CST Microwave Studio for the SRR No. 3 described below. However, a broadband frequency sweep is time consuming, depending on the used VNA, and thus not suitable for LC applications with short peak width. Here, the resonance frequency needs to be recorded continuously. Therefore, another measuring principle is used in this work based on measuring the amplitude of the transmitted signal at a fixed frequency shown in Fig. 2. In this example, the permittivity of the sample liquid is changed from ε_r = 29.3 (pure deionized water) to ε_r = 29 at t = 50 s and back to ε_r = 29.3 at t = 100 s.

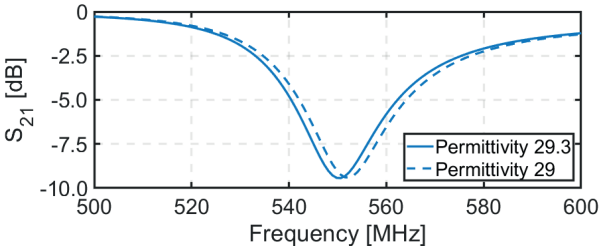

Fig. 1: Simulated frequency sweep between 500 and 600 MHz using CST Microwave Studio for permittivities ε_r = 29 and ε_r = 29.3 inside the split of the SRR No. 3 described below.

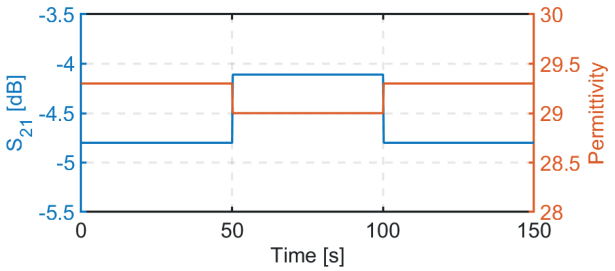

Fig. 2: Simulated transmission (CST Microwave Studio) of the SRR No. 3 at 540 MHz when changing the permittivity from $\varepsilon_r = 29.3$ to $\varepsilon_r = 29$ at t = 50 s and back to $\varepsilon_r = 29.3$ at t = 100 s.

Electronics

To enable continuous recording of the resonance frequency as required in LC applications we use an envelope detector giving a continuous output voltage at a fixed frequency that corresponds to the resonance frequency. If the permittivity of a sample placed in the split changes the resonance frequency, the amplitude of the transmitted signal at a fixed frequency also changes.

To measure the change of the amplitude of the transmitted signal, we use our self-developed electronics shown in Fig. 3 that is equipped with a controllable excitation source and two envelope detectors, one for the excitation source and one for the transmitted output signal. A temperature controlled crystal oscillator, a phase locked loop with voltage-controlled oscillator, a divider and a phase frequency detector are used to generate the output frequency. Additionally, a low pass filter for filtering the harmonics and an adjustable output amplifier are integrated. The output frequency can be set between 23.5 MHz and 6 GHz with a minimum measurable frequency change of 826.4 Hz. The frequency stability is high. In 20 s of measurement time, a maximum delta of just 840 mHz could be measured with a N9030A PXA Signal Analyzer from Keysight Technologies. The excitation source stability is also high. The measured source frequency differs by a maximum of 0.002 dBm.

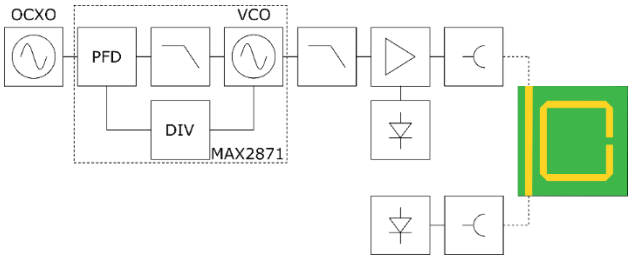

Fig. 3: Basic block diagram of the developed measuring electronics.

Experimental

Here, we present three different split-ring resonator topologies with different fluidic setups. The challenge is to increase the sensitivity while realizing a simple fluidic concept that does not imply any memory effects. The first SRR shown in Fig. 4 consists of a simple printed circuit board (PCB) with two microstrip lines. The PCB material used is Rogers RO4350B, which is suitable for high frequency applications. The split-ring itself is a quadratic microstrip line with a capacitor enlarged towards the center. Here, the board is slit and edge metalized to form a large capacitor. A glass capillary with a square cross-section, used as a fluid channel, is placed inside the split.

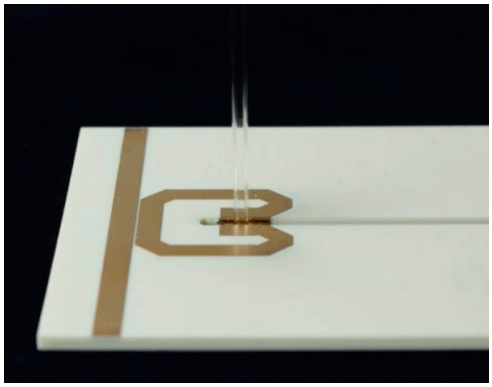

Fig. 4: Split-ring resonator No. 1 with glass capillary inside the split.

The second SRR setup shown in Fig. 5 (a) also consists of a PCB, slit and edge metallized in the split similar to the PCB shown in Fig. 4. The fluid channel shown in Fig. 5 (b) is realized by two PEEK-blocks with holes and internal channels. Thus, the fluid is guided as shown in blue in Fig. 5 (b). One major advantage of this SRR compared to the first SRR setup is the direct contact between the fluid and the edge metallized capacitor over a large electrode area giving higher sensitivity. Furthermore, the setup is more robust and easier to use.

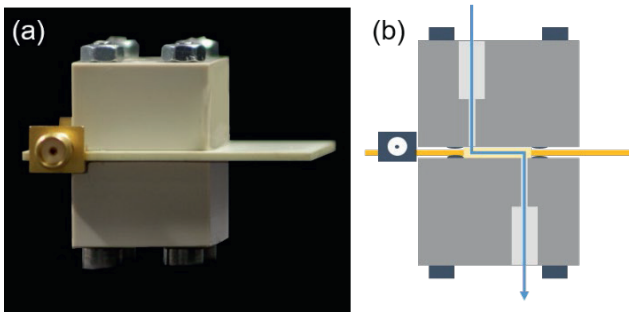

Fig. 5: (a) Split-ring resonator No. 2 with integrated flow channel in two PEEK blocks, (b) cross sectional view showing the flow channel.

The third SRR model named capillary split-ring resonator (CaSRR) is shown in Fig. 6 and consists of a microstrip line on a PCB, while the split-ring itself is made of a stainless steel capillary and a PEEK-union. The split capacity is formed inside the PEEK-union between the two opposing capillaries.

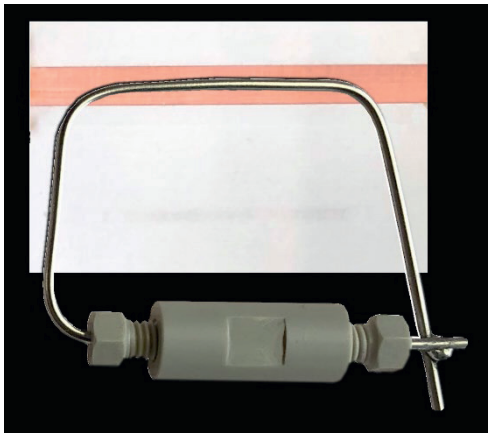

Fig. 6: Split-ring resonator No. 3: Capillary split-ring resonator.

Results

To compare the three different split-ring resonators, we use mixtures of deionized water and isopropanol to determine the sensitivities of each SRR. First measurements were performed with a vector network analyzer. To demonstrate the reversibility of the measurements shown in Fig. 7, the concentration of isopropanol in deionized water was increased in 20% steps from 0% up to 100% and afterwards decreased in 20% steps from 90% to 10%. The concentration is converted to the permittivity. The permittivity of deionized water is $\varepsilon_r = 29.3$ and the permittivity of isopropanol is $\varepsilon_r = 18.6$ at T = 20 °C [11]. The split-ring resonator with glass capillary shows an operating point dependent sensitivity between 0.31 MHz/$\Delta\varepsilon_r$ for pure deionized water and 22.61 MHz/$\Delta\varepsilon_r$ for pure isopropanol. For measurements in aqueous solutions, the SRR has a low limit of detection of $\Delta\varepsilon_{r,min} = 1.75$. To enhance the sensitivity the second SRR has nearly the same topology but direct contact between the fluid and the edge metallized capacitor over a large electrode area. This model shows higher sensitivity between 10.07 MHz/$\Delta\varepsilon_r$ for pure deionized water and 217.81 MHz/$\Delta\varepsilon_r$ for pure isopropanol giving improved limit of detection of $\Delta\varepsilon_{r,min} = 0.07$ in aqueous solutions. Unfortunately, this second SRR shows memory effects, especially if acetonitrile is used as a solvent as needed for many LC applications. The memory effect might be caused by the porous surface of the PCBs, which is not fully protected by the edge metallization. In addition, the PCB material used has a layered structure that could further enhance the observed memory effect. Therefore, a new type of split-ring resonators was developed. This SRR consists of standard stainless steel capillaries. The split is located inside a PEEK-union between the two opposing capillaries. This SRR shows a sensitivity between 7.89 MHz/$\Delta\varepsilon_r$ for pure deionized water and 15.44 MHz/$\Delta\varepsilon_r$ for pure isopropanol and a limit of detection of $\Delta\varepsilon_{r,min} = 0.09$ in aqueous solutions. So far, a vector network analyzer was used for all measurements.

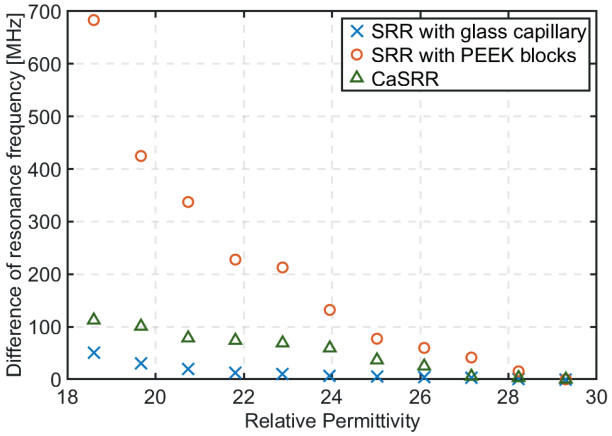

Fig. 7: Comparison of the three different SRR topologies. The resonance frequency for pure deionized water ($\varepsilon_r = 29.3$) is used as reference and subtracted from the resonance frequency measured for the isopropanol-deionized water mixtures.

From the three different SRRs, the capillary split-ring resonator has the highest sensitivity without any memory effects. Thus, this SRR topology is used in the following together with the developed electronics for continuous measurements at a fixed frequency of 650 MHz. Due to the increased sensitivity, the isopropanol-deionized sample mixtures just contain small fractions of isopropanol. The isopropanol concentration now increases in steps of 1% up to a maximum of 5%. Afterwards, the isopropanol concentration decreases from 4.5% in steps of 1% down to 0.5% and finally pure deionized water. The output voltage and the corresponding permittivity are plotted over time in Fig. 8. The mean value of every output voltage per permittivity is then plotted over permittivity in Fig. 9. From the linear regression $f(x) = -9.50\,\mathrm{mV} \cdot x + 371.69\,\mathrm{mV}$, the sensitivity is determined to 9.50 mV/$\Delta\varepsilon_r$. Considering the noise of 0.074 mV, the limit of detection is further improved to $\Delta\varepsilon_{r,min} = 0.03$ within an averaging time of just 24 ms.

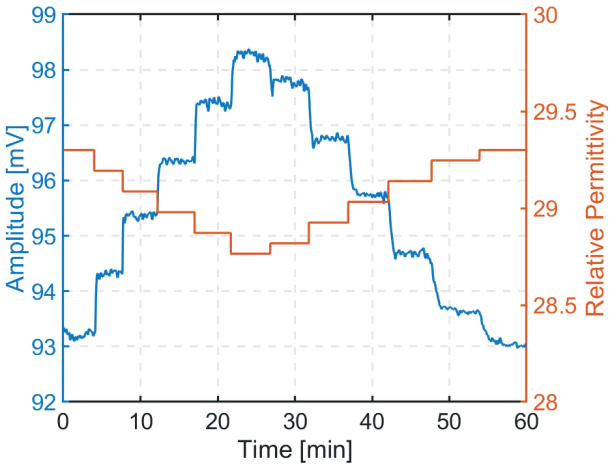

Fig. 8: Continuous measurement of small isopropanol concentrations in deionized water with the capillary split-ring resonator and the electronics developed for continuously recording of liquids.

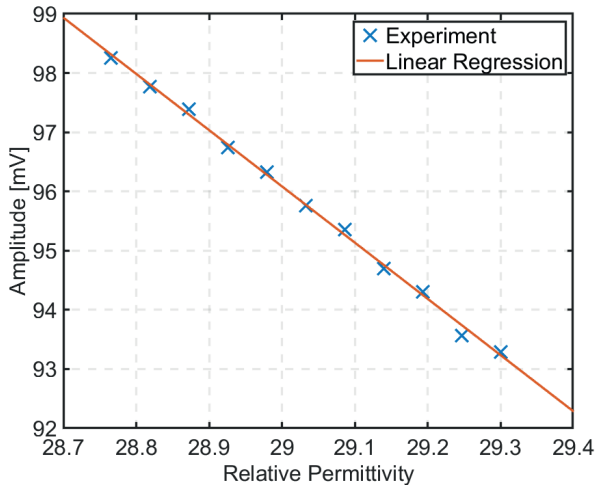

Fig. 9: Mean value of output voltage per permittivity from Fig. 8 and linear regression with $f(x) = -9.50\ \text{mV} \cdot x + 371.69\ \text{mV}$.

Conclusion

In this work, we present three different split-ring resonators with different fluidic concepts. The split-ring resonator with glass capillary shows high reproducibility and reversibility but low sensitivity. Direct contact between the sample and the electrodes of the split capacity as for the second split-ring resonator with flow channel integrated in PEEK-blocks the sensitivity increases but memory effects are observed. The new capillary split-ring resonator shows good limits of detection of $\Delta\varepsilon_{r,min} = 0.03$ for isopropanol in deionized water and also high reversibility and reproducibility. Nevertheless, the sensitivity has to be further enhanced to achieve sufficient sensitivity for liquid chromatography, e.g. by enlarging the surface of the electrodes of the split capacity and therefore enlarging the capacitance of the LCR resonant circuit. Furthermore, better limits of detection can be achieved by using a higher averaging time, which is limited by the temporal width of the LC peaks.

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