SAPPHIRE DIELECTRIC RESONATORS FOR MICROFLUIDIC COMPOSITIONAL ANALYSIS

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ABSTRACT

Cylindrical sapphire dielectric resonators (SDRs) have been developed for in-situ analysis of solvent composition within microfluidic ducts. The SDRs operate in the TE_{011} mode, chosen such that its microwave electric field is parallel to a circular duct milled into the sapphire. This results in very little depolarization of the electric field, giving very sensitive dielectric characterization of the fluid within the duct. A miniaturized SDR operating at 22.7 GHz has a fluid sample volume of ~56 nl and has been demonstrated to have volumetric detection limits of ~3 ppm of acetonitrile in toluene and ~6 ppm of water in acetonitrile.

KEYWORDS: Microwave resonator, dielectric properties, solvent composition

INTRODUCTION

The ability to interrogate precisely the composition of liquid mixtures by non-contact techniques in both static and flow situations (including extreme environments) is highly desirable for a variety of industrial, analytical and quality control procedures. In this context, microwave resonators have the useful dual roles of (a) sensitive characterization of the dielectric polarization and loss of a sample for small applied electric fields, and (b) efficient volumetric heating of the sample (if its dielectric loss is large enough to permit heating) for high microwave input powers. Heating will not be considered in detail here, but the design considerations of suitable resonators for both materials characterization and efficient heating of the same sample are identical (i.e. if it can be detected, it can also be heated).

Here, sapphire dielectric resonators (SDRs) are described for ultra-sensitive dielectric measurements of microfluids. Previously, we have demonstrated miniaturized, distributed (i.e. hairpin) resonators [1] and a lumped element (i.e. split ring) resonators [2] for the successful in-situ analysis of a microcapillary containing a mixture of polar solvents. Whispering gallery mode SDRs have also been described but with low fluid filling factors within the resonator [3]. The use of the split ring resonator was found to increase significantly the measurement sensitivity due to decreased resonator volume, but it (and the hairpin resonator) suffered from the large depolarization of the applied electric field of the liquid samples. The SDRs described here have high quality (Q) factors (e.g. 40000 at 5.3 GHz) owing to the low loss tangent of single crystal sapphire. The TE_{011} mode resonant mode is chosen to provide a divergence-free electric field \( E \) which is parallel to any circular duct, resulting in unambiguous, ultra-sensitive compositional analysis of highly-polar solvents since the electric field is not reduced by polarization. Test solutions are toluene:acetonitrile (i.e. high difference in polarity), and acetonitrile: water (more challenging since both are highly polar).

THEORY

If a dielectric sample (liquid or otherwise) is inserted into the electric field (of magnitude \( E_0 \)) of a resonator there will be a decrease of its quality factor (Q) and decrease of resonant frequency due to the sample's dielectric loss and polarization, respectively. These changes can be expressed using resonator perturbation analysis in the following form

\[
\frac{\Delta Q}{Q} = -\frac{\Im(\alpha)}{V_{\text{eff}}} \quad (1) \quad \frac{\Delta f}{f_0} = -\frac{\Re(\alpha)}{2V_{\text{eff}}} \quad (2)
\]

where \( f_0 \) is the unperturbed resonant frequency, \( \alpha \) is the sample’s electric polarizability (defined by the induced electric dipole moment \( p = \alpha_0 E_0 \)) and \( V_{\text{eff}} \) is the effective volume occupied by the electric field energy (which scales roughly with the resonator volume). Hence, conditions for both highly sensitive characterization and extreme, highly localised, volumetric heating of a dielectric sample are achieved within a resonator that has (a) suitable orientation of the electric field relative to the sample to maximise its dipole moment, and (b) miniaturised volume for electric energy storage.

Figure 1 shows an idealized, thin, cylindrical liquid column subject to an applied electric field. In case (a) the sample has low polarizability (defined as \( \alpha_b \) per unit length) since the internal electric field is reduced by the polarization charges developed on the curved surface of the liquid column, especially if the relative permittivity \( \varepsilon \) of the liquid is large, as will be the case for polar solvents. In case (b) the internal electric field differs little from the applied field and results in maximum polarizability (\( \alpha_a \)), and hence maximum measurement sensitivity. The ratio of the two is approximately

\[
\frac{\alpha_b}{\alpha_a} \approx \frac{\varepsilon(\varepsilon + 1)}{2(\varepsilon - 1)} \approx \frac{\varepsilon}{2} \quad (\varepsilon >> 1)
\]

For water at low frequencies, \( \varepsilon \approx 80 \) so that \( \alpha_b/\alpha_a \approx 41 \), and for acetonitrile (MeCN) \( \varepsilon \approx 37 \) so that \( \alpha_b/\alpha_a \approx 20 \). Hence, these factors can be large and so can provide major enhancements in measurement sensitivity (and sample heating).
**EXPERIMENTAL DETAILS**

Unfortunately, case (b) in Figure 1 is hard to achieve in a microwave resonator without increasing the resonator’s effective volume, thus offsetting the sensitivity gains obtained by sample orientation (from Equations (1) and (2)). An elegant solution for microfluidic ducts is shown in case (c), where the duct follows a circular path. This follows the circular electric field lines in a TE_{011} cylindrical SDR, so the applied electric field is always parallel to the surface of the duct, resulting in maximum polarization. The high relative permittivity of the dielectric material of the resonator (for sapphire $\varepsilon \approx 9.4$ in its basal plane) results in a small effective volume $\propto \varepsilon^{1/2}$, so the gains in measurement sensitivity are two-fold.

A schematic diagram of the SDR with a milled, circular microfluidic channel is shown in Figure 2. The microwave couplings (not shown) are via identical, loop-terminated RG405 coaxial cables and the transmitted power $|S_{21}|^2$ is measured in the frequency domain using an Agilent PNA-X network analyzer. The SDRs used here are variants of the split-post resonator used for characterizing sheet samples [4]. In the TE_{011} mode the two resonator halves behave as one since the $E$-field in the gap region is parallel to the dielectric interfaces. The resulting electric energy density has been computed (using FEM) and is shown in Figure 3. Two prototype SDR sensors have been developed: one operates at 5.3 GHz with a pair of sapphire pucks each of radius 10 mm and length 5 mm, another at 22.7 GHz with pucks of radius 2.25 mm and length 1.0 mm. The 5.3 GHz SDR contains a circular Teflon AF microcapillary (ID 250 μm, OD 500 μm), supported within a Teflon AF carrier slotted into a 1 mm gap between the pucks. The 22.7 GHz SDR has circular microfluidic channel of diameter 3 mm, width 100 μm and depth 60 μm, ablated with a 157 nm excimer laser into one of the pucks at the position of the maximum $E$-field. The pucks were bonded together using a 1.2 μm thick spin-coated film of Teflon AF 1600, and fused silica microcapillaries (ID 100 μm, OD 160 μm) were used to interface with the microchannels.

**RESULTS**

Experimental results are shown in Figures 4 and 5 for the miniaturized (i.e. 22.7 GHz) SDR containing a solution of acetonitrile (highly polar) in toluene (relatively non-polar). The resonant frequency decreases and the 3 dB bandwidth (i.e. $f_0/Q$) increases as the % volume of acetonitrile increases due to increased polarity. Such monotonic variations are expected theoretically when the $E$-field is not depolarized, giving unambiguous compositional analysis. This should be compared with our earlier data [1],[2], where depolarization effects result in multi-valued compositional analysis based on microwave loss. The fluid volume in the miniaturized SDR is 56 nl and the sensitivity (resonant frequency shift) is $\approx$ 80 Hz decrease for a 1 ppm increase in acetonitrile (Table 1). The smallest measurable change of $\approx$200 Hz using the PNA-X network analyzer sets a detection limit of $\approx$ 3 ppm of acetonitrile in toluene, i.e. absolute detection volume of just 0.6 pl.

![Micrograph of lower disk](image)

Figure 2: Configuration of the miniaturized sapphire disk resonator (SDR) with laser-ablated microchannels. Inset: micrograph of the fabricated lower sapphire disk.
Table 1: Summary of the key parameters of the two sapphire dielectric resonators (SDRs) used in this study

<table>
<thead>
<tr>
<th></th>
<th>Quality factor (empty)</th>
<th>Active fluid Volume</th>
<th>Sensitivity* MeCN:toluene</th>
<th>Sensitivity* MeCN:water</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDR @ 5.3 GHz</td>
<td>40 000</td>
<td>2.31 μl</td>
<td>10 Hz</td>
<td>≈ 6 Hz</td>
</tr>
<tr>
<td>Miniaturized SDR</td>
<td>21 000</td>
<td>0.056 μl</td>
<td>81 Hz</td>
<td>37 Hz</td>
</tr>
</tbody>
</table>

*Sensitivity* is the magnitude of the frequency shift for a 1 ppm increase in MeCN concentration.

CONCLUSIONS
The properties of the sapphire dielectric resonators described here afford high sensitivity in the analysis of polar/non-polar fluid mixtures, enabling applications from on-column HPLC mobile phase diagnosis and solvent QA to petrochemical industrial applications such as oil drilling, geo-prospecting and QC. The robust and resilient nature of the resonator structures and the non-invasive principle of the technique allow for operation in extreme environments (temperature, pressure, pH etc) and with optically opaque fluid matrices. The measurements are fast (sampling rates > 100 Hz are possible) and have been made ultra-sensitive by a combination of (a) suitable orientation of the microwave electric field relative to the sample, and (b) miniaturised resonator volume. Detection limits of around 3 ppm (by volume) of acetonitrile in toluene and around 6 ppm of water in acetonitrile have been measured. Future work will involve the development portable, cost-effective, yet high performance instrumentation architecture as an alternative to the vector network analyzer.

ACKNOWLEDGEMENTS
We thank Dr. Oliver Castell and Dr. Chris Allender, of the School of Pharmacy at Cardiff University, for help with the experiments and useful discussions.

REFERENCES

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2013