Cavity Perturbation for In-Situ Monitoring of Microplastics in Water

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Abstract

To date, no inexpensive and easily implemented in-situ monitoring solution exists for the measurement of microplastic particle concentrations in water. State-of-the-art measurements require much effort for sampling and laboratory analysis. We investigated the cavity perturbation method with modified data processing as a tool for in-situ monitoring. Simulation results are promising in that particles as small as 10^{-6} of the measurement volume appear to be detectable. Laboratory experiments confirmed this sensitivity for a microplastic particle in an air-filled cavity.

1 Introduction

1.1 State of the art

The pollution of rivers and oceans with microplastics is an ongoing problem and is a threat to the wildlife and to human health [1]. Definitions for the size of microplastic particles vary, but most authors set the upper diameter limit between 1 mm and 5 mm [2]. Despite the research effort of recent years, there is still a lack of data regarding the concentration and distribution of microplastics around the globe. This is mainly because no widely available technology for in-situ measurement exists [3]. The challenge for the measurement is the quite small concentration of microplastics in the water. It typically ranges between 1 and 100 particles per cubic meter of water [4–6]. Hence, the volume fraction of microparticles is between 0.5 and 50 ppb when a mean diameter of 1 mm is assumed. Current methods require large amounts of water (say 100'000 liters) to be filtered with fine-pitched nets to obtain measurable amounts of particles. The filter cake is then processed manually in a lab [7]. A recent study suggests that researchers regularly contaminate the probes during this laborious process [8]. In-situ methods could lower the risk of probe contamination as no human needs to be in contact with the probes.

One proposed in-situ method utilizes impedance spectroscopy [9, 10]. An advantage of this method is the ability to classify the measured particles. However, the limited measurement volume poses problems when small particle concentrations are involved. For example, with concentrations of 100 particles per cubic meter, a channel with a cross section of a few square millimeters as in [9] would require hundreds of thousands of measurement cell fillings to detect but a single particle with substantial probability. The method clearly calls for higher particle concentrations, i. e., by prior sample preparation.

Another method possibly suitable for in-situ measurements is microwave reflectometry. The setup in [11] uses a planar sensor. Measured reflection coefficients ($\underline{S}_{11}$ parameters) are evaluated to determine the resonance frequency and quality factor of a resonance at about 5 GHz. The particle presence is then inferred from changes in the resonance characteristics. The method resolves particle concentrations of 100 ppm, but again lacks a sufficiently large measurement volume.

1.2 Proposed method

We are investigating whether the microwave cavity perturbation method can meet the contradictory requirements of high sensitivity to microplastic particles and large measurement volumes. As a resonant system, a cavity is inherently sensitive to geometrical and electrical material parameter changes. At the same time, the cavity may be made almost arbitrarily large, a key advantage in the current context. And, as we have shown before, the required electronics may be made inexpensive to further wide application [12, 13].

We employ a circular cylindrical cavity resonator with grids at the two ends so that microplastic particles can enter and leave the cavity. In the field application, the whole cavity would be submerged in flowing water, e.g., a river or a creek. The resonance frequency change depends on the position of a particle and the observed resonant mode [14, pp. 256]:

$$\frac{\Delta f}{f_2} = -\mathrm{Re}\left\{ \frac{1}{2} \left(\quad \frac{\varepsilon_{\mathrm{r,MP}}}{\varepsilon_{\mathrm{r,water}}} \right) \frac{\iiint_{V_{\mathrm{MP}}} \vec{E}_1^* \circ \vec{E}_2 \, \mathrm{d}V}{\iiint_{V_{\mathrm{c}}} \left|\vec{E}_1\right|^2 \, \mathrm{d}V} \right\}. \quad (1)$$

Here, Δf denotes the change in resonance frequency due to the particle, f_2 is the absolute resonance frequency in the presence of the particle, $\vec{E}_1$ is the electrical field strength without the particle and $\vec{E}_2$ is the electrical field strength inside the particle. Both electrical fields are complex valued. The integrations respectively extend over the volume V_{MP} of the microplastic particle and the cavity volume V_{c}. It is obvious that the change in the resonance frequency results from a different relative permittivity of the particle and the background medium. The values for plastic and water are $\varepsilon_{\mathrm{r,MP}} \approx 2 \ldots 4$ (e.g. PE: 2.25 [15, p. 453]; PP: 2.3 [16, p. 316]; PS: 2.55 [15, p. 454]; PA: 3.06 [17]; Phenol resin: 3.73 [17]) and $\varepsilon_{\mathrm{r,water}} \approx 80$, respectively [15, p. 455].

The difficulty with the perturbation eqn. (1) is that the fields $\vec{E}_1$ and $\vec{E}_2$ are usually unknown. Different strategies are proposed in the literature, e.g., calibration measurements with particles of known permittivity, shape, and position or the simple approximation $\vec{E}_1 \approx \vec{E}_2$ (no change in the field by the presence of a particle). While the latter approximation comes with a rather large error, it serves to

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estimate the order of magnitude of the expected resonance frequency shift Δf . Numerically, a microplastic sphere of diameter 1 mm placed inside a cylindrical cavity of length c = 25 mm and radius a = 25 mm changes (c.f. Fig. 1) the resonance frequency by about $\Delta f / f_2 \approx 5 \cdot 10^{-6}$.

The key task of the perturbation method is the precise determination of the resonance frequency. Usually cavity resonators have a high quality factor, which makes the determination of resonance frequencies with small uncertainties possible. In our case the conductivity of non-distilled water lowers the Q-factor to quite low values (below, say, 100). With such low Q-factors, the error and uncertainty of measured resonance frequencies increase.

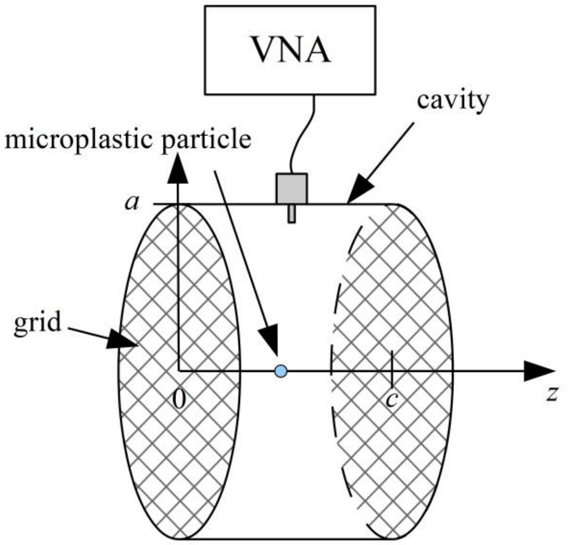

Fig. 1 Schematic drawing of a circular cylindrical cavity with grids at both ends. The cavity is connected to a vector network analyzer (VNA) via a stub coupler on the side wall.

2 Experimental validation

2.1 Numerical experiments

The commercial field computation software Ansys HFSS was used to investigate the effect of placing a microplastic sphere on the axis of a circular cylindrical cavity resonator. The dimensions were as follows: sphere diameter: 1 mm; cavity length: $c = 25$ mm; cavity radius: a = 25 mm. This gives a ratio of microplastic volume to cavity volume of about 10 ppm. The relative permittivity of the particle was set to $\varepsilon_{\mathrm{r,MP}} = 2.25$ (PE). To make the simulation realistic, fresh water with a conductivity of $\sigma = 10\,\mathrm{mS/m}$ and a permittivity of $\varepsilon_{\mathrm{r,water}} = 80$ was chosen as homogeneous background medium in the cavity.

The resonance frequencies of the TE_{111}-mode (fundamental mode) and the TE_{113}-mode were extracted from the simulated reflection coefficient (S_{11}) spectra for various positions of the microplastic particle. Figure 2 shows the relative change of resonance frequency with regard to the resonance frequency without the particle for the TE_{111}- and TE_{113}-mode. The dependence of the resonant frequencies on the particle position is clearly visible as long as the particle is located in a region with high electric field strength. At the cavity ends, where the field vanishes, or near other nodes of the field, the particle cannot be detected. For better comparison, the electric field strengths of the TE_{111}- and TE_{113}-modes are visualized in Fig. 3.

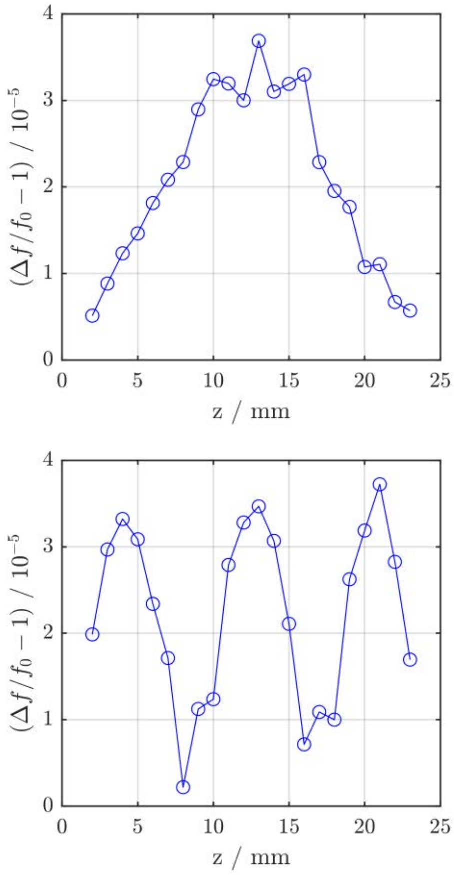

Fig. 2 Relative change of the resonance frequency due to the presence of a microplastic particle on the cavity axis. See text for details. (a) TE_{111}-mode. (b) TE_{113}-mode.

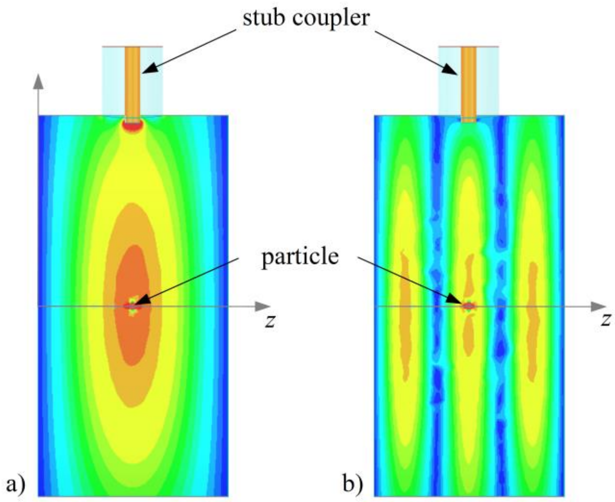

Fig. 3 Normalized electric field strength magnitude in the longitudinal symmetry plane of the cavity when the plastic particle is located in the cavity center. Blue: zero magnitude; red: maximum magnitude (unity). a) TE_{111}-mode. b) TE_{113}-mode.

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According to these numerical results, it should not only be possible to detect a particle that takes only 10 ppm of the cavity volume, but to also estimate its position.

The described method can also cope with the conductivity losses of water. The resonance curves, however, then become quite flat. Without measurement noise, the resonance frequencies can still be extracted easily from the S_{11}-parameter curves, but the presence of noise will increase the uncertainty of the extracted resonance parameters.

The described noise problem in the presence of (large) losses calls for a different signal processing approach, viz., one that avoids the determination of resonance frequencies. As one is mainly interested in the resonance frequency shift when a particle moves through the cavity, it suggests itself to compare a measured spectrum with a reference spectrum. The latter may be the spectrum obtained in the absence of a particle or with the particle at a known location. A suitable quantity then is the relative spectrum

$$A(f) = \frac{\left|\underline{S}_{11,\,\mathrm{new}}(f)\right|}{\left|\underline{S}_{11,\,\mathrm{cal}}(f)\right|}. \qquad (2)$$

In the investigated case, the reference spectrum was taken to be the spectrum obtained with a particle in the cavity center. Figure 4 shows the numerical results for the TE_{111}-mode. It is expected that the method is generally applicable to cavities and particles of arbitrary shape as long as the volume fraction of the particle is in a similar order of magnitude as in the example case.

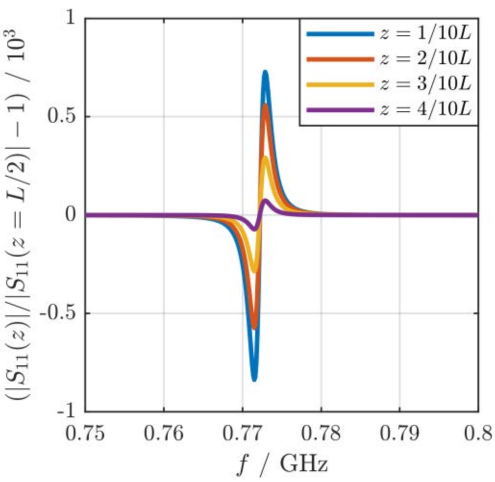

Fig. 4 Simulated relative spectrum $A(f)$ of the fundamental TE_{111}-mode for various particle locations. See text for geometry details.

2.2 Laboratory measurements

In laboratory experiments, a circular cylindrical cavity with dimensions c = 400 mm and a = 62.5 mm was used (Fig. 5). A plastic particle (PLA, $\varepsilon_{\mathrm{r,MP}} \approx 2.8$ [18]) with a volume of 10 mm³ was inserted through a grid at one cavity end. Hence, the ratio of particle volume to cavity volume amounted to 1.9 ppm. To hold the particle at a desired position, a polyamid string with a diameter of less than 200 µm was used. Reference measurements with string and without particle proved the influence of the string on the measured spectrum to be negligible.

Fig. 5 Physical realization of a cavity for experimental purposes. A plastic particle is visible near the inner corner of the ruler.

The measurements were performed with plastic particles placed at various locations along the axis of the otherwise air-filled cavity. Figure 6 shows some results for the fundamental TE_{111}-mode.

As expected from the results of the numerical results, the particle position can be estimated from the relative spectrum $A(f)$. A generalization to cavities and particles of arbitrary shape appears feasible, but the numerical details will depend on these boundary conditions.

We cannot state yet whether the method is also applicable to water-filled cavities. The high losses introduced by the water need to be carefully considered and maybe fought by better coupling the cavity to the source.

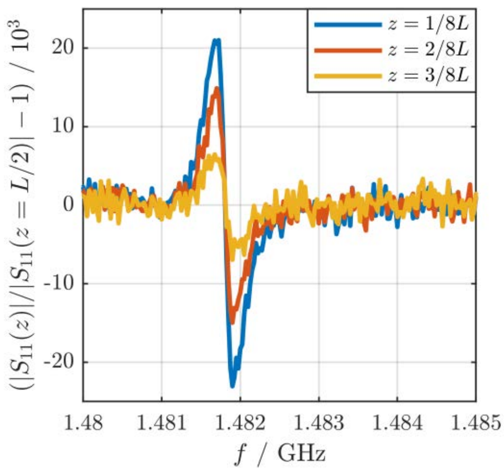

Fig. 6 Measured relative spectrum $A(f)$ of the fundamental TE_{111}-mode for various particle locations. See text for geometry details.

3 Conclusion

Available in-situ monitoring methods for microplastic particles suffer from either low sensitivity and/or small measurement volumes. We have demonstrated that the cavity perturbation method may be a viable alternative. Numerical simulations and laboratory experiments have produced promising results with measuring cell volumes as large as several liters and a ratio of particle volume to measuring cell volume as small as a few ppm.

4 Literature

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