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Free and/or bound water by dielectric measurements

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Abstract

In the past few years, the research on new methods (FTIR, NMR, microwaves) to measure the quantity and quality of water has been largely improved, particularly in the agricultural industry. Numerous studies have been made in order to establish a relationship (BET, GAB, ...) between parameters such as temperature, the water content in the matrix and the partial pressure of water vapour. The dielectric spectroscopy in the microwave domain shows a strong discrimination between bound and free water. The measurements in a resonant cavity allow calculation of the complex permittivity. This methodology has been used to quantify the grade of a seed's viability, and by extension, to discriminate between living seeds, containing mostly bound water, and dead seeds, containing particularly free water. This was explored with the society CLAUSE, in tomato, pimento and melon seeds. In a resonant cavity, the dielectric response of each seed is dependent on the weight, the heterogeneity of the shape (depolarisation factor of the electric field), and the anisotropy of density distribution of water in the matrix. Consequently, in order to take into account these parameters, the rotation of the seed in the electric field gives the total dielectric response or the dielectric signature of each seed. In this first approach, using only four perpendicular positions of the seed in the cavity, the mathematical envelope of the dielectric response is usually greater when the seed is dead.

Keywords: Free/bound water; Resonant cavity; Microwaves; Complex permittivity

1. Introduction

Water content in biological tissue and cells is very high, and can be considered an essential substance for the stability and function of biological systems. Nevertheless, the dielectric behaviour of water in cells is hard to understand.

Using dielectric spectroscopy, Hasted (1973) shows that water has three relaxation domains, solid water (ice), which relaxes in the kHz domain, bound water (b_w) relaxing around MHz, and free water (f_w) relaxing in the microwave region.

In the GHz region, the ratio of the imaginary parts of the complex permittivity, for free and bound water, ($\varepsilon''_{fw}/\varepsilon''_{bw}$), can be very strong, between 1 and 10 000, in hydrated materials. Then, using a dielectric measurement, we can obtain a good discrimination between free and bound water (Henry, Houitte, Costa, & Serpelloni, 2000).

2. Materials and methods

To support the use of this new dielectric metrology it was necessary to develop the simulation of the seed's dielectric response. The seed can be identified as an heterogeneous material (m) including *free water* (f_w) with an anisotropic distribution in the seed, *bound water* (b_w) or associated water on polar sites of the material, and *tegument and embryon* (m_x *for matrix*). Table 1 summarises the simulation of dielectric constants of these elements, at 5 and 9 GHz.

In this case, we have used the additivity of dielectric contributions of each element included in the seed, as in the Wiener law. If we refer the index m to the effective material, V_m to the total volume of the seed ($V_m = V_{mx} + V_{fw} + V_{bw}$) and φ_i to the volume fraction, we can write

$$\varepsilon^*_m V_m = \varepsilon^*_{mx} V_{mx} + \varepsilon^*_{fw} V_{fw} + \varepsilon^*_{bw} V_{bw} \tag{1}$$

$$\varepsilon^*_m = \varepsilon^*_{mx}\varphi_{mx} + \varepsilon^*_{fw}\varphi_{fw} + \varepsilon^*_{bw}\varphi_{bw} \tag{2}$$

and separating the real (ε'_m) and imaginary (ε''_m) parts of the complex permittivity,

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$$\varepsilon'_{m} = \varepsilon'_{mx}\varphi_{mx} + \varepsilon'_{fw}\varphi_{fw} + \varepsilon'_{bw}\varphi_{bw} \tag{3}$$

$$\varepsilon''_{m} = \varepsilon''_{mx}\varphi_{mx} + \varepsilon''_{fw}\varphi_{fw} + \varepsilon''_{bw}\varphi_{bw} \tag{4}$$

- In living seeds, for a relative humidity RH = 70%, this domain gives the massive repartition of constituents as 80% for matrix, 18% for bound water and 2% for free water.
- For dead seeds, the repartition is estimated to be 80% for matrix, 2% for bound water and 18% for free water.

Table 1
Dielectric constants of each element included in a seed at 25 °C and at 5 and 9 GHz

	ε'		ε''	
	5 GHz	9 GHz	5 GHz	9 GHz
Matrix	≈3	≈2.6	$\approx 10^{-2}$	$\approx 10^{-10}$ to 10^{-1}
Bound water	≈10	≈6 to 24	$\approx 10^{-1}$	$\approx 10^{-5}$ to 0
Free water	≈70	≈55	≈30	≈29.7

We observe an inversion between free and bound water. Table 2 summarises this situation with the different dielectric contributions.

Therefore, we can observe that for living seeds, the contribution of the dielectric losses of free water (ε''_{fw}) is greater than that of bound water (ε''_{bw}), and the discrimination ratio between free and bound water is greater than 30. On the other hand, for dead seeds, the contribution of dielectric losses of free water (ε''_{fw}) were more important than that of bound water (ε''_{bw}), and the discrimination ratio between free and bound water is greater than 270. For a relative humidity of only 10%, the constituent repartitions are 80% for the matrix, 19.5% for bound water and 0.5% for free water in the case of living seeds, and 97.5% for the matrix, 2% for bound water and 0.5% for free water for dead seeds. A simulation for RH = 10% is reported in Table 3, in which it can be seen that it is not

Table 2
Dielectric properties at 25 °C, 5 GHz and 70% of humidity

	Dielectric parameters 5 GHz		Living seeds			Dead seeds		
	ε'	ε''	%	ε'	ε''	%	ε'	ε''
Matrix	3	0.01	80	2.4	$0.8\ 10^{-2}$	80	2.4	$0.8\ 10^{-2}$
Bound water	10	0.1	18	1.8	$1.8\ 10^{-2}$	2	0.2	$0.2\ 10^{-2}$
Free water	70	30	2	1.4	$60\ 10^{-2}$	18	12.6	$540\ 10^{-2}$
Total contributions				5.6	$62.6\ 10^{-2}$		16.2	$541\ 10^{-2}$

Table 3
Dielectric properties at 25 °C, 5 GHz and 10% of humidity

	Dielectric parameters 5 GHz		Living seeds			Dead seeds		
	ε'	ε''	%	ε'	ε''	%	ε'	ε''
Matrix	3	0.01	80	2.4	$0.8\ 10^{-2}$	97.5	2,92	$0.97\ 10^{-2}$
Bound water	10	0.1	19.5	1.95	$1.9\ 10^{-2}$	2	0.2	$0.2\ 10^{-2}$
Free water	70	30	0.5	0.35	$15\ 10^{-2}$	0.5	0.35	$15\ 10^{-2}$
Total contributions				4.7	$17.8\ 10^{-2}$		3.48	$16.2\ 10^{-2}$

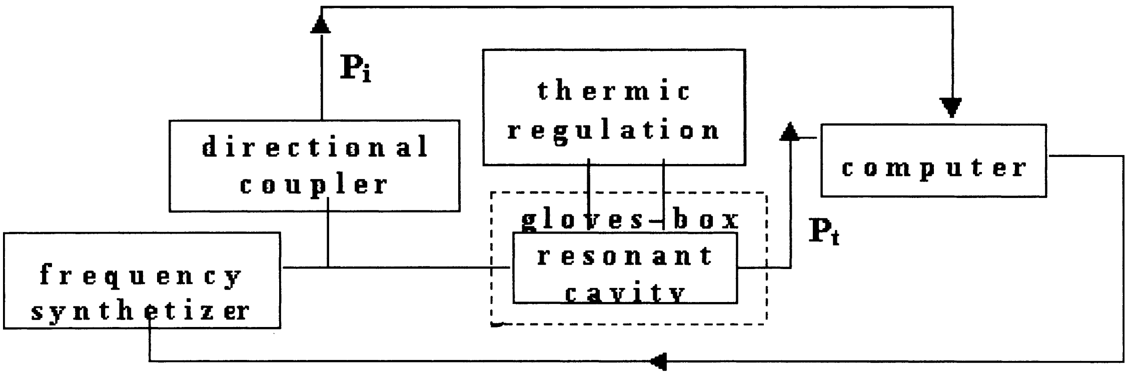

Fig. 1. Experimental set-up represented in a block diagram.

possible to discriminate between a living and a dead seed.

Finally, with these simulations, we can observe that it is easier to distinguish between a living and a dead seed using the dielectric losses (ε'').

The microwave method involves measuring the shifts in the resonant frequency and quality factor of a long cavity (Kraszewski & Nelson, 1996), caused by the insertion of the sample. The shift in the resonant frequency of the cavity, Δf, caused by the sample, can be related to the real part of the complex permitivitty, ε', while the change in the reciprocal of the quality factor of the cavity, $\Delta(1/Q)$, gives the imaginary part, ε'' (Henry, 1982). Using the small perturbation theory of resonant cavities, and separating the real (ε'_m) and imaginary ($\varepsilon''_{total} = \varepsilon''_{dipolar} + \sigma/2\pi\varepsilon_0$) parts of the complex permittivity, we can write,

$$\frac{\Delta f}{f_0} = K\frac{V_m}{V_c}\left(F\left(\varepsilon'_m, \varepsilon''_m\right) - 1\right) \quad \text{and} \quad \Delta\left(\frac{1}{2Q}\right) = K\frac{V_m}{V_c}G\left(\varepsilon''_m, \varepsilon'_m\right) \tag{5}$$

where f_0 is the resonant frequency in the empty cavity, and V_m and V_c are the volumes of the seed and cavity, respectively.

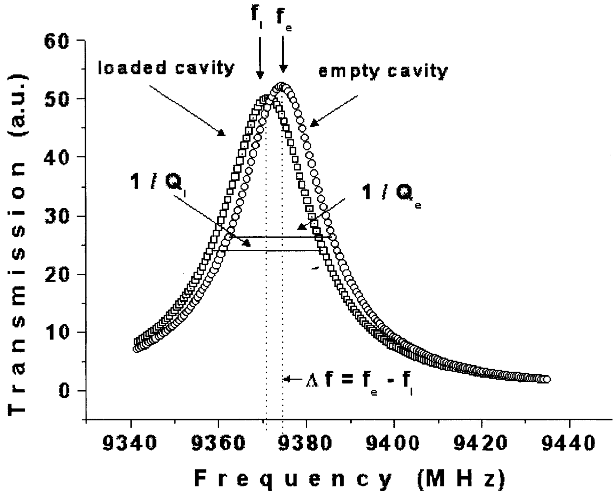

Fig. 2. Variation in the cavity transmission, when the seed is inserted.

The measured perturbation is then proportional to the products $F(\varepsilon'_m, \varepsilon''_m)$. V_m and $G(\varepsilon''_m, \varepsilon'_m)$. V_m and inversely proportional to the volume of the resonant cavity. For a sample parallel to the electric field, $F\left(\varepsilon'_m, \varepsilon''_m\right) = \varepsilon'_m$ and $G\left(\varepsilon''_m, \varepsilon'_m\right) = \varepsilon''_m$.

The depolarisation factor K is dependent on the shape and the repartition of water in the seed. Before the determination of the dielectric parameters in a resonant cavity, we must condition all the seeds at constant temperature and humidity (Pfost, Mourer, Chung, & Milliken, 1976). During 3 weeks, we conditioned them at 25 °C and RH = 50% [with a saturated solution of $Mg(NO_3)_2$], or RH = 70% (with a saturated solution of NH_4Cl).

3. Results and discussion

The experimental set-up is represented in block diagram in Fig. 1. The accuracy measurements have been made in resonant cavities at 5 and 9 GHz, at controlled temperature and humidity (Chen, 2000), of at

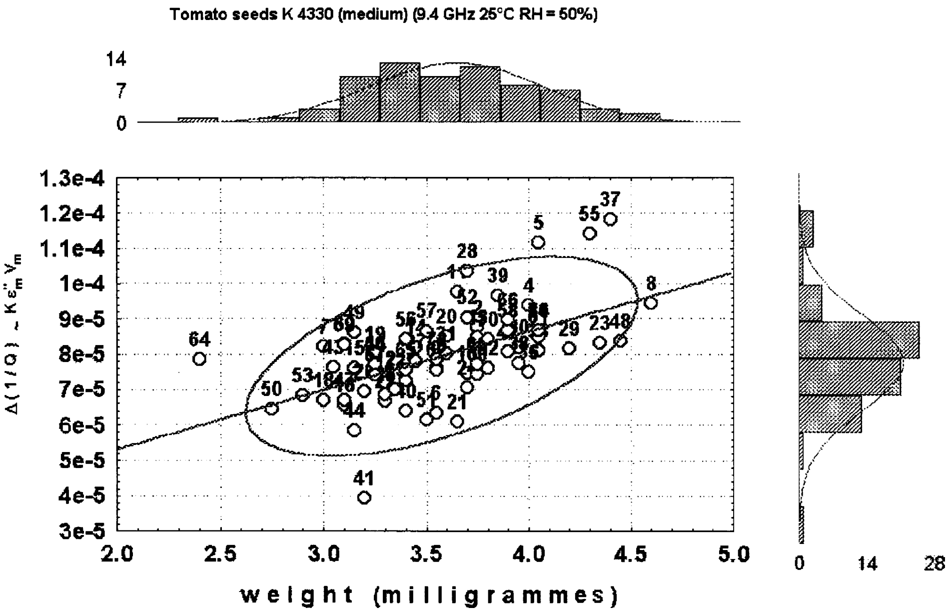

Fig. 3. $\Delta(1/Q)$, proportional to ε'', versus weight of the tomato seeds.

least 120 units of conditioned seeds of tomato, pimento and melon.

The variation in the cavity transmission, when we insert a seed, can be seen in Fig. 2. After the precise determination of the dielectric parameters $\left(\Delta f/f_0 \approx \varepsilon'_{\mathrm{m}}\ \text{and}\ \Delta(1/Q) \approx \varepsilon''_{\mathrm{m}}\right)$ of each conditioned seed, at a fixed position of maximum of electric field in the resonant cavity, we have attempted to find the best graphical representation, in order to see the preponderant factors.

Thus, we have correlated dielectric experimental data on each seed with their calculated volume and weight. Particularly, we can observe that:

- the dependence of dielectric parameters on weight is greater than on volume; and
- the linear dependence is less effective for ε'' (Fig. 3) than for ε' (Fig. 4).

In consequence of the small perturbation theory,

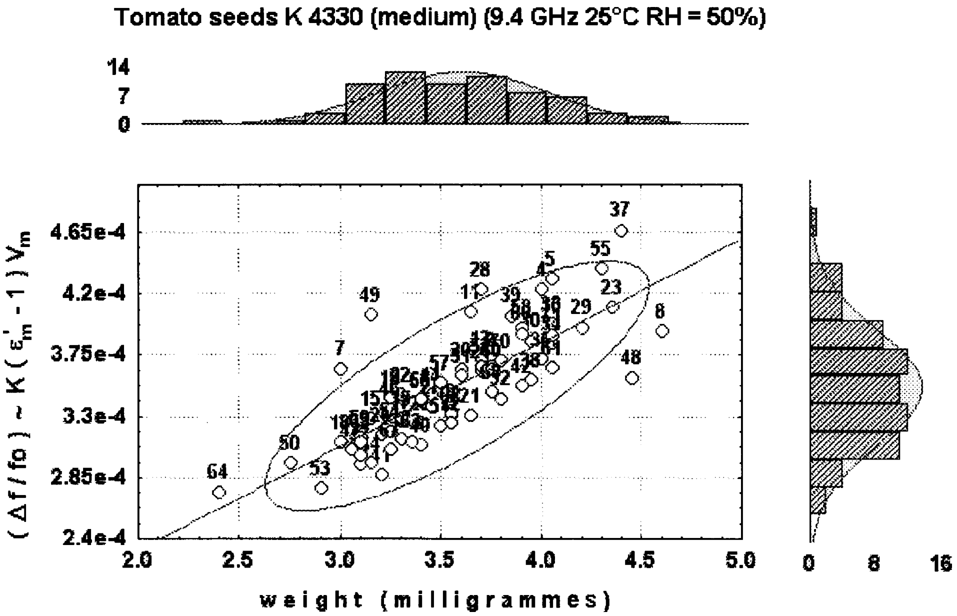

Fig. 4. $\Delta f/f_0$, proportional to ε', versus weight of the tomato seeds.

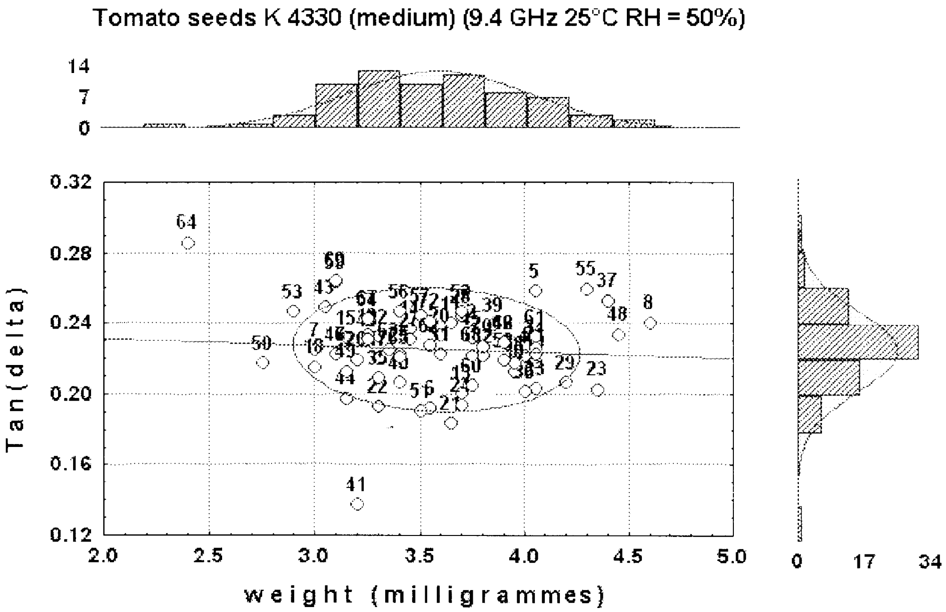

Fig. 5. Tan(δ) versus weight of the tomato seeds.

$$\frac{\Delta f}{f_0} = K(\varepsilon'_{\mathrm{m}} - 1)V_{\mathrm{m}} \quad \text{and} \quad \Delta\left(\frac{1}{Q}\right) = \frac{K}{2}\varepsilon''_{\mathrm{m}}V_{\mathrm{m}}, \tag{6}$$

the ratio

$$\frac{\Delta(1/Q)}{\Delta f/f_0} = \frac{\varepsilon''_{\mathrm{m}}}{\varepsilon'_{\mathrm{m}} - 1} \approx \tan(\delta) \tag{7}$$

should allow us to eliminate the dependence on volume (V_{m}) and depolarisation factor (K) (Fig. 5).

In fact, tg δ, being almost independent of the volume and weight of the seed, cannot be used to discriminate between dead and living seeds. Observing that the permittivity, ε', is more sensitive to the weight, and the dielectric loss, ε'', is more sensitive to the quantity and quality of water presented in each seed, we have decided to use a new graphic representation—ε'' versus ε', for each seed.

In Fig. 6 we present $\Delta f/f_0$ versus $\Delta(1/Q)$, for tomato seeds. There, we observe the linear fit obtained, expressing

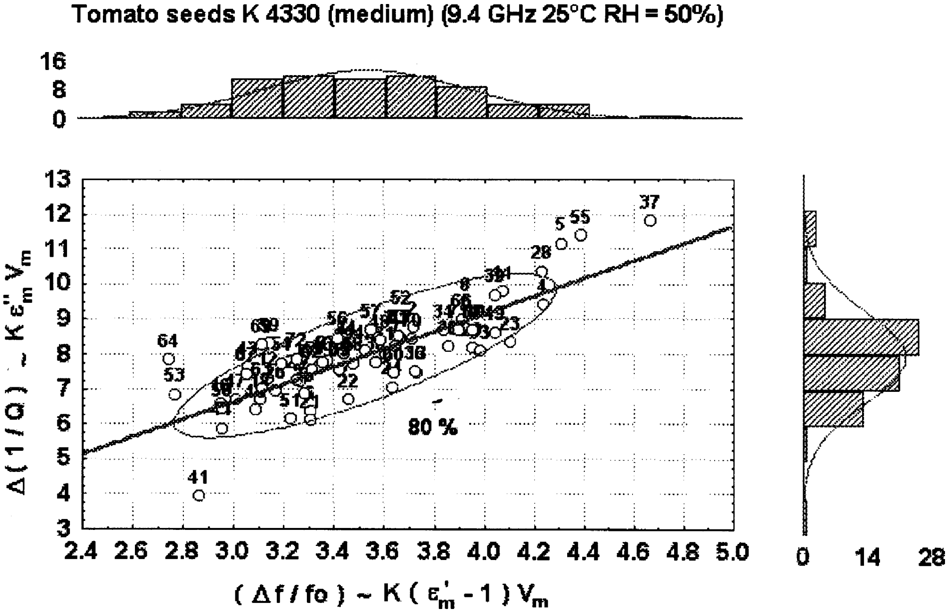

Fig. 6. ε'' versus ε', for the different tomato seeds, identified by a number. The statistical ellipsoid is also presented, in order to estimate the dead seeds.

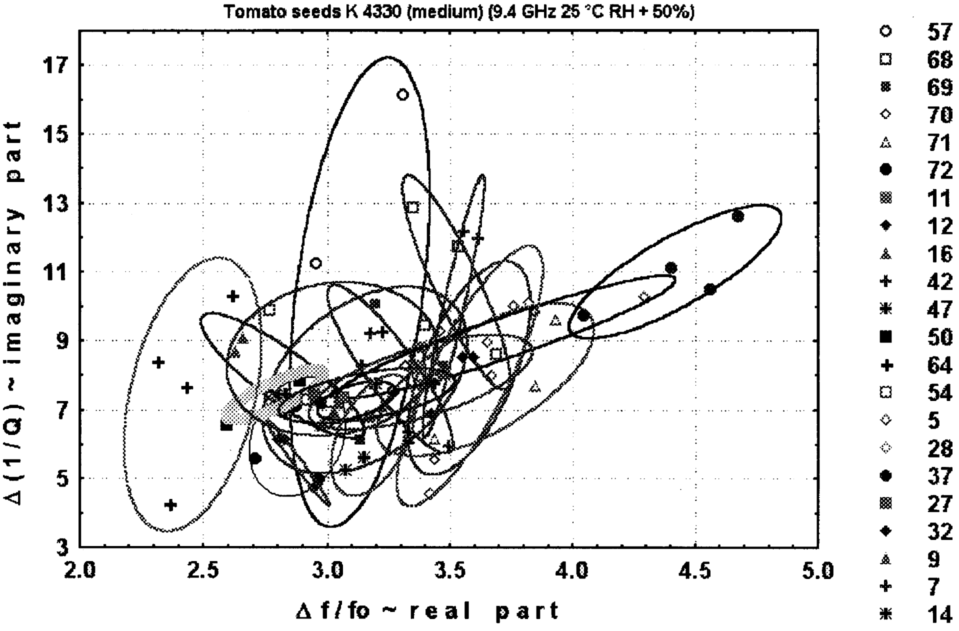

Fig. 7. ε'' versus ε', for the different tomatoes seeds, in four different positions. The anisotropy is shown with the help of the ellipsoids.

the dependence of parameters, whose slope is proportional to tan(δ).

We also present a statistical ellipsoid for the data. Regarding the numbered seeds in this figure, we can conclude that the seeds outside the ellipsoid are probably dead. They have a high quantity of free water (the seeds in the superior range) or they have already lost this water (the seeds in the inferior range).

As the seeds are not homogeneous in shape, an anisotropy in the dielectric properties is anticipated. Nevertheless, this anisotropy should be amplified if the seed is dead. The existence of higher dielectric loss in some cells provokes that amplification. To test this hypothesis, we repeated the measurements, rotating each seed in the cavity.

The results can be observed in Fig. 7. For each seed, the four perpendicular measurements allow a new ellipsoid. It is confirmed that the "probably dead seeds", clearly located outside the statistical ellipsoid reported in Fig. 6, present an anisotropy, which results in ellipsoids with higher surface area or/and higher ratio between the principal dimensions, as observed in Fig. 7.

4. Conclusions

The reported method is a powerful technique to quantify the seed's viability degree and to discriminate between live and dead seeds.

In order to eliminate the dead seeds, we have operated with a statistical approach on the numbered seeds, in two ways. First, we have drawn the dispersion ellipsoid of $\Delta(1/Q)$ versus $(\Delta f/f_0)$, which allows identification of the probably dead seeds. Second, we have checked that the rotation of seeds in the resonant cavity, gives greater variations of dielectric parameters, indicating a stronger anisotropy.

To use the method in the industry, it is appropriate that each seed should cross and rotate in the resonant cavity, in a sample holder, constructed with a material not absorbent of the microwave radiation, for example, Teflon. The acquisition and calculation time must be shorter than the seed residence time in the cavity, which demands a very rapid synthesiser.

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