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Rapid moisture measurement with microwave resonance technology in infant formulas

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Abstract

Besides breast milk, infant formula is the only other milk product that the medical community considers nutritionally acceptable for infants under the age of one year.

Water content is a very important value for the quality especially for the physical, microbial and shelf-life properties of a product. Accurate and rapid measuring of water or moisture content is the basis for producing dried powdered food like infant formula. For this purpose different methods, for example NIR spectroscopy or microwave resonance technology, can be used.

Microwave resonance technology is a non-destructive, non-chemical and very fast method to determine moisture in various kinds of food.

For measuring moisture, a low-energy microwave field is generated which shows a sensor specific resonance. Solid products and water molecules that are brought into the microwave field influence the resonance frequency and the resonance bandwidth. Because of their dipole property, the free water molecules permanently realign with the alternating field and so absorb energy. Frequency shift and attenuation of the resonance are measured and converted into a moisture value that is independent of varying product density.

To achieve accurate results with this method it is important to calibrate correctly with an adequate reference method. This was done by different methods like oven drying, volumetric Karl-Fischer-Titration and an automatic Karl-Fischer-Titration heating oven.

Depending on the kind of infant formula it is possible to calibrate the microwave resonance device with these different methods.

Keywords: No more than seven key words will be specified, with a font of TNR 10.

1. Introduction

Besides breast milk, infant formula is the only other milk product that the medical community considers nutritionally acceptable for infants under the age of one year.

Water content is a very important value for the quality especially for the physical, microbial and shelf-life properties of a product. Accurate and rapid measuring of water or moisture content is the basis for producing dried powdered food like infant formula. For this purpose different methods, for example NIR spectroscopy or microwave resonance technology, can be used.

Microwave resonance technology is a non-destructive, non-chemical and very fast method to determine moisture in various kinds of food.

2. Materials and Method

2.1. Microwave resonance technology

Moisture measurement with microwave resonance technology is based on the changing of the resonance behaviour of a specific sensor.

Therefore a low-energy microwave field is generated. If dipole molecules, especially

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water molecules, are brought into the microwave field the resonance frequency of the sensor is shifted and the bandwidth of the frequency curve increases. This is shown in Figure 1. The frequency is shifted from f_0 to f_1, the bandwidth increased from b_0 to b_1.

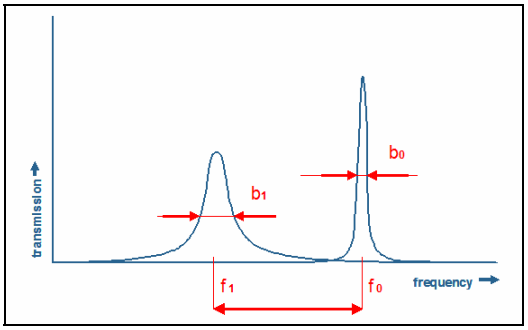

Figure 1: Shifting of the resonance frequency and enhancing of the bandwidth. [1]

Two Parameters are measured. Parameter A is the shift of the resonance frequency ($f_0 - f_1$), parameter B is the increase of the bandwidth ($b_1 - b_0$).

The interrelation between these parameters is shown in Figure 2.

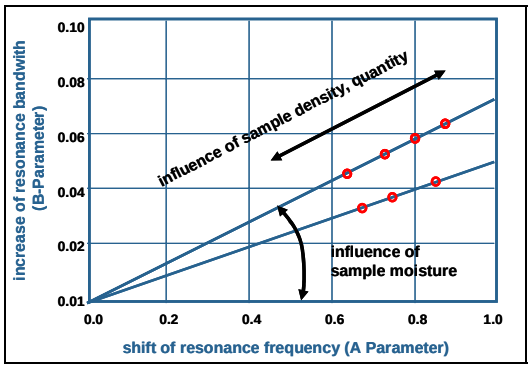

Figure 2: Interrelation between resonance frequency and bandwidth. [1]

The parameters A and B are both dependent on mass in the same way. The quotient of B and A is independent of mass, and is only addicted on the moisture of the measured sample.

Therefore the density independent microwave-moisture-value is calculated as:

$$\Phi = arctan \frac{B}{A}$$

Φ is directly proportional to the moisture content of the material. In most common cases, a linear calibration can be applied [2].

For the experiment a microwave resonance device MW 3150 (TEWS, Hamburg) was used.

2.2. Problem of calibration

The moisture concentration of a sample must be measured with a direct method which serves as a relation method. The values found by this technique are often called "true values".

A secondary method cannot yield more accurate results than the reference method used. It is therefore an essential condition for correct results obtained by the indirect method that the reference values are correct. The reference values must really be "true" [3].

2.3. Drying technique

Drying techniques, which are the "classical" oven drying, vacuum drying, freeze drying, infrared or microwave drying, do not distinguish between water and other volatile substances. The result of all of these methods is not water content but the mass loss the product undergoes under the conditions applied. These conditions (sample size, temperature, pressure, time, energy input, criteria to stop the analysis) can be chosen in principally freely. The result depends very strongly on these conditions can, however, be reproducible. The above mentioned techniques lead to different results when the parameters are changed, and the results cannot all be correct.. Water content is a sample property which has a certain, though unknown value. From the scientific point of view, the results of drying methods should therefore not be called "water content" but rather "mass loss on drying" with indication of the drying conditions [3].

For the calibration curves different samples were dried in a drying oven (FD 115 Binder) at 80 °C, 100 °C and 120 °C, and in a vacuum drying oven (VRTK, Elektro-Wärme-Aachen) at 50 °C.

35 – 45 g of product were weighed into 16 glasses with a twist-off lid.

They were dried at different temperatures. In regular time steps always 2 samples were taken out of the oven.

After cooling down their loss of mass was measured, the microwave-moisture-value registered and the water content determined by Karl Fischer titration or gas extraction followed by Karl Fischer titration.

2.4. Karl-Fischer-Titration

The most important primary method to determine water content is the Karl Fischer titration. It is based on a chemical reaction selective for water:

$$ROH + SO_2 + Z \rightarrow ZH^+ + ROSO_2^- \quad (1a)$$

$$ZH^+ + ROSO_2^- + I_2 + H_2O + 2\,Z \rightarrow$$

$$3\,ZH^+ + ROSO_3^- + 2\,I^- \quad (1b)$$

Overall reaction:

$$3\,Z + ROH + SO_2 + I_2 + H_2O \rightarrow$$

$$3\,ZH^+ + ROSO_3^- + 2\,I^- \quad (2)$$

Z is a base (very often imidazole), ROH is an alcohol, usually methanol, recently also ethanol in special reagents. [4]

In this case a 2-component-reagent-system (Hydranal®-Solvent, Hydranal®-Titrant 2) was used.

In a double-coated titration vessel at a temperature of approximately 40 °C, a mixture of 30 ml Solvent and 10 ml Hydranal®-Formamide were pretitrated.

5 replicates were titrated with an extraction time of 10 min (Titrando 841, Metrohm).

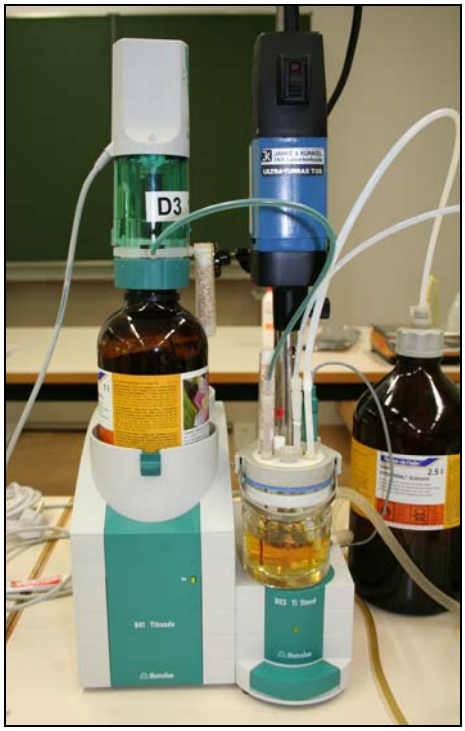

Figure 3: Karl Fischer titrator with a heatable titration vessel.

2.5. Automatic Karl Fischer titration with heating oven

The automatic Karl Fischer titration with heating oven (KFT-ho) is a combination of a drying method and the coulometric Karl Fischer Tttration.

A vial witch contains the sample is automatically placed into a small heating oven. Then a stream of dry air or nitrogen is led into the vial. The released water is transported into the titration vessel by the carrier gas stream. The contained water is then determined by coulometric Karl Fischer titration.

This can be done at different temperatures from 50 °C up to 250 °C.

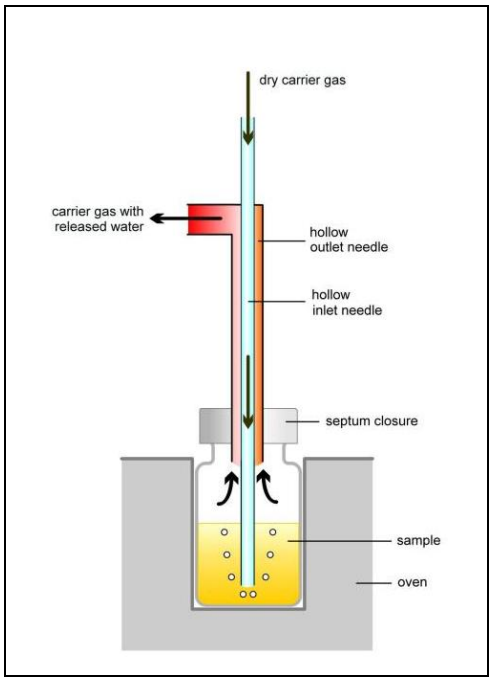

Figure 4: Karl Fischer titration with gas extraction. [5]

By using a temperature ramp and increasing the temperature of the oven at a rate of 2 °C per minute it is possible to monitor the water releasing behaviour of a sample.

Figure 5 shows the water released at the respective temperature (drift in µg / min) and the sum of the total water determined (water in µg).

At the beginning of the heating process and below 120 °C surface water and weakly bound water is released. At higher temperatures the sample is disintegrated and water is produced.

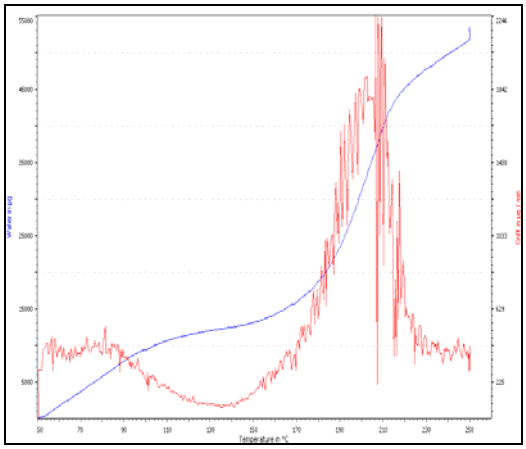

Figure 5: Temperature ramp of Bebivita from 50 °C to 250 °C.

As is generally the case in drying samples there is no sharp boarder between releasing weakly bound water and disintegrating the sample. Therefore, a temperature of 105 °C was chosen to evaporate nearly all of the weakly bound water and to avoid the browning of the sample.

Under these conditions the found water contents are very close to those determined by conventional Karl Fischer titration.

The advantage of the KFT-ho is the automated measurement of up to 35 samples and the possibility to measure samples in sealed air-tight vials.

This is especially important for the calibration of hygroscopic powders like infant formulas.

Figure 6: Sample rack of the automated Karl Fischer titration with heating oven.

2.6. Generating samples by drying

The great challenge for the calibration is to generate samples with different water content. The range of the directly available water contents, in the same product, is very small.

For the experiment only products bought from a store were available. The different water contents were generated by drying the samples.

All sample conditioning was done by drying to avoid a re-crystallisation during moistening up, as the sorption isotherm shows.

Water is adsorbed and is bound into the lattice and cannot be dried out under "soft" conditions.

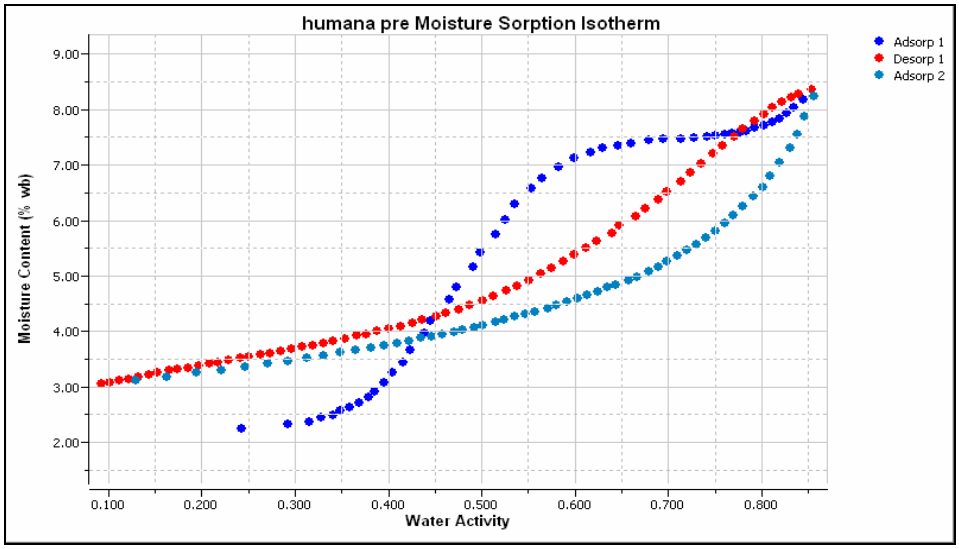

Figure 7: Sorption isotherm of Humana pre recorded with an "Aquasorp" isotherm generator (Decagon Devices).

3. Results and Discussion

A calibration based on the data set of the drying curve at 80 °C was possible.

The calibration straight is shown in Figure 9.

A correlation of 0.9865 could be achieved.

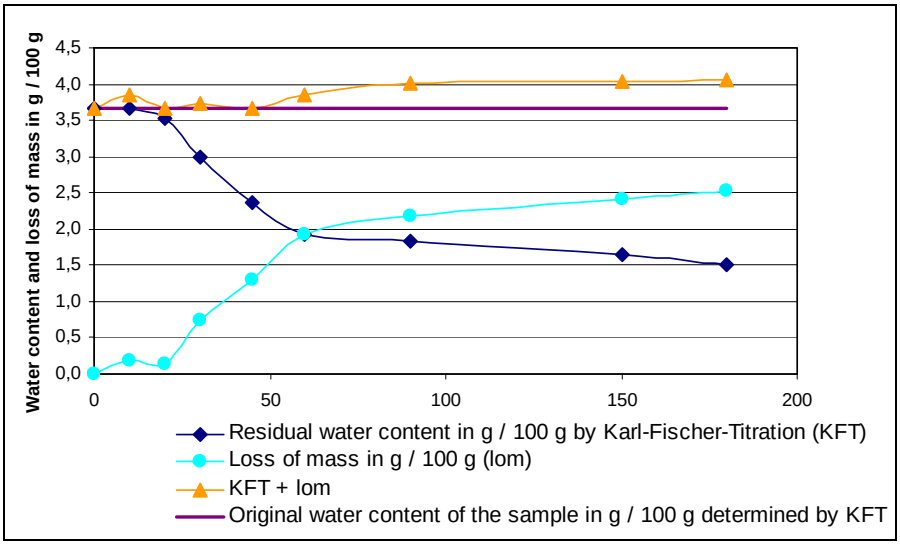

Figure 8: Drying curve of Bebivita 1 dried at 80 °C. Water content was measured with conventional KFT.

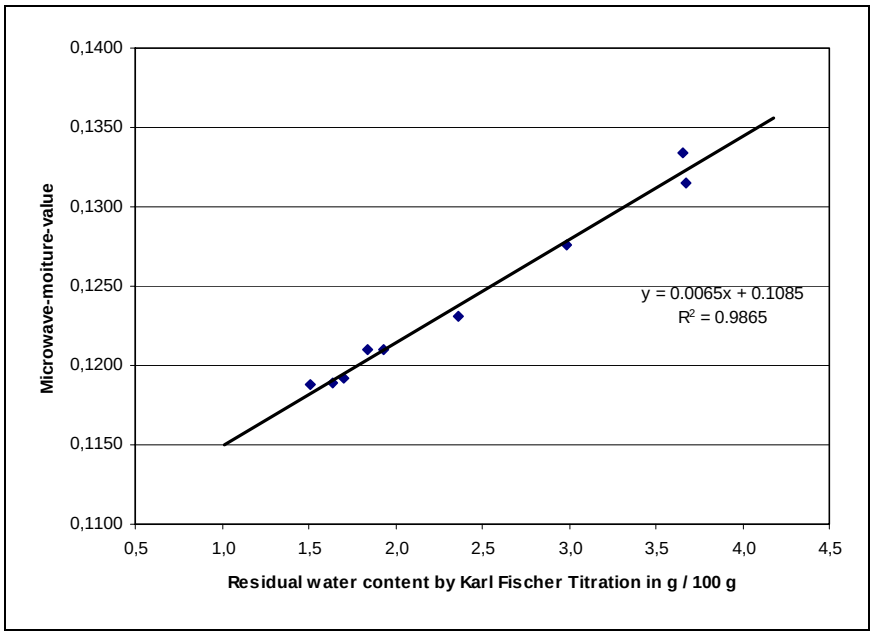

Figure 9: Calibration of Bebivita 1 with conventional Karl Fischer titration as reference.

The automatic Karl Fischer titration with heating oven (KFT-ho) brought some important advantages for the calibration.

It was possible to seal the samples in vials at the same moment the microwave-moisture-value was measured.

This was very important for the handling of the hygroscopic powders.

During the measurement by conventional Karl Fischer titration it could be observed that the samples absorb water from the environment.

Using the KFT-ho as reference method the correlation increased to 0.9985 and a well balanced drying curve was obtained.

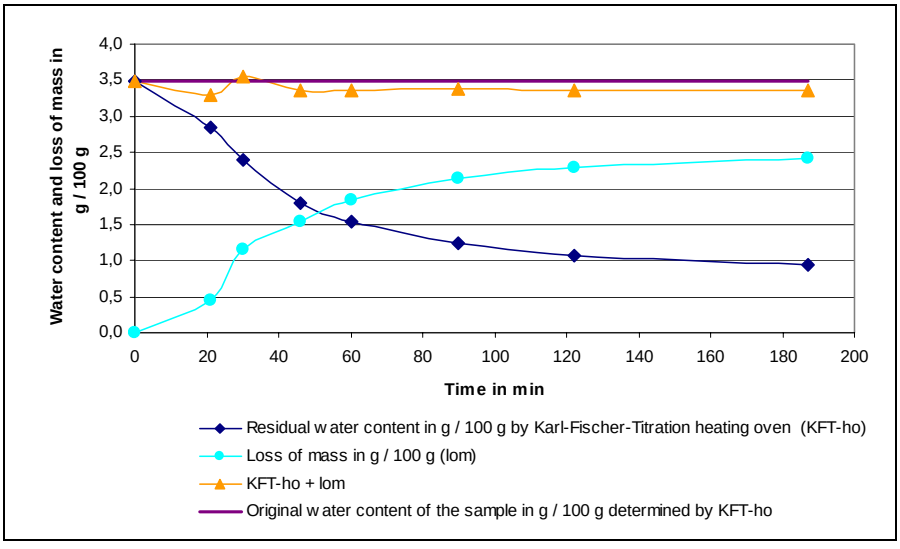

Figure 10: Drying curve of Bebivita 1 dried at 80 °C. Water contents were measured by KFT-ho.

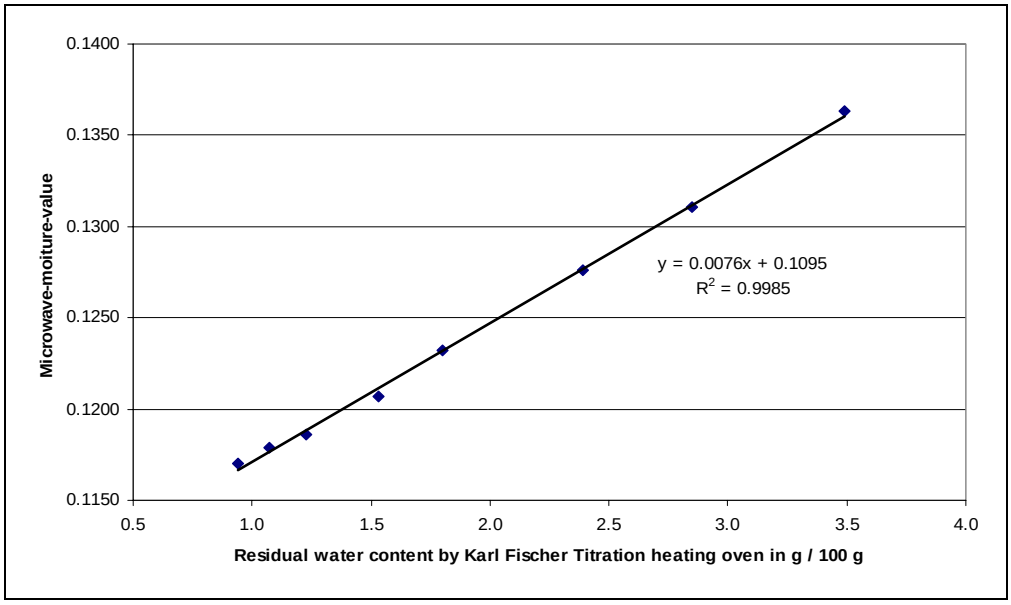

Figure 11: Calibration of Bebivita 1 with Karl Fischer titration with heating oven as reference.

Similar results were found for all the products investigated.

The transfer of calibrations for one product to another was not possible. Every product has to be calibrated separately. Even small changes of the product formulation or different kinds of lots lead to different microwave-resonance-values.

Figure 12 shows the attempt to calibrate two lots of the same product with a small change in the formulation. No acceptable calibration is possible.

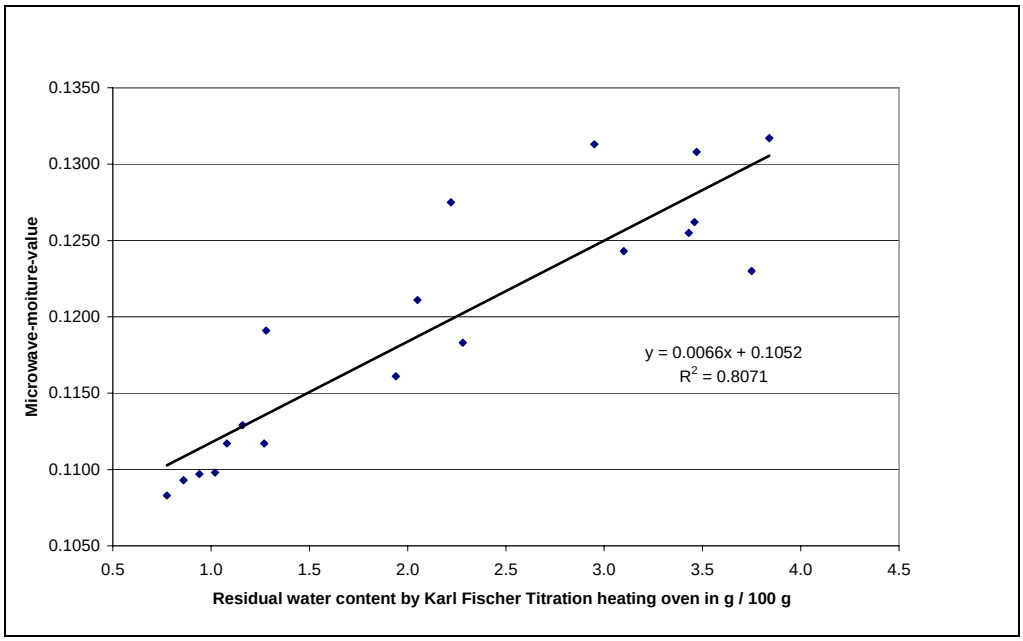

Figure 12: Calibration of two drying curves at 80 °C of Bebivita 1 with Karl Fischer titration with heating oven as reference

4. Conclusion

The microwave resonance technology can be used for rapid measurements of the moisture content in infant formulas.

The calibrations are highly affected by the production parameters of the product. It is very important to choose the right kind of reference method to calibrate the system. The Karl Fischer titration with heating oven seems to be a very acceptable method. It can be carried out very quickly, easily and automatically.

The major benefit of the microwave resonance technique is the very short testing time and the possibility to use it online.

5. References

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