Applications of microwave spectroscopy in process analysis

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Microwave (MW) spectroscopy has the potential to be used in process analysis for the monitoring and control of industrial processes. It is an ideal process analyser as it is:

- non-invasive: a transmitter and receiver can be retrofitted to the outside of the reaction chamber
- non-destructive
- can be used for solids, liquids, gases and suspensions: microwave spectra are a result of the dielectric constant, which are different for different types of material
- can be used for dark coloured samples
- analyses the whole sample: microwaves diffuse out from the transmitter though the entire sample
- analyse large sample volumes

MW spectroscopy is the rotational spectra of molecules due to an interaction with microwaves. The range usually measured is 0.25–3.20 GHz. Microwaves can penetrate materials with low dielectric constants, such as plastics, glass, ceramics and composite materials, even when they are several centimetres thick. However, they are reflected by metal surfaces, so any metal microwave vessels must have windows made from materials such as plastics to allow non-invasive analysis.[1]

Microwave spectra are the result of two properties:

1. Dielectric constant (ε′)

This is a reduction in the velocity of the microwave across the chamber. As an electromagnetic wave passes through a sample it causes an alternating polarisation within the material. The material stores some of the wave energy, and releases it back to the wave slowly, therefore reducing the wave's velocity:

$$\varepsilon' = \frac{(V_{VAC})^2}{(V_{MIX})^2}$$

Samples with different dielectric constants can be distinguished between.

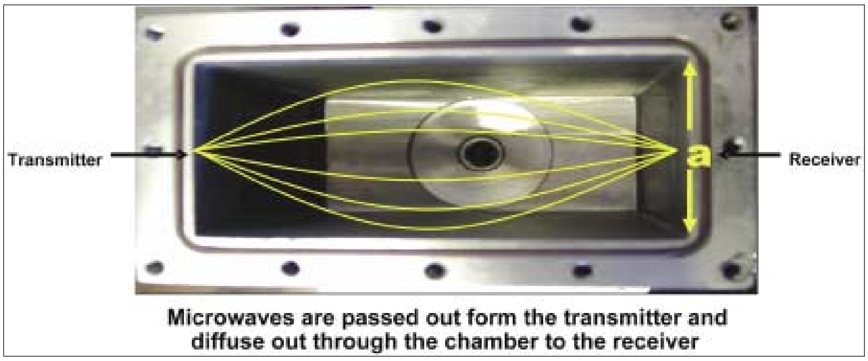

Figure 1. Microwave chamber showing microwaves diffusing out inside a chamber.

2. Dielectric loss (ε″)

This is a reduction in the magnitude of the wave. As molecules orientate in the electric field, energy is lost due to friction, reducing the magnitude of the wave.[2]

Microwave spectra are complex due to relaxation in liquids and solids. This means multivariate analysis must be used to interpret the spectra. The technique is less sensitive than similar spectroscopic methods but this is compensated for by the analysis of large sample volumes.

Waveguides

Waveguides are usually used in microwave spectroscopy. The Guided Microwave Spectrometer (GMS), used in this work, has two parallel metal surfaces between the send and receive antenna. These two metal surfaces form a waveguide which steers the wave front towards the receive antenna. A waveguide has the characteristic of only transmitting waves that have a wavelength shorter than twice the distance between the two parallel surfaces, called the *a* dimension. Larger waves will not fit into the waveguide and are "cut-off"[2] (see Figure 1).

Traditional microwave spectroscopy

Traditionally microwave spectroscopy is defined as "the high resolution absorption spectroscopy of molecular rotational transitions in the **gas** phase".[3] The spectra are dominated by molecular moments of inertia, which depend on the atomic masses and geometric structure of the molecule, hence it is mostly use for qualification of products. Much work has been carried out regarding species determination in the gaseous phase. The first experiments on gaseous spectroscopy in the microwave region were carried out in 1934 by Cleeton and Williams,[4] in which the absorption of ammonia vapour was investigated. There is high accuracy available with microwave spectroscopy, allowing much more detailed and exact information can be obtained than infrared spectroscopy.

Use of MW in process analysis

It was predicted as far back as 1990[5] that microwave spectroscopy could be used as a useful technique for process control. Few papers exist describing the application of microwave spectroscopy for quantification. This technique has largely been ignored for on-line analysis as the spectra are often broadband without clearly defined peaks. Multivariate calibration is necessary to correlate the spectra to either chemical or physical process changes.

Microwave spectroscopy provides a non-invasive method of analysis. A transmitter and receiver are fitted to either side of a reaction chamber. The vessel must be sufficiently transparent to microwaves, or have windows, e.g. mica, glass or teflon, which allow microwaves through. Microwaves radiate out from the transmitter through the sample, and the attenuation of the microwaves is measured by the receiver. This allows for the entire sample to be analysed simultaneously, removing the need for sampling, and capturing a true picture of the reaction process.

There have been some applications already published in the literature which demonstrate the utility of GMS for a range of different chemical analysis, for either solids or liquids.

The feasibility of using a general calibration model based on guided microwave spectroscopic data for the determination of moisture in various tobacco types was described in Reference 6. Importantly, it was determined that the method is sensitive to the weight of the sample used, and that best results were obtained when weight is included as a variable, whereas the position of the sample in the field had little effect. The paper suggests several experimental adaptations to improve the data and thus increase the predictive ability of models based on this data. However, the method described compared very well with the standard NIR on-line analysis, but with many fewer samples required in the calibration model (25 versus nearly 1500). The requirement of fewer samples is probably due to the fact that the surface effects which add complexity to NIR spectra are not apparent in the GMS spectra.

Loades and Walmsley[7] reported the determination of acetonitrile or ethanol in water. A wide range of different concentrations was used (up to 30% v/v), combined with partial least squares (PLS) and weighted ridge regression was applied to generate a model for prediction, based upon the microwave spectra. A high level of co-linearity was observed in both of the sample data sets and this was reduced by background subtraction. The prediction ability for the two types of regression models were found to be comparable with the error of prediction being approximately 2.5% for the acetonitrile samples and 1.1% for ethanol samples.

Current work is on-going in the areas of monitoring drying (microwaves are extremely sensitive to the end point of

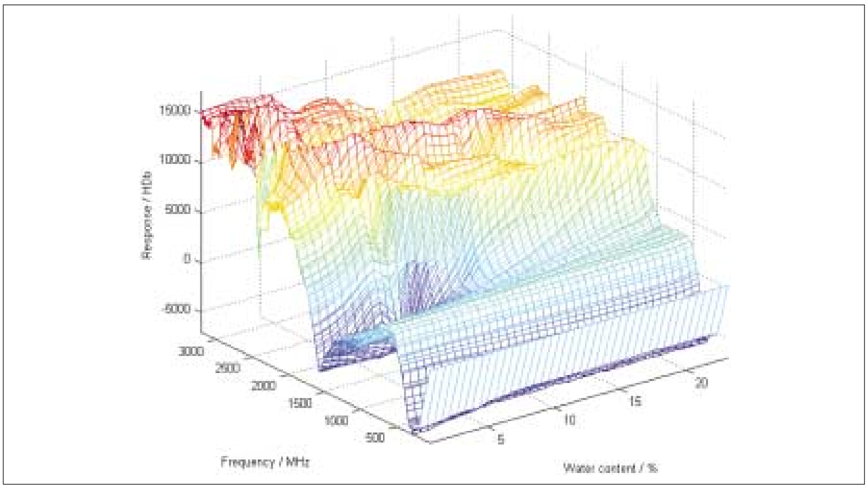

Figure 2. Plot of the microwave spectra after the addition of aliquots of water to sand.

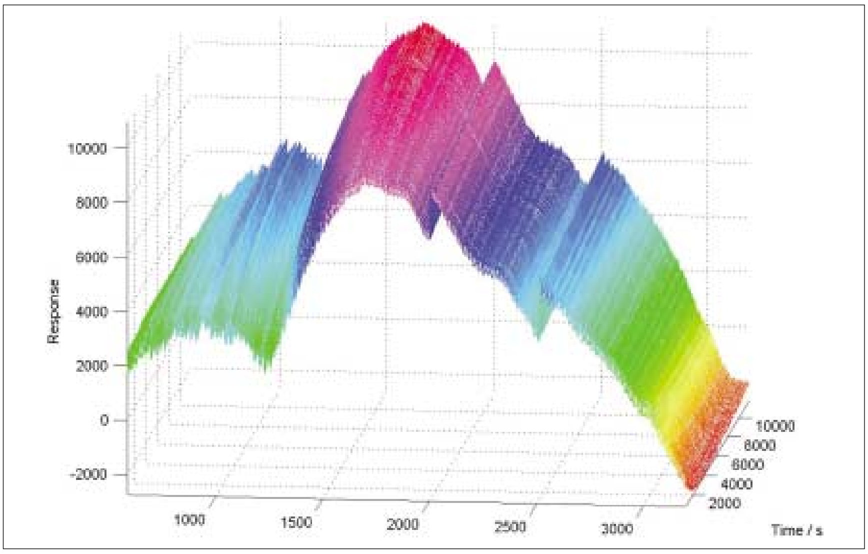

Figure 3. Plot of the microwave spectra obtained over time for the batch esterification reaction.

the drying process) and monitoring of batch reactions.

Monitoring of a simulated drying process

The drying process in industry is one that is hard to monitor. Huge cakes of wet material are dried in big vessels. The cake must be sampled to ensure it is dry, but where should this sample be taken from? Will it really be representative? Microwave spectroscopy analyses the whole sample simultaneously so removes the need for sampling, and gives a representative picture of the process. As the dielectric constant for water is high, microwave spectroscopy should be suitable for monitoring the drying process.

An example that has been looked at is the drying of water from sand, and propanol from ascorbic acid. At present these two materials have just been wetted to imitate the drying process, as a method had not yet been found to mimic industrial drying.

Figure 2 shows example spectra of water added to sand in 1 mL aliquots. It can been seen that there is a big difference in the spectra of sand with 25% water and dry sand, particularly around the 2000 MHz region.

A PLS model had been constructed, and six latent variables (LVs) were needed to model the concentration data. This gave a root mean square error of validation (*RMSEV*) of 1.0 mL (0.6%). This is quite high as the modelled range is 1–40 mL of water. From the spectra it can be seen that the spectra not only change in response to concentration, but also the peaks move frequency. This indicates non-linear data and so a non-linear method of calibration is required.

This example shows the potential of microwave spectroscopy for the monitoring of drying processes. The spectra clearly change with respect to water concentration, and changes can be seen down to low concentrations of water.

Monitoring of a batch esterification reaction

During an esterification reaction, the dielectic constant of the reaction mixture changes, so this can be monitored by microwave spectroscopy. Using microwaves eliminates the need for sampling, either by a sample loop or physical removal of sample. The batch reaction investigated was the esterification of butanol by acetic acid.

The reaction was performed in a microwave chamber (~500 mL) at different temperatures to enable important kinetic information to be obtained. The spectra were obtained at minute intervals for three hours. The collected data is analysed by curve resolution techniques to extract the concentration profiles and spectra of the pure components, without the need for time consuming reference measurements.

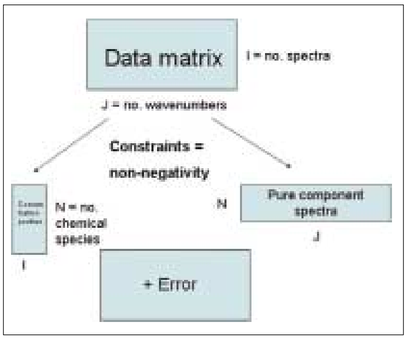

Figure 4. Schematic diagram to illustrate the basis of curve resolution techniques.

Multivariate curve resolution methods are employed to try to recover the true pure underlying spectral and concentration profiles causing the "chemical" variance observed. The main aim of curve resolution techniques is to determine the true value of *C* (concentration profile) and *S* (pure component spectra) shown in Figure 4.

Initial estimates of the spectra and concentration profiles obtained from evolving factor analysis are used in the subsequent alternating least squares step, which uses these initial starting points

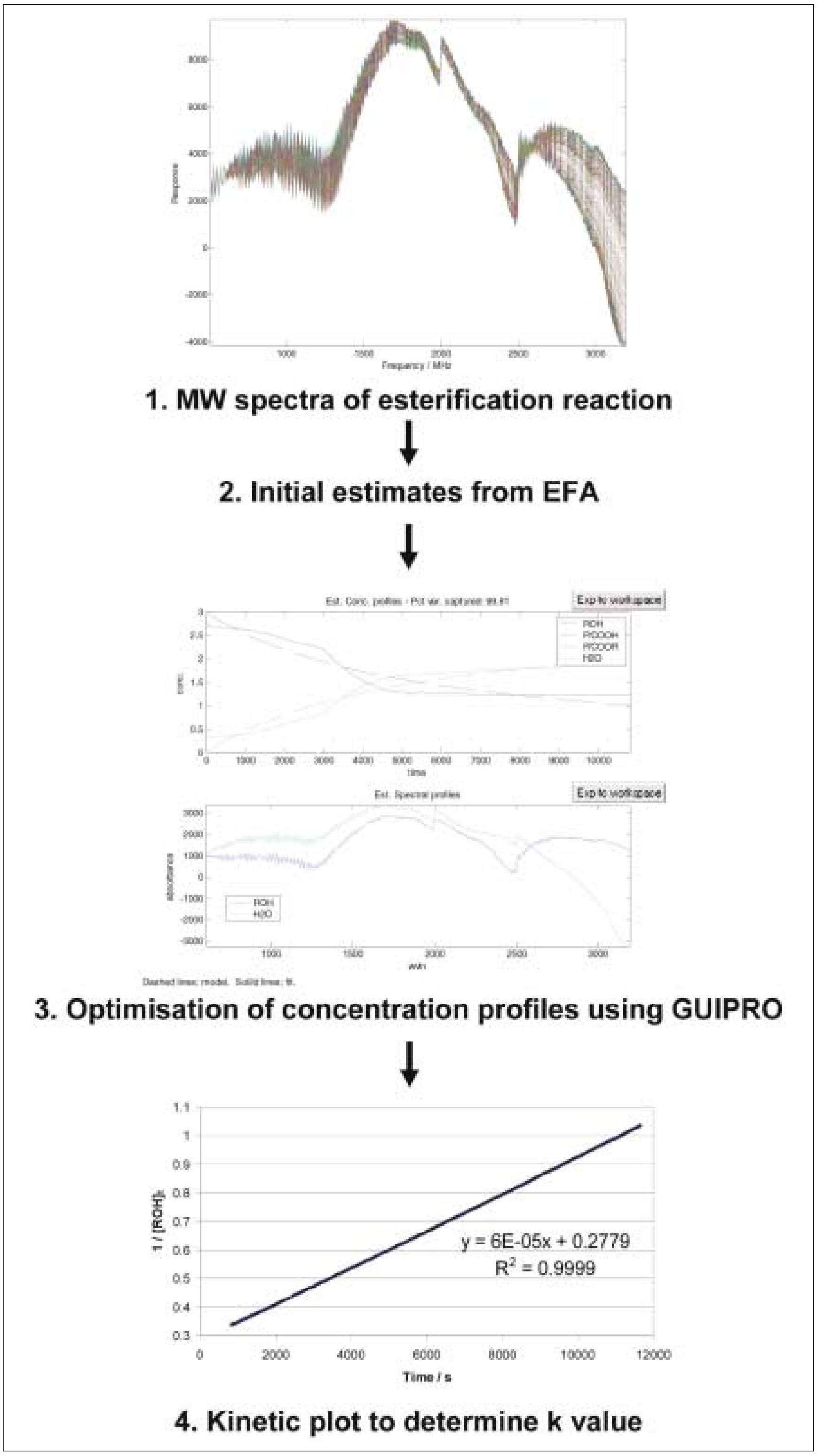

Figure 5. The stages of required to determine the *k* value of a reaction.

and refines them in an iterative process. The number of chemical species present is obtained directly from the "chemical rank" of data matrix. There can be a problem with rank deficient data in which the true number of components are not resolved. Constraints, such as non-negativity and kinetic constraints, can be included to aid optimisation, and break the rank deficiency.

The GUIPIRO software developed by Paul Gemperline[8] was used to analyse the data to extract the concentration profiles and kinetic from the reaction.

Table 1. *k* values for the esterification of butanol by acetic acid at different temperature.

Molar ratio	Temp (°)C	*k* values
2 : 1	25	8.6E–05
2 : 1	35	8.6E–05
2 : 1	50	1.8E–04
2 : 1	60	3.0E–04

The *k* value of a reaction is expected to increase with increased temperature, as the reaction should be faster. Table 1 shows the results for *k* obtained.

As can be seen from the results, the *k* values do increase with temperature over the range 35–60°C. This indicates it is in fact the *k* values being extracted from the spectra. This can be proved by monitoring the reaction using reference measurements and compare the calculated *k* values.

This initial work proves that microwave spectroscopy can be used along with curve resolution techniques to monitor reactions. No reference measurement is needed. This technique has the potential to be used in real time to allow control of the reaction as it progresses.

References

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