

Measurements of Accurate Temperatures in the Microwave Reactors

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Abstract: A broad range of research on chemical reactions by microwave heating has been conducted, because unlike reactions by conventional heating, reactions by microwave heating underwent a reaction acceleration phenomenon. The microwave effect on chemical reactions has been previously discussed as a thermal or non-thermal effect without universal knowledge. Measuring temperature accurately is essential for discussing reaction kinetics such as reaction acceleration, however, it is difficult to measure temperature distribution accurately in a microwave reaction vessel. This mini- review introduces recent researches on the measurements of temperature distributions in microwave reaction vessels using multiple fluorescent fiber optic thermometers, and also proposes precautions on how to measure temperatures for microwave-assisted chemical reactions. Furthermore, this mini- review presents a new thermometer for measuring local heating by microwave irradiation.

Keywords: Microwave, fiber optic thermometer, infrared thermometer, Raman spectroscopy.

INTRODUCTION

Microwave heating is applied in various areas such as plasma generation [1-3], food processing [4, 5], extraction [6, 7] and ceramic sintering [8-10]. Since Gedye [11] and Giguere [12] first used microwave heating in organic synthesis in 1986, a numerous number of research papers have been reported concerning chemical syntheses using microwave heating [13-15]. Many reports of reduction in reaction time and improvement in product selectivity have been published in microwave-assisted chemical syntheses, in which the authors claimed that these syntheses were conducted under the same temperature conditions in conventional syntheses. Such effect is called "nonthermal effect", and is expressed as a special effect different from "thermal effect" which features rapid, uniform and internal heating. However, no definite proof of the existence of such a "nonthermal effect" has been provided until now, and the nonthermal effect has yet to be proven separately from the special thermal effect of microwave.

Some problems in accurately measuring temperatures during microwave heating have made it difficult to verify the nonthermal effect of microwave. For temperature measurement, thermocouples are generally used. In the case of microwave heating, however, the thermocouple sheath itself generates heat caused by the microwave energy, and thus fails to measure the temperatures of objects accurately [16]. There is also the problem of sparks, which are caused by plasma generation. Although these sparks can be controlled by grounding, the risk cannot be completely eliminated [17]. Infrared (IR) thermometers have also been generally used for temperature measurements during microwave irradiation. Because an IR thermometer measures a blackbody radiation from the surface of the object using an infrared sensor, it can measure the surface temperatures of an object without contacting it. It means, however, an IR thermometer can measure only the surface temperatures of reactors, not the internal reaction temperatures. Some other measurement methods using magnetic resonance imaging (MRI) and Raman spectroscopy techniques have also been proposed for measuring temperatures under microwave irradiation [18-23]. While MRI simultaneously measures the multipoint temperatures in an object, it is difficult to precisely duplicate the actual conditions in the microwave equipment. In addition, MRI highly costs to operate. On the other hand, the temperature measurement from Raman spectroscopy, which measures Raman peak line shifts on solid surfaces such as silicon and diamond, is hardly applicable to the chemical reactions in liquid solutions. Thus, a definite method has yet to be established.

A fiber-optic (FO) thermometer does not interfere with microwave and since it is a contact-type thermometer, it can accurately measure the temperatures inside microwave reactors. It uses the mechanism that when an ultrathin phosphor attached to the tip of an optical fiber is irradiated with light through the optical fiber, its fluorescence decay varies greatly depending on the temperatures [24]. The temperature can be measured by measuring this fluorescence decay. Since the optical fiber covered with PTFE possesses low microwave absorption, being barely influenced by microwave irradiation, contact measurements of optical sensors conducted inside the reactors can provide accurate temperatures.

This mini- review introduces a recent research on the measurements of the temperature distributions in microwave reaction vessels by using multiple fluorescent FO thermometers and proposes precautions for temperature measurement in microwave-assisted chemical reactions. Furthermore, this mini- review presents a new thermometer for measuring local heating by microwave irradiation.

Temperature Difference Between Infrared (IR) and Fiber Optic (FO) Sensors

Kappe *et al.* assumed that the difference between the temperature in a reaction vessel and that measured by an IR thermometer is misinterpreted as a non-thermal effect, and they attempted to verify this assumption [25-27]. A FO thermometer was developed to accurately measure the internal reaction temperature (Fig. 1). An IR sensor installed on the microwave synthesis device measured the temperature at the bottom of the reaction vessel. The temperature measured by the IR thermometer was about 100°C in a 10 ml quartz reaction vessel containing 5 ml NMP. The optic fiber thermometer on the same area read 130°C, which was higher by 30°C (Fig. 2). Temperature distributions were also measured inside the reaction vessel, which showed the higher temperature in the upper part of the reaction vessel, although IR sensor showed about 100°C, the upper part of the reaction vessel reached 170°C. Namely, the existing temperature in some areas of the reaction vessel is actually higher than the one indicated by the IR thermometer in microwave synthesis device. The difference between the temperatures shown by the FO and IR thermometers was reduced to about 6°C by effective stirring. The well-designed experiments to eliminate temperature difference by controlling the temperatures under microwave at the same temperature of the oil-bath heating demonstrated the disappearance of the microwave-assisted effect observed in the organic synthesis. These results demonstrate the importance of an accurate temperature measurement under microwave heating and at the same time demand that the previous results of the microwave-assisted chemical reactions should be reconsidered.

Additionally, Kappe *et al.* performed simultaneous temperature measurements using IR and FO thermometers during ionic liquid syntheses under the microwave irradiation to investigate the differ-

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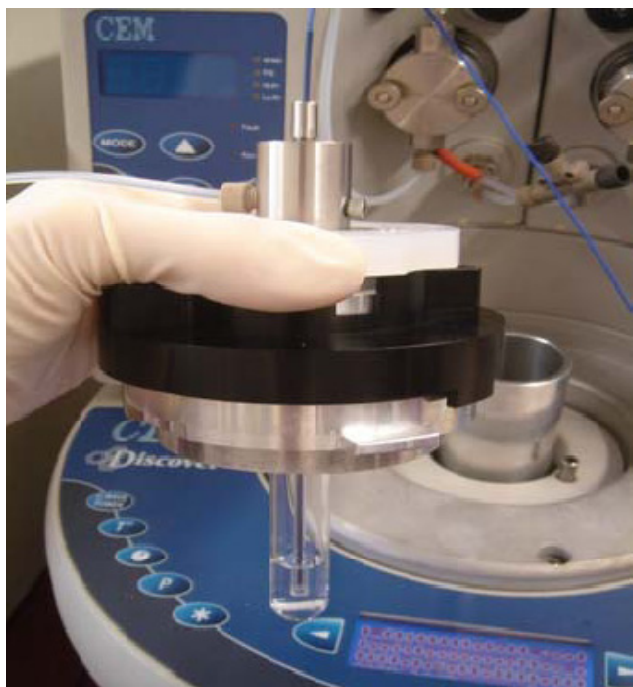


Fig. (1). Set-up for Monitoring Internal Reaction Temperatures with Fiber-Optic Probes. (Reprinted with permission from ref 27. Copyright 2007 American Chemical Society.)

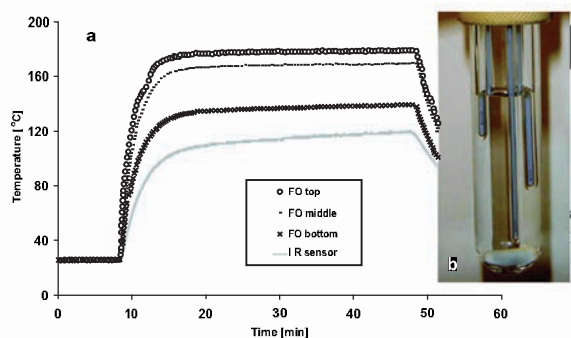


Fig. (2). (a) Temperature profiles for a sample of 5 mL of NMP contained in a 10 mL quartz vessel equipped with three internal fiber-optic sensors. The sample was irradiated with constant 50 W magnetron output power without stirring for 40 min (CEM Discover). Shown are the profiles for the three internal fiber-optic probes and for the external IR sensor located at the bottom of the instrument. (b) Multiple fiber-optic temperature probe assembly (Reprinted with permission from ref 25. Copyright 2008 American Chemical Society.)

ence between the thermometers [28]. The FO thermometer indicated higher temperatures than the IR thermometers in the two single-mode microwave irradiation equipment, Discover made by CEM and Monowave300 by Anton Paar. Overheating in the heating process, in particular, was prominent in media such as ionic liquids, which absorb microwave quite efficiently (Fig. 3). This phenomenon was probably caused by the high thermal resistance of the thick glass of the reaction vessel walls. Indeed, no overheating was observed in the reaction vessels that were made of SiC, which have higher microwave absorptivity and thermal conductivity. Moreover, reports have also been published showing that short intermittent microwave irradiation has a better effect on reaction promotion compared to continuous irradiation [29, 30]. Therefore, the possibility seems to exist that the overheating effects play an important role on the acceleration of microwave-assisted chemical reactions.

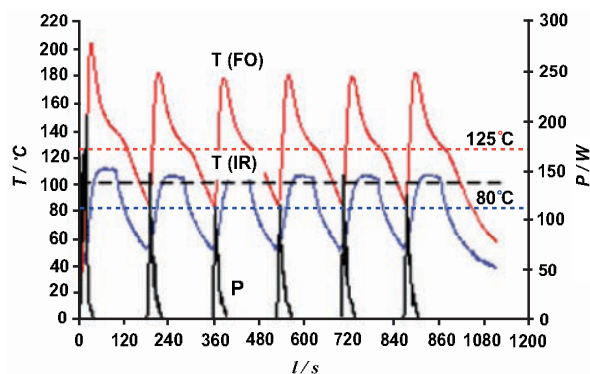


Fig. (3). FO/IR temperature (T) and power (P) profiles for a 3 mL sample of bmimBr heated in an Anton Paar Monowave 300 single-mode reactor using external IR temperature control (FO sensor as slave). Six cycles applying a set temperature of 100 °C (1 min hold time) were programmed, magnetic stirring on (600 rpm), 10 mL Pyrex vial. (Reprinted with permission from ref 28. Copyright 2010 Royal Society of Chemistry.)

Temperature Distribution in the Microwave Reactor

As discussed above, IR and FO thermometers showed different temperatures in the microwave reaction. This difference is caused by the fact that an IR thermometer measures the temperature of the outer surface of vessels, whereas an FO thermometer monitors internal vessel temperature. There is temperature difference between the inside of vessels and the outer surface. Kappe *et al.* also measured temperatures using FO thermometer at three different heights inside the reaction vessel, which demonstrated that there was temperature distribution inside the reaction vessels [25]. The temperature distribution became greater when the reaction was not stirred sufficiently. These observations have led us to an important fact that the temperature is greatest at the microwave focus point, and decreases as this distance increases.

Stankiewicz *et al.* investigated the temperature distributions inside the reaction vessels by monitoring temperature distribution in solid samples, which possess low diffusion properties [31]. The group used two kinds of solid samples, Al₂O₃ and CeO₂-ZrO₂, which had different microwave absorptivities. It is known that Al₂O₃ has better absorptivity than the other, though the absorptivity of the both solid samples is low. In the comparison between IR and FO thermometers, the difference in the temperature of the CeO₂-ZrO₂ sample, which absorbs little microwave, was as small as 9°C at a heating temperature of 70°C. On the other hand, the difference in the temperature of the Al₂O₃ sample, having better microwave absorptivity than that of CeO₂-ZrO₂, was about 50°C at a heating temperature of 90°C. Furthermore, temperature differences in the horizontal direction, between the center and the edge of the sample, were monitored in the microwave reaction vessel using the probe thermometers (Fig. 4). As a result, the temperature at the edge of the reaction vessel was somewhere between these at the center and the outer surface of the vessel. This revealed that there is a temperature gradient inside the microwave reaction vessels.

Microwave heaters are generally classified into two kinds of reaction devices: One is a single mode, which concentrates its electromagnetic field at a single spot; the other is a multi-mode, which has more than one electromagnetic field mode, as in microwave ovens. Each mode is employed to make use of its advantages. Multi-mode heating is widely used, and is suitable to large-capacity synthesis. In the temperature distribution of single-mode devices, the temperature in the center of the reaction device is highest, indicating lower temperatures toward the edges, as shown above. On the other hand, Corner *et al.* investigated the influence of the temperature distribution in multi-mode devices by heating up water and zeolite precursor solution and introducing FO thermometers at multiple locations in a 40mm diameter reaction vessel (Fig. 5) [32]. The

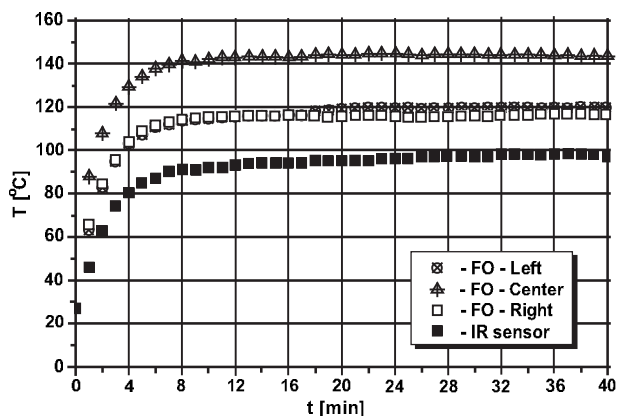


Fig. (4). Horizontal temperature distribution profiles obtained with FO inside a 2 g Al_2O_3 sample 6 mm above the bottom of the glass vial. The black square dots denote the IR temperature indication. (Reprinted with permission from ref 31. Copyright 2010 Institute of Physics.)

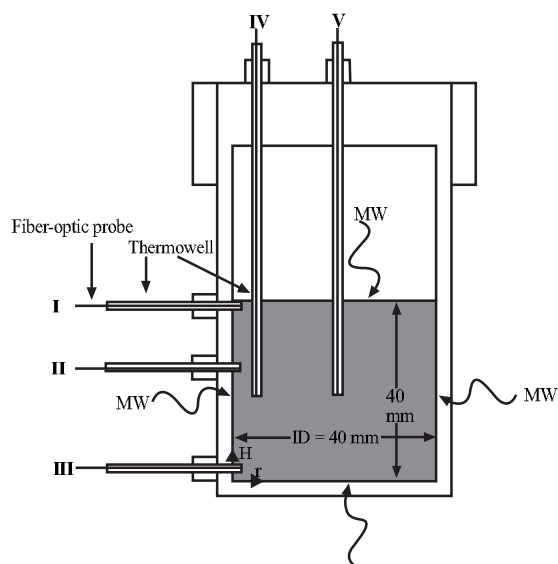


Fig. (5). Schematic drawing showing the vessel constructed to measure the temperatures at different points under microwave heating. (Reprinted with permission from ref 32. Copyright 2009 American Chemical Society.)

microwave penetration depth of multi-mode microwave against the water and zeolite precursor solution was calculated in the relation between the amount of microwave absorption and the increase of temperature. The microwave penetration depth of water became larger as the dielectric loss coefficient was lowered due to the higher temperature. However, its penetration depth was measured to be as much as about 40 mm, deep enough for a 40 mm diameter reaction vessel. Accordingly, little temperature distribution in multi-mode heating of water was observed. Meanwhile, zeolite precursor solution showed much higher dielectric loss coefficient than water, which has a high dielectric loss coefficient itself. Its penetration depth was calculated to be approximately 10 mm for the zeolite precursor solution. Furthermore, the zeolite precursor solution, with its high viscosity, showed low diffusion efficiencies, resulting in a large temperature distribution in the solution. There was indeed a large temperature distribution demonstrated not only by measuring with multi-spot FO thermometers, but also by observing an IR thermograph immediately after heating (Fig. 6). Interestingly, it should be noted that the external temperature was higher than internal temperature in multi-mode heating when a solution with high dielectric loss was irradiated, while it has been shown that the interior was higher in temperature in single-mode so far.

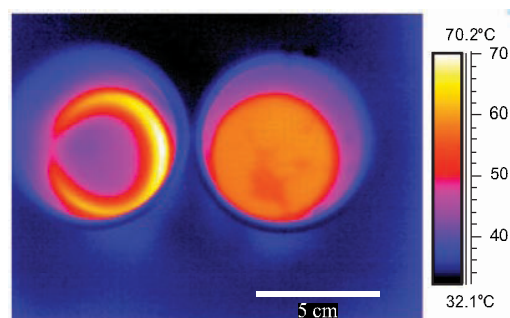


Fig. (6). Ex situ IR images (top view) for NaY synthesis solution (left sample) and water (right sample) heated under 320 W at the end of the heating period. (Reprinted with permission from ref 32. Copyright 2009 American Chemical Society.)

The difference in the tendencies in temperature distribution is reflected on the nature of microwave synthesis: that is, the result of reaction depends on the kind of reaction devices. Particle size and shape of zeolite were changed by changing the temperature and the agitation in microwave reactors. It has also been reported that there was a change in the form of zeolite particles by microwave radiation [33, 34]. This may have been influenced by the unique temperature distribution in the microwave reaction vessel.

New Thermometers to Accurately Measure Temperature in a Microwave Reactor

An FO thermometer is a very useful tool to measure temperature, especially when directly measuring internal temperatures of a chemical reaction. However, its area of measuring temperatures is relatively wide, providing only an indication of the average temperature in the reaction solution. It is said that there is a reaction acceleration effect due to local heating, which is characteristic of microwave heating. The assumption is that there is an occurrence of superheating in which active species for reaction is locally heated up by microwave, which leads to an unusually higher temperature than those of surroundings. It is difficult to use a FO thermometer to observe such an occasion of superheating in a direct manner, and so this effect has not yet become a proven property of microwave-assisted chemical reactions. That is why the temperature measurement method using Raman spectroscopy for measuring temperature in microwave reaction vessels was proposed and established (Fig. 7) [35].

In Raman scattering, there are Stokes and anti-Stokes shifts that can also be observed at the same shift values as those of the Rayleigh scattering [36]. While this represents transitions between

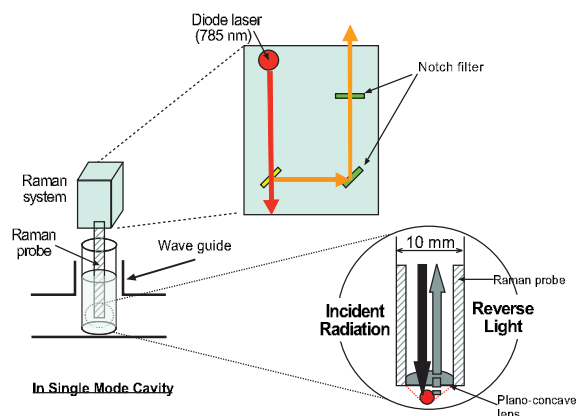


Fig. (7). Experimental setup for in situ observation of Raman spectroscopy. (Reprinted with permission from ref 35. Copyright 2010 American Chemical Society.)

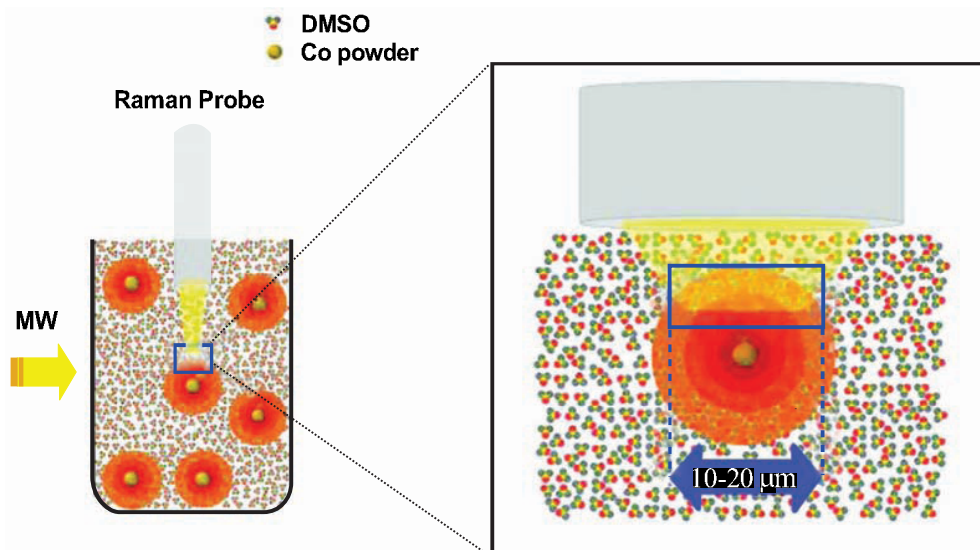


Fig. (8). Image of “nonequilibrium local heating”, which is defined as the phenomenon of heating domains at much higher temperatures than a bulk solution temperature induced under microwave irradiation. The laser beam for Raman scattering was focused to 10-20 μm . (Reprinted with permission from ref 35. Copyright 2010 American Chemical Society.)

the same vibrational levels, their intensities are different. These intensity ratios are expressed as a function of temperature in accordance with the Boltzmann distribution. Thus, the temperature is known from their intensity ratio. When ca. 10 μm of the spot size of the light source for Raman spectroscopy is used, in situ measurement of the local temperatures becomes possible under the microwave irradiation. This thermometry method was applied to heterogeneous systems to measure local temperatures (Fig. 8) [35]. With Co particles dispersed in a DMSO solvent, the temperature of the DMSO, present in proximity to the surface of the Co particles locally and selectively heated by microwave, was measured. During the microwave heating, abnormally high temperatures than those of typical Raman scattering of the surrounding bulk DMSO solvent were detected. It is noteworthy that the higher temperature (473K) than the boiling point of DMSO (462K) was detected therein (Fig. 9). It can be inferred that the Co particles locally heated by micro-

wave incidentally caught by the spot of the Raman light source, resulted in observation of the abnormal heating of the DMSO. This is the first evidence ever that the presence of localized heating was observed in a concrete way. Furthermore, dehalogenation reactions of the organic compounds on Co and Fe particles acting as a reducing reagent showed the acceleration under the microwave irradiation, where the temperatures of reaction solutions were measured with an FO thermometer. This acceleration should be attributed to “Non-equilibrium local heating” of the metal particles as the reaction field. It was not the influence of how the temperatures were measured but the essential effect of the microwave itself. It is thus obvious from these findings that the special effects of microwave do exist without doubt. It is necessary to establish more accurate thermometry methods to prove this discovery.

CONCLUSIONS

This mini-review summarized accurate temperature measurements for chemical reactions utilizing microwave heating. IR thermometers, measuring the temperature on the outer surface of reaction vessels, are unable to measure accurate temperatures inside the vessels. The use of FO thermometers makes temperature measurements more accurate, but they are not best suited where there are temperature distributions inside the reaction vessels. Thus further studies will be needed taking into consideration the drawback of this type of thermometers. The special effects of microwave that have been reported in several thousands of studies to date seem particularly necessary to be re-verified. The investigations on the effects of microwave under accurate temperatures are considered to contribute to the future progress of chemical processes using microwave.

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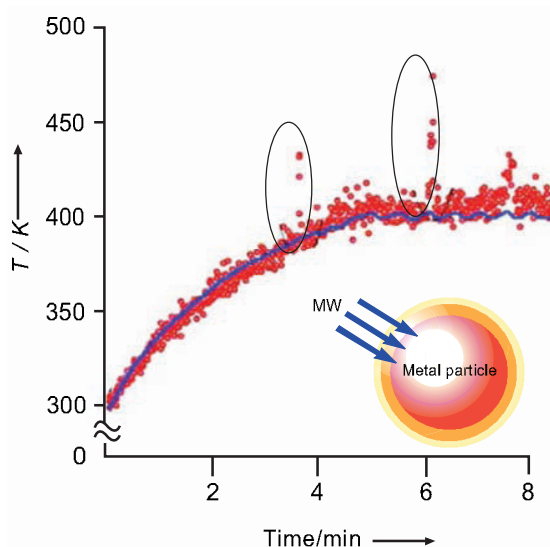


Fig. (9). Nonequilibrium local heating induced by microwave irradiation. Time-dependent Raman spectra of DMSO heated by microwave irradiation at 0.25 s intervals for 8 min in the temperature range 300-500 K (Reprinted with permission from ref 35. Copyright 2010 American Chemical Society.)

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