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OPTICAL, MOLECULAR SENSITIVE, IMAGING MONITORING TECHNIQUES AND APPLICATIONS IN THE MICROCHANNEL

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ABSTRACT

In this conference paper, we will not discuss the particularities of microchannels per se or their possible applications, as we assume that this will be sufficiently explained in other contributions of this conference. Rather, we focus on remote control techniques that may not yet be so widespread. For copyright reasons, we mainly use own measurements from the CeMOS Research Center and do not claim a complete representation of the state of the art.

Optical time and space resolved measuring technologies in the UV- and visible range are predestined for the control and better understanding of flows, mixing processes and reactions in microchannels. Common image analysis results in two-dimensional images. Those can be obtained in reflected light or - if the microchannel has been specially manufactured - in transmitted light. For transmitted light images bottom and lid of the microchannel must be transparent. An increase of contrast can be obtained. This is supplemented by restrictions in the temperature control of the fluids.

Other restrictions result from the depth of field of the classical image analysis. Only a narrowly defined detection plane is imaged sharply or mean values are obtained for randomly distributed concentrations in the vertical axis. This is remedied by scanning instruments which require more time to capture the images.

But indeed does classical methods with microscopy and image analysis allow insights into the spatial distribution of gases and fluids and their temporal development. Optical contrasts are required. This can be done by contrasting the moving phases.

Fluorescence marking is common in this context as it requires low concentrations of markers. The Main Disadvantage is the influence of the marker on the fluidics and the lack of selectivity. Self-fluorescence detection is only possible in very few cases.

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The local and time-resolved concentration controlled identification of molecular species and a possible tracking of mixtures, inhomogeneities, reactions or deviations in the reaction behavior and the occurrence of by-products cannot be detected with these techniques.

The fluid scientist wishes for measuring systems that combine a high spatial and temporal resolution with molecular selectivity and no disturbance of the fluidics.
In principle, optical technologies outside the range of perception of the human eye can be considered here.
All known approaches have advantages and disadvantages and the state of the art will be explained below.

Near infrared spectroscopy: NIR spectroscopy uses the fact that almost all fluids in the NIR range have absorption bands. Thus they are usually distinguishable. In the world of chemical monitoring, these methods have made massive inroads since it is easily possible to transport the light via glass fibers and thus build fiber-optic sensors to be integrated into chemical reactors. Fiber optic probes can be miniaturized so that they can also be easily integrated into microchannels. The excitation of second or higher harmonics of vibrational-rotational transitions of molecules caused by the photons is used. Thus the extinction is relatively weak and only higher concentrations (above approx. 0.1% in fluids) can be detected.

MIR spectroscopy: With this type of spectroscopy fundamental oscillations of the molecules are scanned which, in contrast to NIR spectroscopy, have much higher excitation cross sections. The advantage of this is the possibility of detecting even small concentrations down to the parts per million region. Due to the sharper bands, the selectivity towards NIR is also greatly increased. A disadvantage is the complex technology hence a robust design of the device is handicapped. Existing fiber technologies are unstable, have limited spectral range and cannot be used for long periods in harsh environments. In practice the extremely high absorption of water also proves to be disadvantageous. Water-containing substance systems are massively superimposed by the water absorbance and other substances – especially with low concentrationsare only found with difficulty.

Raman spectroscopy: The Raman technology also scans the fundamental oscillation of the molecules but in contrast to MIR spectroscopy by exploiting the polarizability of the molecules. Stimulated with photons in the visible range, the molecules are short time excited into a virtual state and fall back instantaneously into another vibrational-rotational state of the electronic basic level. This has the advantage that classical fiber-optic sensors can be used for Raman measurement techniques and the high selectivity of MIR spectroscopy is also present.
On the other hand, the Raman effect is extremely weak. Strong lasers have to be used up until now and long integration times are necessary. This situation is strongly and positively changing in present times.

Elastic light scattering:
Scattered light technologies can be used for precipitating products or those that change the dispersivity in the microchannel - such as emulsifying, crystallizing, precipitating or dissolving.
This contribution includes how these technologies can be used if local selectivity is achieved in addition to the known molecular selectivity or particle size.

The discussed molecule-selective measuring methods are now to be adapted for obtaining location-selective information in image-analytical or scanning systems. This can be achieved - as in classical imaging - in 2 ways:
- Design of an imaging system with capturing all pixels simultaneously.
- Integration into a scanning system, which scans the locations one after the other, reducing the measurement speed but being eligible for higher wavelength resolution, depth of field or contrast if necessary.

NIR image analysis:
Analogous to image analysis in the UV/VIS range, CCD cameras are used and wavelength selectivity with optical filters is utilized either on the emitter or on the detection side.
In the NIR range, however, cameras on silicon based chips cannot be used due to the limited spectral range of those systems.. Instead cameras based on indium gallium arsenide (InGaAs) are used which are sensitive in the 900-1600nm range [4]. In combination with NIR light-emitting diodes (NIR LEDs) images can be

generated with wavelength selected brightness levels according to the absorption bands of fluids for locally fluctuating concentrations. It is advantageous to also take reference images without the presence of any absorbing substances. Computer based optimization of images, like anti-shading methods, can be used to compensate for inhomogeneous illumination problems. The advantage of NIR LED illumination as an alternative to broadband illumination and the use of sequentially used filters is in the simplicity of the design and the fast change of wavelengths. Without special equipment image sequences of 25 full frames/second can be achieved and thus moderately fast changing processes can be captured. With individual wavelengths, pulses down to microseconds can also be recorded.

MIR image analysis:

Such techniques are known from the field of thermal imaging. However, depth of field and contrast are usually not sufficient for scientific purposes. The method of MIR scanning proves to be more favourable. Commercial devices typically reach scanning velocities of1-2 measuring point per second. Thus the generation of images is very time-consuming. A 2-stage procedure for data acquisition proves to be more favorable. The first stage, an image scanning with full spectrum width, is selected for each pixel. Here the assignment of interesting statements to the suitable wavelengths can be assigned via gold standards for narrowly defined local conditions[6]. In the following the interesting wavelengths and target cutout are selected and monitored with an up to 300 000 measurements per second fast scanning mode using quantum cascade lasers for routine sample measurements. [3]. With these techniques unequal surfaces with topographies can be sampled and coatings with a layer thickness of less than one micrometer are eligible for molecule selective detection.

Raman scanning image analysis:

As explained above Raman spectroscopy requires high laser power and long exposure times. On the other hand Raman measuring heads can be precisely focused and installed in scanning equipment. This makes 2D Raman scanning possible [2]. Even 3D-scanning seems to be achievable.

The measurement rate can be increased by tolerating a loss of resolution [1], but this can only be achieved under convenient conditions. Further development towards higher velocities is possible by limiting the numbers of detected Raman-shifts by replacing classical Raman spectroscopy by Raman multichannel photometry [5]. Large-area detectors promote Raman photometry by replacing the necessary dispersion and thus small-area detections in the spectrometer with filter techniques and single photon counters. The area and sensitivity gain lead to a considerable increase in speed.

Scattering light measurement technology:

Scattering light techniques (elastic light scattering) can be used to control the formation of disperse phases, e.g. due to product failures. In the example a fiber optic based backscattering [7] technique is used. The fast detection is mandatory to visualize the precipitation of inorganic products in the millisecond range. Microchannels in particular allow strong concentration gradients and thus also pH or temperature gradients. This can lead to extremely fast precipitation processes. Fast measurement technologies are required. In geometries with constant flow and events occurring constantly for each location, kinetic fields for precipitation processes can be developed in combination with fast backscatter measuring systems with scanning equipment.

Combination techniques:

An example shows how the different modes described can be built into one device. This allows, for example, the distribution of lipids via Raman scanning. The additional information of the local moisture from NIR scanning to be used for helpful information on wound healing, but also for reaction monitoring in the microchannel.

An optimal control technology seems to be the combination of different techniques and selective wavelength information generated by different wavelength regimes. The combination provides a flexible application for divers scientifique problems.

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