Inline Process Analysis With Lif(t) Fluorescence Spectroscopy

LIF(t) is an in-situ analysis system for the quantitative analysis in liquid and powders or on surfaces based on laser-induced and time-integrating fluorescence spectroscopy. Using ultraviolet laser radiation through quartz fibres the matter to be proved is analysed directly in the process, eliminating sample preparation.

This article gives an overview on the physical and technical bases of LIF(t) laser-induced and time-integrating fluorescence spectroscopy. This measuring procedure shows its efficiency in applications from the most diverse areas of process analysis. The patented procedure of time-integrating LIF offers a solution to measurement problems, which were considered insolvable before.

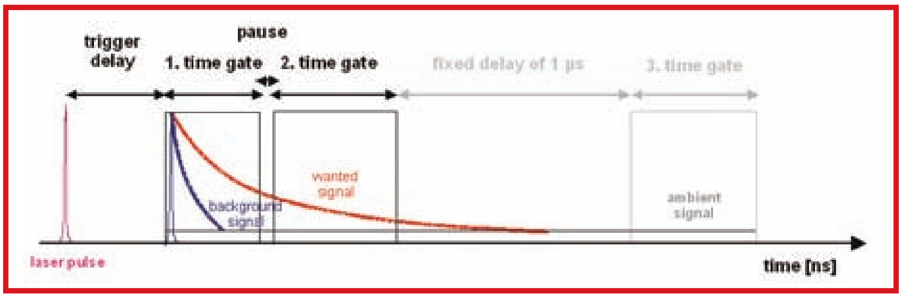
Physical And Technical Principle

The basic principle of the laser-induced fluorescence spectroscopy (LIF) is the absorption of laser radiation by the substance to be proved. The radiation energy is absorbed by the molecules and is emitted again in nanoseconds (10-9s), the so-called fluorescence phenomenon. Compared to other spectroscopic methods this procedure is especially suitable to prove very low material amounts because of its high sensitivity. But the use of applied laser wavelengths (e.g. 266 or 355nm) in the ultraviolet spectral range stimulates not only the fluorophores of the analytical target but also molecules of the surrounding matrix, mainly from organic matter. This means that registering only the spectral intensity distribution of the fluorescence not necessarily leads to a significant separation of the substance spectra. Therefore, a time-integrating approach is included in the procedure to observe the decay times of the fluorescence signals in a suitably chosen wavelength range.

After each single laser pulse excitation, lasting approx. 1ns, the time decay of the fluorescence radiation is registered in two measuring windows as intensity values I1 and I2 .

The differential value (I2 / I1) depends on the amount (concentration, layer thickness, etc.) and allows at the same time a significant separation of annoying background signals. Furthermore the evaluation of this differential value allows for analysis results which are not influenced by disturbances or system specific variations as these affect the overall behaviour of the time decay and thus the total fluorescence intensity in the same way.

Pic.1: LIF(t)-measuring procedure



The optical excitation occurs with an especially developed passive UV microchip laser which generates a pulse frequency of about 10kHz of single laser pulses with wavelengths of 266 or 355nm. Quartz fibre tubes of up to 30m length and application specific measuring heads guide the laser light directly into the process. Using a second quartz fibre, the LIF signals are transferred to the detector. The measuring heads contain no active components which making them suitable for application in rough or demanding surroundings, as well as hazardous areas.

The detector system consists of a photomultiplier which registers the single fluorescence signals (photons) by wavelengths through an application-specific combination of optical filters. By means of a statistical count procedure, the detector signals are evaluated as a function of time, converted by a calibration function into the respective measuring value and displayed in less than a second.

Optical spectroscopy procedures have a long history in lab applications but nowadays they are also used to solve process analytical questions. The fluorescence spectroscopy holds a special position amongst these procedures due to its sensitivity. Classical methods like UV radiation or infrared radiation, which can be applied as transmission or reflection experiment, always need a reference value. In contrast to that the fluorescence spectroscopy works on the basis of registering direct intrinsic radiation.

Process applications in liquids

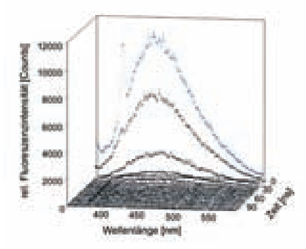
Process applications in liquids, especially the analysis of oil in water always belongs to the standard repertoire of an environmental laboratory. The classical method for the hydrocarbon index is the gas chromatography (ISO EN 9377-2). The procedure requires qualified sampling and test preparation by extraction and clean-up in the lab. However, in many industrial production areas, the need has risen to monitor all possible oil entries into the process streams. Constant supervision allows for fast intervention in the case of leakages to protect the production plants, e.g. cooling water circulations or process-specific condensate streams. The lab analytics mentioned above can be applied here; but because of the necessary sampling and preparing they are time-intensive.

The application of the LIF(t) as a quick in-line procedure introduces the measuring head with its fibre-optical coupling directly into the process stream and supervises continuously the calibrated values of mineral oil or hydrocarbons.

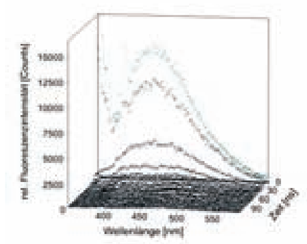
Picture 2 shows the typical fluorescence spectrum of pure water and its intensity behaviour as a function of time in nanoseconds (ns). Beside the peak of the Raman scatter of the H2O molecule, a very broad band is visible which is caused by the always present humine acids. In presence of mineral oil (10ppm) the spectrum (picture 3) shows a very similar band contour to that of pure water, so that an oil entry cannot be proved right away. The difference reveals itself by evaluating the respective time-dependent behaviour of the fluorescence intensity (time decay curve) for a wavelength of 400nm. (picture 4 and picture 5).

Here a significant increased time decay of the fluorescence intensity is visible in the presence of mineral oil in the water (picture 5). By capturing the decay curve in the two time windows 1 and 2 (see picture 1 left), the concentration can be calculated immediately and allows for quick and reliable analysis.

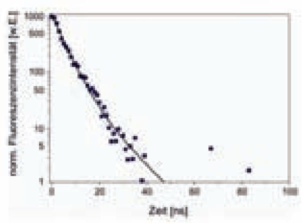
Next to the measurement of oil-in-water, the method is suited for the supervision of oil-on-water. With specific measuring heads oil films on water can be supervised reliably, e.g. surface water in production plants or oil separators and slurry tanks.



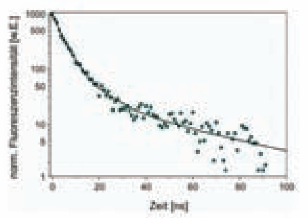
Pic.2: Fluorescence spectra of pure water with time dependence



Pic.3: Fluorescence spectra of a 10 ppm oil-in-water emulsion in water



Pic.4: Time decay curve of pure water



Pic.5: Time decay curve of oil-in-water emulsion (10 ppm)

Process applications on solids

Beside the measurements in and on liquids, LIF(t) can also be applied in process applications on solids, powders and surfaces. Special measurement heads allow direct in-line supervision and process control. Fluorescence delivers intrinsic signals, so it works to a great extent regardless of the geometry of the surfaces to be examined and annoying reflections can be eliminated easily.

An interesting application on solids is the measurement in polymer pellets. In this procedure, material properties (viscosity, yellow index) of polyamide could be correlated with LIF(t) measurement results, allowing for a continuous in-line-monitoring and process control in the production stream.

Further examples are the lubrication or application of process auxiliaries in the industry or metal plate rolling processes , where special oils and emulsions are sprayed on the surface for lubrication or cooling purpose.

Beside the supervision of surface coatings, the continuous monitoring of surface cleanliness is of big interest. The areas of application are very varied here and concern many industrial areas, from the processing and chemical industry to automotive and the medical technology.

Today in the multiple areas of the chemical industry, the most diverse process-analytic applications are daily business. Nevertheless, real in-situ/in-line procedures are only available for a limited range of applications, like the gas analysis. Hence, the LIF(t) procedure finds active interest in this industry. Because of the versatile applicability in liquid phase (oil/solvents) or on/in solid states (powder/granulate materials/polymers) many interesting and rewarding challenges are still to be expected.

In-line process analysis is still rarely found in the bio and pharmaceutical industry, due to strict regulations and the very specific production technology. As an offline technique the fluorescence spectroscopy has already found a very wide application field in these industries. It can be expected, that the method presented here will help to make these areas accessible for in-line process analysis in order to contribute to product quality and offer added value. Author: Dr. Heribert Hohmann

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