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Particle Size and Shape Analysis in the (wet) Process Environment

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ABSTRACT

The interest in quality control of the production results of particle processing operations such as milling, agglomeration, classification, mixing, is as old as the processes themselves. A major information in this context is the particle size distribution (PSD). While early methods such as sieve analysis and sedimentation required a time consuming laboratory operation, modern methods allow for an instantaneous monitoring of particle size and shape of the production directly in the process environment. Today, instruments basing on laser diffraction, image analysis and ultrasonic extinction are dominating this field. As the precision of the analysis results is mainly limited by sampling errors, representative sampling and an adequate sample size are of decisive importance for high quality measurements. A sufficient sample size is especially critical for counting methods, such as image analysis. Current solutions for at-line, on-line and in-line process applications are presented and discussed, including equipment for hazardous areas (ATEX) and instruments adapted to the requirements of good manufacturing practice (GMP).

Introduction

The instantaneous monitoring of the particle size distribution (PSD) in the process environment requires fast and robust measuring methods. They all have specific advantages depending on the application.

Measuring Methods

Laser Diffraction (LD) is a fast absolute measuring technique [1], which has proven its suitability for particle size distributions (PSDs) ranging from below 0.1 µm to about 10 mm in dry and wet applications. In a typical set-up the concentration has to be adapted by dilution with suitable fluids. In order to measure the size of the primary particles, the sample has to be well dispersed. The introduction of a powerful dry dispersing unit in 1984 [2] has overcome the former limitation of this method to wet applications. Especially for dry applications LD allows for large sample sizes of even above 100 grams and has an excellent statistical relevance of the data [3]. It is standardized by ISO 13321-1:1999.

Dynamic Image Analysis (DIA) is a fast absolute measuring technique, covering a size range of about 1 µm to above 10 mm. The images of the particles are captured, allowing for direct visual inspection and shape analysis in addition to particle sizing. The requirements for dispersion and dilution are comparable or even higher than for LD, as overlapping particles in the images would require subsequent separation by time consuming software algorithms. A good statistical representation is possible by particle numbers typical in the range of 10^6. In combination with high measuring frequencies [4], which are typically used for process monitoring, this results in very large data volumes. DIA is standardized by ISO 13322-2: 2007.

Ultrasonic Extinction (UE) measures the frequency dependency of the extinction (attenuation) of sound waves propagating in suspensions or emulsion. As the required frequency range can currently not be generated in gases, this method is limited to wet applications. It is a non-absolute technique and requires an extended set of parameters for the exact evaluation of size distributions. For process applications an empirical evaluation method of these parameters has been found to be superior to approaches basing strictly on physical models. Size ranges from above 10 nm to about 3 mm can be monitored directly at concentrations up to 70 %Vol. without dilution. The robust method covers wide temperature ranges up to 150°C and pH 1 to pH 14 [5]. The acquisition of UE spectra has been standardized by ISO 20998-1, the standard for the conversion into size distributions is still in progress.

Application types

Today, the reproducibility of these methods is very high. So sampling errors usually dominate all other errors.

In the classical laboratory or **off-line** application the sample is taken manually, is manually adapted to the needs of the measuring equipment, and manually measured. In the process environment three main types of applications are defined:

At-line is the fully automated analysis in a laboratory. The sample is still taken manually or by stand-alone devices. The sample is transported to the laboratory, e.g. by pneumatic delivery. Several hundred samples can be measured per day allowing for precise quality control of slow processes. At-line LD is e.g. widely used for quality control in the cement industry.

On-line places the measuring device in the process environment close to but not into the production line. The fully automated system includes the sampling but the sample is transported to the measuring device. Mainly LD, UE, and DIA are used.

In-line implements sampling, sample preparation and measurement directly in the process, keeping the sample inside the production line. This is the preferred domain of LD (mainly dry), DIA, UE, and focused beam techniques. The latter are measuring chord length rather than size distributions.

Because of the importance of precise sampling, we have started the development of suitable sampling devices as soon as LD became available. Beginning with the presentation of a first representative sampling probe for aerosols in 1978 [6, 7], an application of a continuous representative sample

coupler "ROPRON" was published in 1989 [8] for particle size analysis in dry fall shaft applications in combination with LD. In the same paper a Sample Finger Robot (SAFIR) was described for particle size analysis at concentrated suspensions, performing all the necessary steps automatically, such as sampling from a process pipe, the dilution and circulation to the LD system.

Current Realisation

ROPRON and SAFIR have been successfully used in several at-line and on-line applications. The experiences with these early applications have built the basis for today's solutions.

Sampling

Today, the work horse for all our process application requiring representative sampling is the TWISTER, which has been introduced in 1998 with a specially adapted LD sensor with built-in dry disperser MYTOS [9]. They enabled a real in-line particle size analysis for the very first time.

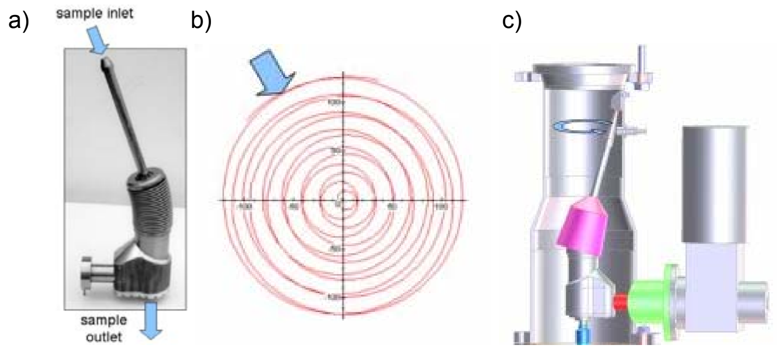

Fig. 1: a) Sampling finger with sample inlet and outlet. The protection shield is removed for clarity. b) Spiral path of the sampling pipe over the cross-section of the process pipe. The arrow indicates the parking position. c) TWISTER cross-section showing the process pipe and the spinning sampling pipe in the parking position.

The concept of the TWISTER is a sampling pipe, which is moved from a shielded parking position on a spiral line towards the centre of the process pipe and back. For representative sampling, the velocity is controlled in a way that equal areas are covered in equal times. The particle transport is performed by a flow pump or for dry applications preferably by the injector of the dry disperser of the subsequent measuring device.

Since its introduction a continuously growing family of samplers have been developed, covering diameters of the process pipe from 50 mm to 660 mm as well as versions adapted to the ATEX and GMP requirements [10].

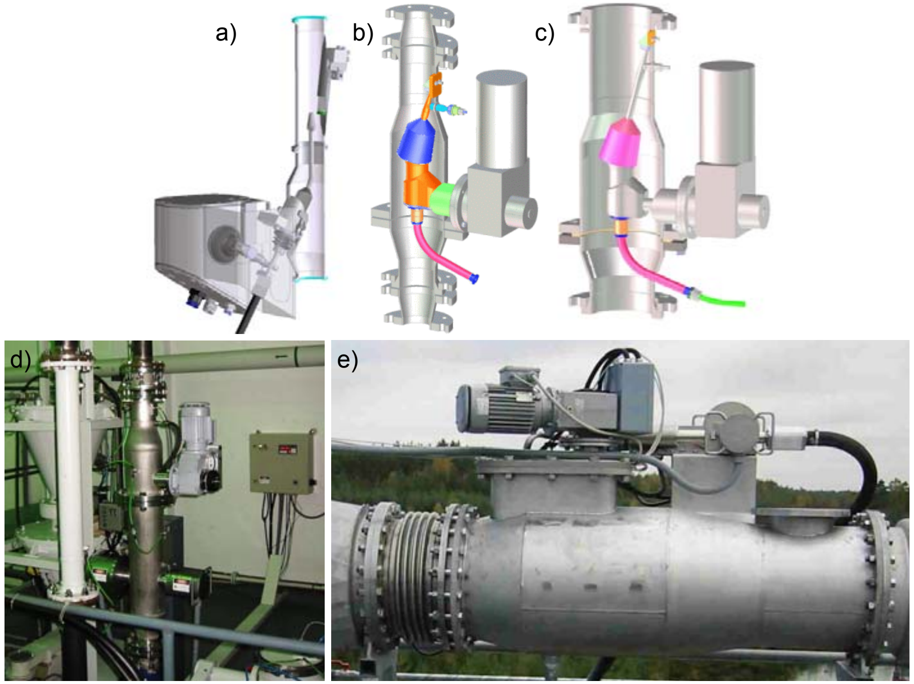

Fig. 2: a) Representative samplers TWISTER 50 mm ∅, ATEX/GMP with drive unit, b) TWISTER, 100 mm ∅ with pipe reduction to 80 mm ∅, c) TWISTER 150 with sample outlet stage, d) typical inline application with TWISTER & MYTOS, integrated in a pipe of 100 mm ∅, e) typical on-line out-door application with TWISTER in a pipe of 400 mm ∅ and piggy-back on-line MYTOS.

For applications with narrow size distributions or where the partial sample can be taken from a well mixed, homogeneous volume, static mixers or even simple probes have been used successfully, as an alternative.

Particle Size and Shape Sensors

The preceding sampling principle can be combined with LD, DIA and UE for on-line and in the cases of LD and UE for true in-line applications. As almost identical components have been used for the sensors in the laboratory and process environment, including e.g. light sources, dispersers, optics, detectors and software, a good comparability was achieved for the different fields of applications. Currently three different sensor families are available:

- The MYTOS/MYTIS family, basing on LD,
- the PICTOS/PICTIS family, basing on DIA,
- and the OPUS family, basing on UE.

Fig. 3: a) at-line MYTOS and vibratory feeder, b) MYTOS Module with control rack, c) on-line TWISTER 150 with on-line MYTOS, d) in-line TWISTER 150 and in-line MYTOS 150

The **MYTOS family** is combining the renowned dry disperser RODOS [2] with the well established technology of the off-line sensor HELOS [1] in a robust IP65 stainless steel housing. Particle sizes from 0.25 μm to 3,500 μm are covered by 6 widely overlapping measuring ranges. At-line applications are realized with preceding vibratory feeder, as a stand alone unit or as module in a protection housing.

On-line applications can be realized with the same set-up by connecting the device to a preceding sampling station. For in-line application the sensor is available as part of the process pipe with diameters 100, 150 and 200 mm.

For coarser particles the MYTIS family has been introduced, replacing the powerful dry disperser by the gentle gravity disperser GRADIS. It covers the size range from 0.5 µm to 3,500 µm in two overlapping measuring ranges in at-line and on-line applications.

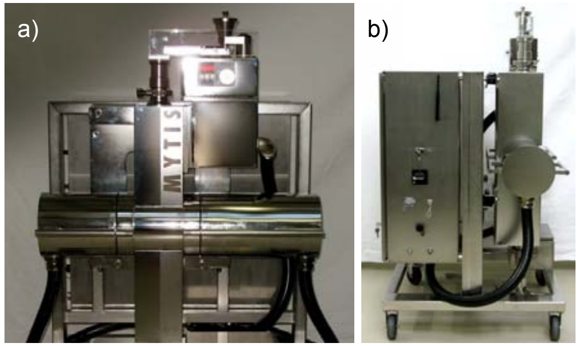

Fig. 4: a) MYTIS with built-in gravity disperser and vibratory feeder, control box on the rear, b) side view.

The **PICTOS family** combines the dry disperser RODOS with the DIA sensor known from the QICPIC off-line sensor [4].

The unit is capable to capture images of particle flows with 1024x1024 pixels at up to 500 frames per second, process and store the results in real-time. A special nanosecond pulse light source limits the motion blur to far below one pixel size for all measuring ranges. Currently overlapping measuring ranges cover size ranges from 5 µm to about 3.5 mm. Similar to MYTIS the PICTIS family combines the high speed image analysis of QICPIC with the gentle

dispersion of the gravity disperser GRADIS in a singe robust instrument, covering a size range from 5 µm to 10,000 µm.

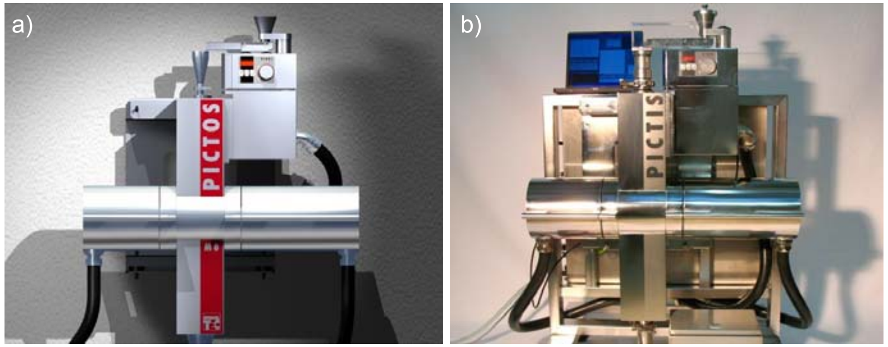

Fig. 5: a) PICTOS and b) PICTIS at-line IA sensor equipped with the vibratory feeder VIBRI, both units support GMP applications.

The **OPUS family** is designed as finger probes and can be adapted to nearly all kinds of process pipes or vessels by a variety of process adapters and probe lengths ranging from 33.6 cm to 3.5 m using a DN 100 flange.

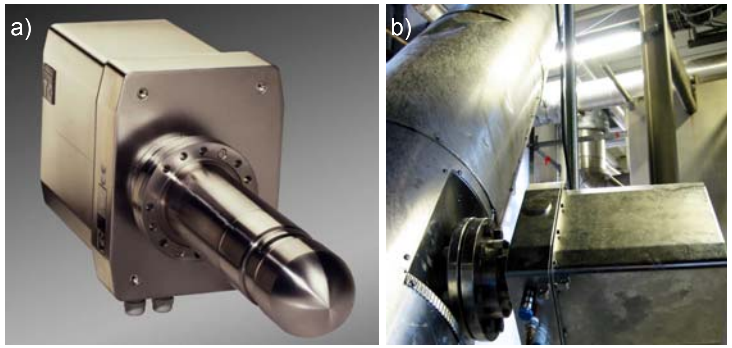

Fig. 6: a) OPUS System, suitable for rugged process applications: 0 to 40 bar, 0°C to 120°C, PH 1 to PH 14; b) In-line application of an OPUS probe monitoring a crystallization process in a large vessel.

Process adapters cover pipe diameters from 10 mm up to a few meters. For small diameters, 10 - 25mm, FT- (Flow-through) adapters are applied to couple OPUS with the process. Since the complete product flow is introduced to the measuring zone, sampling is not an issue any more. FT 15, FT 20, FT 25 with inner diameters of 15 mm, 20 mm and 25 mm are available as a standard, other diameters are available on request. They can also be combined with a preceding TWISTER and a subsequent flow pump.

Pipe diameters from 50 - 200mm are covered by BP- (By-pass) Adapters. In this case the product is partially passing the measuring zone and partially flowing around the OPUS probe. This adaptation is best suited to be installed in a turbulent flow. BP 50, BP 100, BP 150. BP200 to inner diameters of 50 mm, 100 mm, 150 mm and 200 mm are available as a standard, other diameters are available on request [11].

Software

One single software package is used for the control and evaluation of all instruments mentioned above. It allows for the concurrent operation of several measuring system of the same or different types in a network environment. The database Firebird™ is used in combination with an application server for the storage of the measurement conditions and the measured data. The software is compliant with CFR 21 rule 11 for the storage of electronic data and signatures.

Results

Due to the strict confidentiality of most of the applications, only a few results can be published without indication of the exact process parameters.

Laser Diffraction

In a first example a TWISTER 50 is used to monitor the outlet of an AFG 100 jet mill in a pharmaceutical production. A MYTOS Module is used to monitor the particle size distribution. The results displayed in Fig. 7 are constant at

constant operation conditions. The decrease of the optical concentration indicates the emptying of the mill. The cycle time of a full TWISTER scan was set by software to only about 40 seconds. So any change of the parameters during the set-up of the milling conditions could be observed immediately.

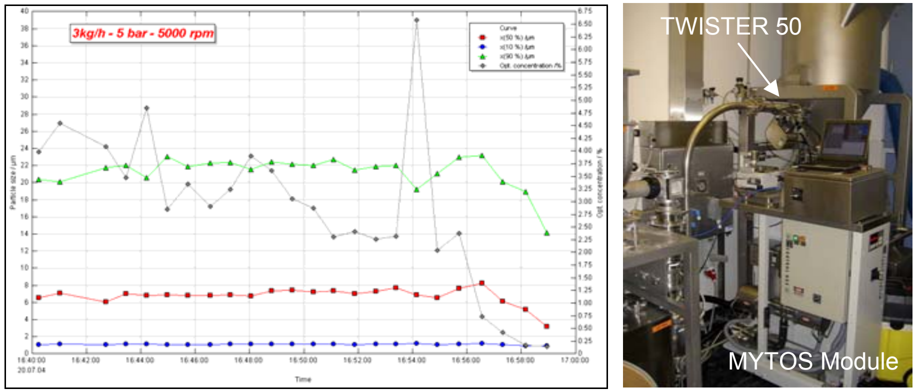

Fig. 7: Trend diagram of the particle size x_{10}, x_{50}, x_{90} in a pharmaceutical production using TWISTER 50 & MYTOS Module.

In a second example a TWISTER & MYTOS combination with 100 mm pipe diameter is used in a SiO-production to monitor the particle size distribution directly in the outlet of a mill/classifier stage.

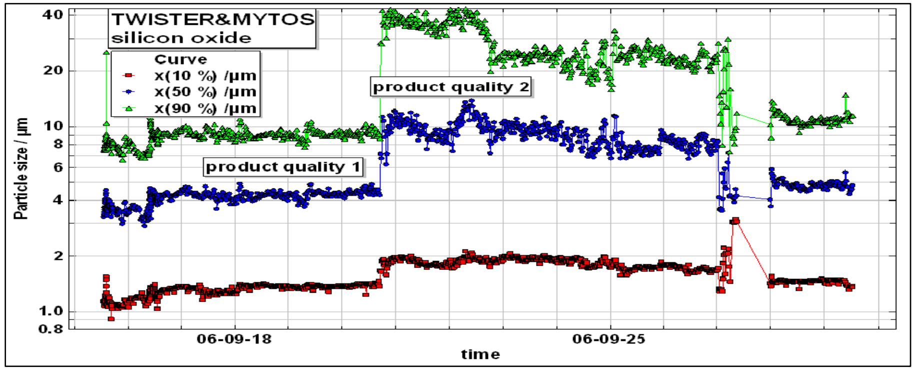

Fig. 8: Trend diagram of the particle size x_{10}, x_{50}, x_{90} in a silicon oxide production over two weeks using TWISTER & MYTOS

The instant reaction of the measuring system allows for the test of different settings to reach the desired PSD, as displayed in Fig. 8. The step in the particle size is related to a chance of the product from product quality 1 to quality 2. The change in the x_{90} in product quality 2 is a result of a fine tuning of the production parameters. On the 28th the mill ran empty, followed by the start of a new batch on the 29th.

Image Analysis

As the IA for process applications has been introduced recently [12], no released process data are currently available. Fig. 9 displays data from a PICTOS installation in our test house. At a constant frame rate of 450 fps the data have been acquired by a 2 GHz Pentium-M processor and stored in real time into the database. A second embedded Core-2-Duo processor was used concurrently inside the control-box of the PICTOS for the evaluation and the data reduction. The results were available via the local network and could be visualized as PSD, shape information, particle gallery or trend graphics at any location in real-time.

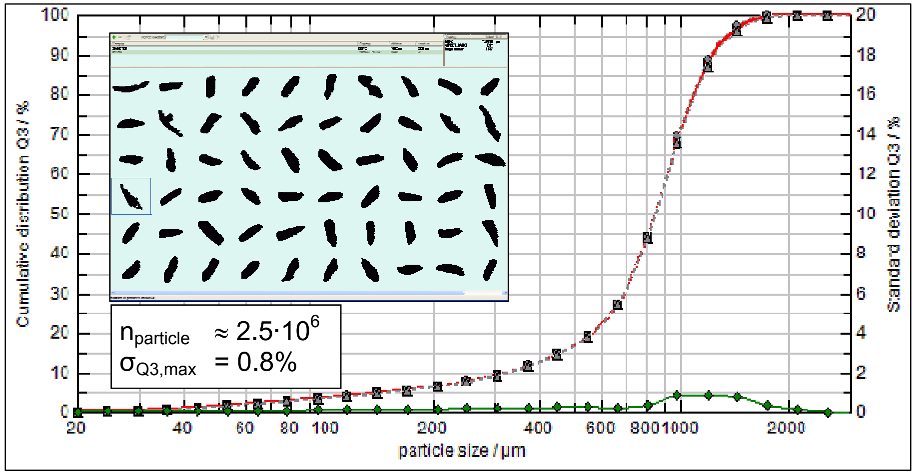

Fig. 9: Subsequent measurements of coffee powder in the test house. More than 10^6 particles are measured for each measurement.

For each measurement more than 10^6 particles have been acquired from about 25 g of sample mass. The resulting rel. standard is below 1% und thus sensitive to very small changes of the produced quality. Each individual particle can be selected, evaluated and displayed by the particle gallery.

Ultrasonic Extinction

Fig. 10 presents some results of a typical in-line installation. In this application the milling process of Aluminium pigments was to be monitored. The challenges were the demanding environmental conditions and the use of benzene as suspension liquid. So the complete installation has to be compliant with the ATEX 95 regulations for hazardous areas.

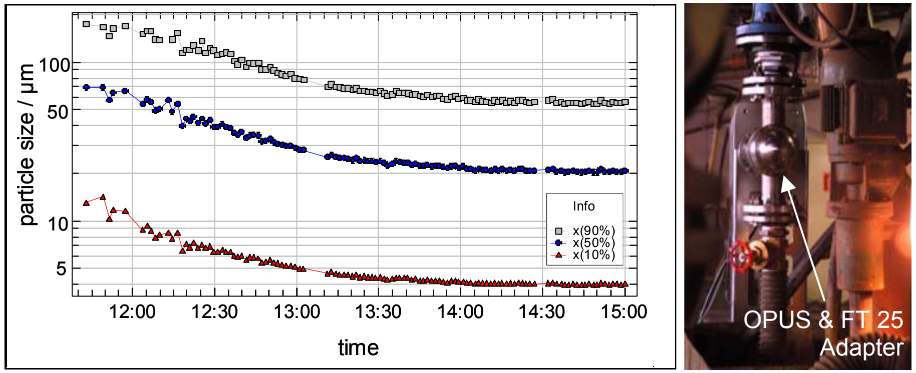

Fig. 10: a) Trend diagram of a milling application for Aluminium pigments in benzene, b) OPUS Probe connected to the process via a flow through adapter.

OPUS allows for the flexible installation in various applications. Fig. 11 demonstrates the use of an OPUS sensor in a complex sampling matrix. It enables the feed from different production lines, so that several stages of the production can be monitored periodically by a single sensor device [13].

Fig. 11: The OPUS Probe installed in a complex sampling station using a by-pass adapter with 50 mm ∅

Conclusion

Today, precise, fast and robust particle size and shape analysis is available for both, laboratory and process environment. A family of representative samplers, mixers and probes adapts to subsequent measuring systems and to the process. At-line, on-line or in-line solutions can be chosen according to the needs of the specific application and the space available at the plant. Sample size and measuring frequency can be adapted by software in real-time to optimize the relevance of the information vs. ware and data volume. Cycle times down to one minute are possible for all methods: LD, DIA and UE. The availability of three methods expands the field of applications to specific needs: LD as an absolute, fast and robust method typically acts as

the standard method for sizing applications in dry and wet regimes. The presented high performance DIA adds shape information and allows for the detection of smallest fractions at the highest size resolution. This is e.g. ideal for the detection of sieve breaks etc.. Both methods do not require parameters and can thus handle batches of different materials easily.

In contrast to LD and DIA, UE is depending on parameters, which have to be evaluated for each specific product in advance. But it can be used for suspension and emulsion at high concentrations and high temperatures without dilution. So it is often the preferred choice for applications in the field of wet milling, crystallization and polymerization. Special versions of the instruments are available for hazardous areas, for GMP, or pharmaceutical applications. The application of particle size and shape analysis in the process environment is currently mainly limited by high temperatures (LD, DIA > ~100°C, UE > 150°C), high pressures (LD, DIA > ~1 to 3 bar) and very low concentrations (LD, DIA << 0.1 % Copt; UE < ~1% CVol.). This will have to be addressed in the future.

Symbol Index

DIA: Dynamic image analysis
Copt: Optical concentration
CVol: Volume concentration
LD: Laser diffraction
PSD Particle size distribution
UE: Ultrasonic extinction

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