on-line Sampling and Sample Splitting
- Principle and Instrumentation *

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1 Introduction

on-line particle size analysis is a vision which has been viewed with increasing clarity by specialists for more than two decades and which is described and proposed to users as a highly promising technique of production control.

For just about twenty years, the laser diffraction method has also been available for analyzing particle size distributions; as a result of this development, too, on-line analysis has evolved from a visionary possibility to the status of concrete utopia during the interim.

On the whole, the on-line applications realized and published during recent years still present a heterogeneous picture with respect to the common characteristics for the achieved or desired performance. Perhaps it would be more appropriate to speak of so-called on-line applications.

However, an appreciable diversity corresponding to the wide range of possibilities with typefying characteristics can develop only if the interested user evolves from the expectant attitude to an appropriate, conscious phase. That is, he must be capable of realizing the meaning of the sample for analysis and coping with the new dimension of available information.

As a manufacturer of analytical instruments for measuring particle size distributions and designer of system solutions, we regard ourselves as a company which performs a bridging function between the arising expectations among potential users and our ensured possibilities. The approaches which we have adopted during the interim and the present capabilities in the field of on-line analysis with laser diffraction are described in the following.
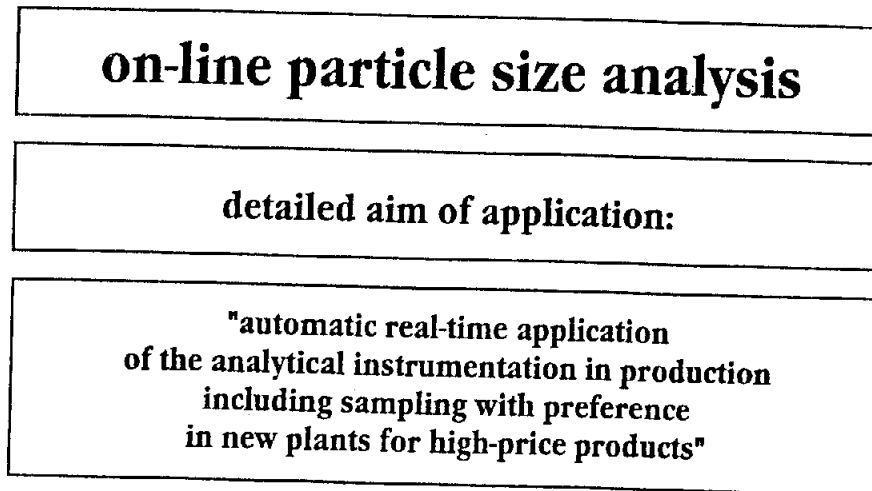
2 on-line particle size analysis

For the present purpose, the concept of on-line particle size analysis encompasses the method as well as the sum of the instrumentation required for obtaining more information faster from the production for the production.
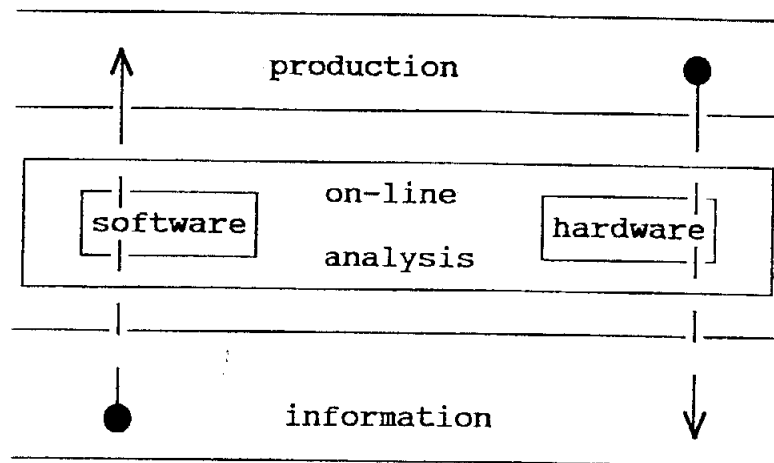
Figure 1: Function blocks for organizing on-line analysis: information from production for production

The on-line hardware procures all information, which is processed by the on-line software in such a way that the respective problem can be solved. At present, the expectations decidedly exceed the capabilities of the available solutions. With the use of information obtained by elaborate methods, the initiation of the most comprehensive actions, or the acquisition and backing of new knowledge, or both, are subsequently demanded.

Our own objectives for the application of on-line analysis of particle size distributions by laser diffraction are stated more precisely against this background:

on-line particle size analysis

detailed aim of application:

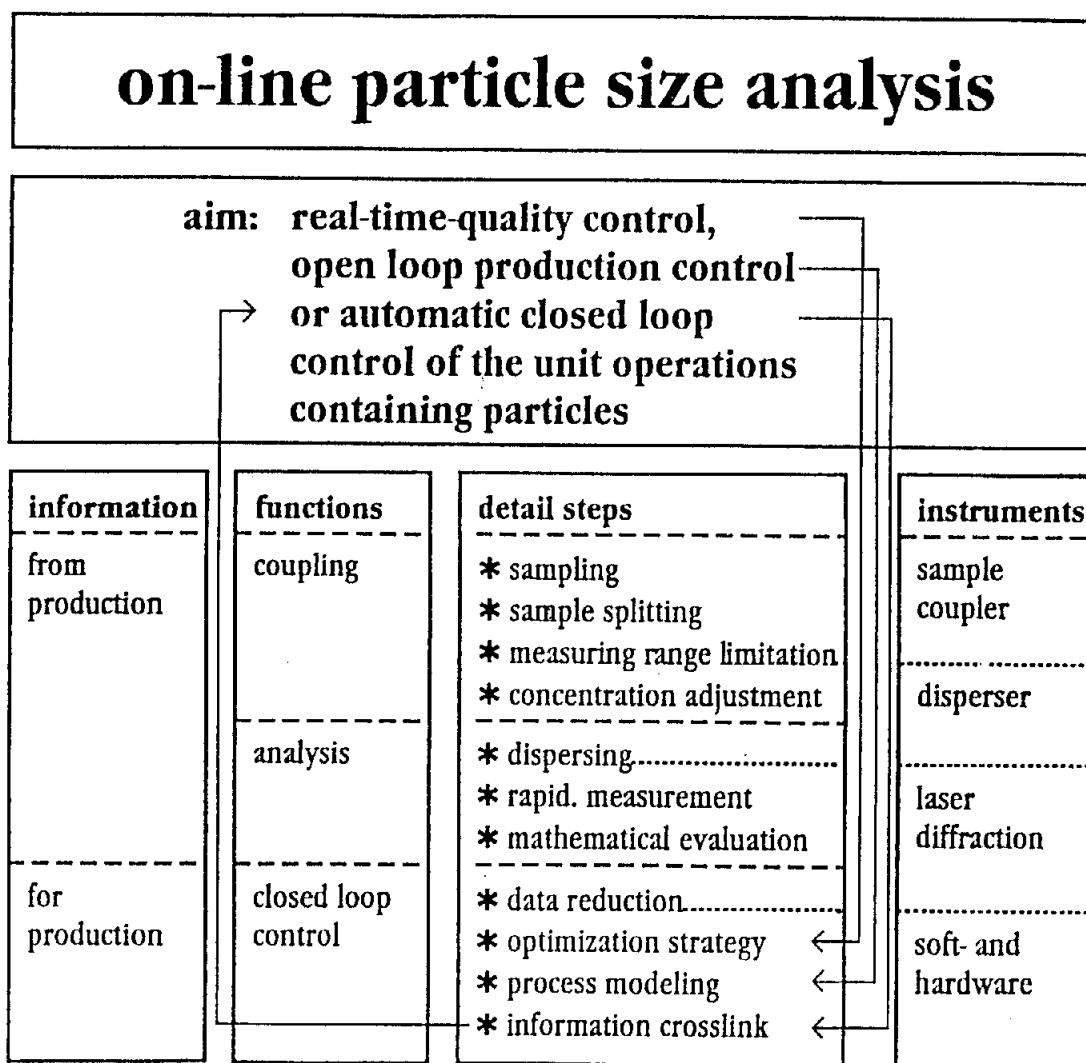| "automatic real-time application
of the analytical instrumentation in production
including sampling with preference
in new plants for high-price products" |
| --- |

Figure 2: Precise statement of objectives for application

This combined market strategic orientation imposes exacting technical demands on innovations and initially concentrates the range of users on efficient partners conscious of the problems involved. This is a desired feature and promotes the continuing development of a mature technology for the long term far more than it undoubtedly hinders an otherwise dilletante propagation.

A further basic requirement imposed on an on-line measuring system is a reaction time which is matched to the process to be characterized. This in turn depends on the collective period which elapses from sampling until the measurement, as well as the subsequent cycling time of the measuring instrument.

Operation in the minute range is feasible for the on-line analysis of particle size distributions by laser diffraction for the purpose of real-time quality control, production control and closed-loop control. A number of partial steps must thereby be mutually matched and executed either in succession or in parallel:

The object of the first five steps is the preparation for the rapid measurement. The quality of the measurement and the value of conclusions derived therefrom with respect to the fundamental operation to be characterized depends decisively on the reliability of the sampling process and the subsequent preparation of the sample for analysis.

on-line particle size analysis

aim: real-time-quality control,
open loop production control
→ or automatic closed loop
control of the unit operations
containing particles

information	functions	detail steps	instruments
from production	coupling	* sampling * sample splitting * measuring range limitation * concentration adjustment	sample coupler disperser
	analysis	* dispersing.................... * rapid. measurement * mathematical evaluation	laser diffraction
for production	closed loop control	* data reduction................... * optimization strategy ← * process modeling ← * information crosslink ←	soft- and hardware

Figure 3: Functions, partial steps, instruments for on-line particle size analysis

The concentration on, or limitation to individual partial aspects, such as the rapid measurement and evaluation, implies neglect of the problem-specific process-engineering integration. This inevitably results in the lack of sufficiently accurate samples for the highly exact, rapid measurement by laser diffraction; as a consequence, the derivation of process control and closed-loop control parameters would be only random, or at best predominantly but only conditionally successful.

The five partial steps which follow the measurement are associated with the individual target ranges.

Real-time quality control has already been realized if the optimization strategy is included as a simple comparative method in the operating cycle.

If, in addition, production line modelling is included, the decisive step has been taken for production control. The production line modelling itself is that section of the overall problem field which is still the least developed. At present, therefore, production line modelling may simply mean that the plant foreman, who is thoroughly familiar with the production facility, knows what he must do after what results. The difference between this approach and true real-time quality control is thus the fact that the results must be available directly to the shop foreman in the plant, rather than in the laboratory.

In this case, a person has closed the information circuit, whereas the inclusion of the last step, designated here as information networking, results in feed-back to the plant facilities themselves and effective control of the basic operation. For automation with reproducible response with time, this approach is certainly the most attractive means of applying on-line particle size analysis.

3 Sampling and sample splitting

The primary task in realizing on-line analysis of particle size distributions is the rapid availability of an appropriate analytical sample from the production process for the measuring instrument to be employed.

The suitability imposes an extensive demand with respect to both the supply of the sample volume and the sample preparation. Requirements must thereby be satisfied in the fields of representative sampling, sample splitting, and fast, reproducible dispersion.

For performing an on-line analysis, it is already evident that the connection must, of course, be established with the product in the process during sampling and sample splitting. However, further decisive intermediate steps are required for a rapid measurement.

In a simplified manner, it may be stated that the measuring task is adapted to the process with respect to the withdrawal interface and volume flow during sampling and sample splitting. Subsequently, however, the measuring principle requires appropriate supplementary adaptation measures for the further preparation of the carefully taken and prepared process samples.

From this extended requirement, it is obvious that a new category of instruments must be developed for supplementary modularization, that is, turn-key availability of the on-line hardware. We designate these instruments as "sample couplers", because they must ensure the process-specific connection with the production plant and the proper preparation of the withdrawn samples for analysis by the measuring instrument downstream.

production ●

A

sample
coupler ●

on-line – hardware B

analysis
system ●

C
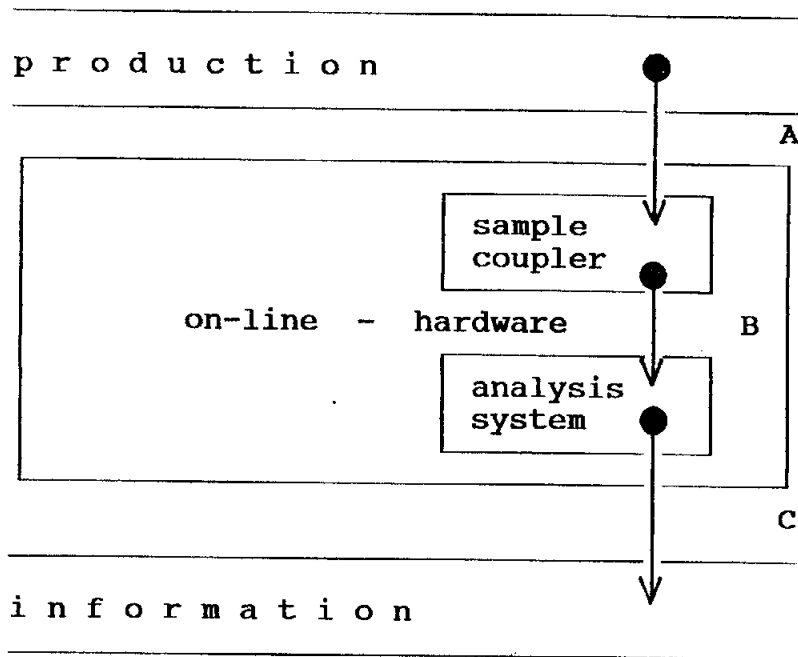
information

Figure 4: on-line-hardware:
information from production

A) Process-specific connection with the production
facility
B) Proper preparation of the process sample for
analysis by the analytical system
C) Transfer of the analytical result to the data
processing system in a form suitable for proces-
sing

With the inclusion of sample couplers, the instrumentation for
procuring reliable information from production is completed. In
each case, the configuration of sample couplers must be appropria-
tely designed for the application in question, whereas the analy-
tical system, comprising a laser diffraction sensor and a product-
specific dispersing device, for example, can be employed as stan-
dard equipment.

4   Sample couplers

4.1 Developmental concept

The configurational versions of sample couplers can be systematically delimited. For understanding the concept, a brief recapitulation on available instrumentation for the analysis of particle size distributions by laser diffraction is provided.

Instruments for off- and on-line analysis

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* Laser diffraction
  sensors   : for the analysis of particle size
                         distributions

                    HELOS-system: KA-series : 0.1 -   875μm
                                   LA-series : 0.1 - 1750μm
                                   VARIO   : 0.5 - 2625μm

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* Dispersing systems   : for the adaptation of the sensors to
                          powders, suspensions, emulsions, sprays

                    dry: RODOS, GRADIS
                    wet: SAFIR, ISIS

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* Sample couplers   : for coupling the analytical systems with
                          production

                    dry: ROPRON, ISOS
                    wet: SAFIR, ISIS

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* Analytical software   : for further processing of psd results
                          and relating with other measuring
                          methods

                    QX, REMO & PARA, TRIMO

Figure 5:   Instrumentation for the analysis of particle size
               distributions

Laser diffraction sensors for the analysis of particle size distributions have been available since the early 1970's. The performance has been recognized during the interim. Our concept is based on the conclusion that the analytical systems must be adapted to match the products, rather than *vice-versa*. The adaptation of the sensors to handle dry powders, suspensions, emulsions, sprays, etc. has been accomplished systematically by means of dispersing systems.

dispersing systems		
principle:		
dispersing	in measuring zone of sensor	
medium	moved	at rest
dry	**RODOS**	**GRADIS**
size ranges	$1 < x < 500\ \mu m$	$100 < x < 1500\ \mu m$
quantity	5.0 - 100 g	5.0 - 100 g
wet	**SUCELL**	**CUVETTE**
size ranges	$0.1 < x < 250\ \mu m$	$0.1 < x < (1000\ \mu m)$
quantity	0.05 - 2.0 g	0.001 - 0.5 g

Figure 6: Principle of the dispersing systems

The function of the dispersing systems is the correct preparation of the products to be analyzed for the measurement, that is, the nondestructive dispersion of the particles. Thus, they interact with the laser beam in the measuring cross section as individual particles and at the most favourable overall concentration.

Products manufactured in the dry state are thereby analyzed in the dry state, while wet products are analyzed in suspension. Thus, conclusive information on the primary size distribution, which is also relevant with respect to the production process, is obtained with the highest probability.

In the measuring cross section of the sensor, the particles in the dispersing medium can move or be at rest in relation to the laser beam. This difference is decisive for the energy transfer; hence, dispersion can proceed in a manner which protects the product, on the one hand, and which is extremely aggressive, on the other hand. Furthermore, an appreciable influence is associated with the required sample quantities and the applicable measuring ranges.

With the use of the four dispersing systems, RODOS and GRADIS (dry), SUCELL and CUVETTE (wet), an adaptation of the laser diffraction sensors to match highly diversified products is feasible largely with standard instruments. The dispersing systmes, which can also be operated automatically in the open-loop mode with a continuous supply of new material for analysis are also well suited for application to on-line analysis. This has been accomplished with all devices with the exception of CUVETTE.

The analytical systems with this configuration of laser sensor and dispersing system have thus been conceptually prepared for coupling with production in combination with the sample couplers in the next step.

sample couplers

principle:			
unit operation		sampling transport medium	
	without		with
dry	**ROPRON**		**ISOS**
operation range	$0 < x < 5000$ µm		$0 < x < 500$ µm
quantity	50 g - 10 kg		5 g - 1000 g
wet	**SAFIR**		**ISIS**
operation range	$0 < x < 500$ µm		$0 < x < 250$ µm
quantity	0.5 g - 500 g		0.05 g - 20 g

Figure 7: Principle of sample couplers

For alterations in the tasks involved, the corresponding developmental principle applies to the sample couplers as far as basic operations subject to dry or wet analysis are concerned.

A new criterion for decision on sampling is the case distinction at the withdrawal interfaces. As dictated by the problem concerned, the sample may have to be taken either with or without transport or dispersive medium. Solution versions are currently available for three of the four resulting cases of application.

4.2 Apparatus design versions

Hence, if an analytical instrument is again ready for measurement, for example, every ten minutes, a check must be performed to ascertain whether the withdrawal of a random sample every ten minutes is sufficient.

It is assumed here that the sample size corresponds exactly to the volume currently required by the analytical system, and that the sequence of events in the production process between the instants of sampling remains unknown. Regardless of this demand, the sampling must be representative with respect to the sampling cross section.

Sampling devices, such as pipettes, sample scoops, sample thieves, immersion collectors, sampling valves, stationary suction probes, sample skimmers, pendular or impact samplers, half-open, slotted extraction tubes, or screw conveyors, attain only a small portion of the cross sections under investigation in the production streams in each case. Consequently, they are unsuited or only conditionally suited for the complicated tasks of on-line operation.

In the case of belt transfer, sampling devices which move intermittently to-and-fro beneath the belt transfer site as so-called slotted samplers are known. These devices provide an applicable sampling solution to this planar, linear sampling problem, if the splitting ratio does not exceed 1:100.

An on-line sampler should be installed in a transport cross section of the production process. It must thereby be ensured that all components of surface area are taken into account during the sampling process, and that a sufficiently large subsample is taken for representative reduction in a sample splitter situated downstream, to yield the sample quantity necessary for analysis.

Conventional partial stream sampling, for example, vacuum extraction through probes, thereby complies with the pertinent VDI guideline, 2066, and scans the cross section punctually by traversal in conformance with a specified grid pattern. This method provides neither high local resolution nor a conclusive integration effect with reference to the total cross section,

since the weighting of the individual sampling points depends on hypothetical assumptions about the quality of quasistationary on coming flow and homogeneity of distribution of the dispersed phase in the cross section.

On the basis of these considerations, a new sampling and sample splitting technique has been developed with appropriate adaptation to the sampling problem with respect to way and time. Thus, the device for withdrawing the partial stream from the main stream is provided with an orifice cross section whose external limits form a circular sector with the aperture angle α; this sector slowly rotates about the sector vertex situated on the pipe axis of the main stream. The speed of rotation should not exceed values for which no reactions interfere with the production stream.

The sampling ratio of the partial stream to the main stream achieved is $\alpha/360$. The radius of the circular sector is at least equal to or greater than the pipe radius of the main stream. All components of surface area are completely spanned once within one revolution. A complete revolution corresponds to the integration over the entire cross section of the main stream. The rotational speed should never be synchronous with possible fluctuation limits of the main stream. The reliability with which the production stream is appraised increases with the number of integration cycles from which the entire subsample is formed summarily.

Since designing of the sampling orifice with sector aperture angles, α, less than 3° is not advisable because of more pronounced edge effects at small angles, the mass flow rate for sampling is at least about 1 per cent of the mass flow rate for the main stream.

For orientation it can be assumed that between 1 and 0.001 per cent of the mass flow rate of the main stream is required for on-line analysis. As just explained, the sampling device can thereby perform the splitting step in the per cent range,

$$\dot{m}_T = \frac{\alpha}{360°}\,\dot{m}$$

$$\dot{m}_A = \frac{\alpha\,\beta}{(360°)^2}\,\dot{m}$$
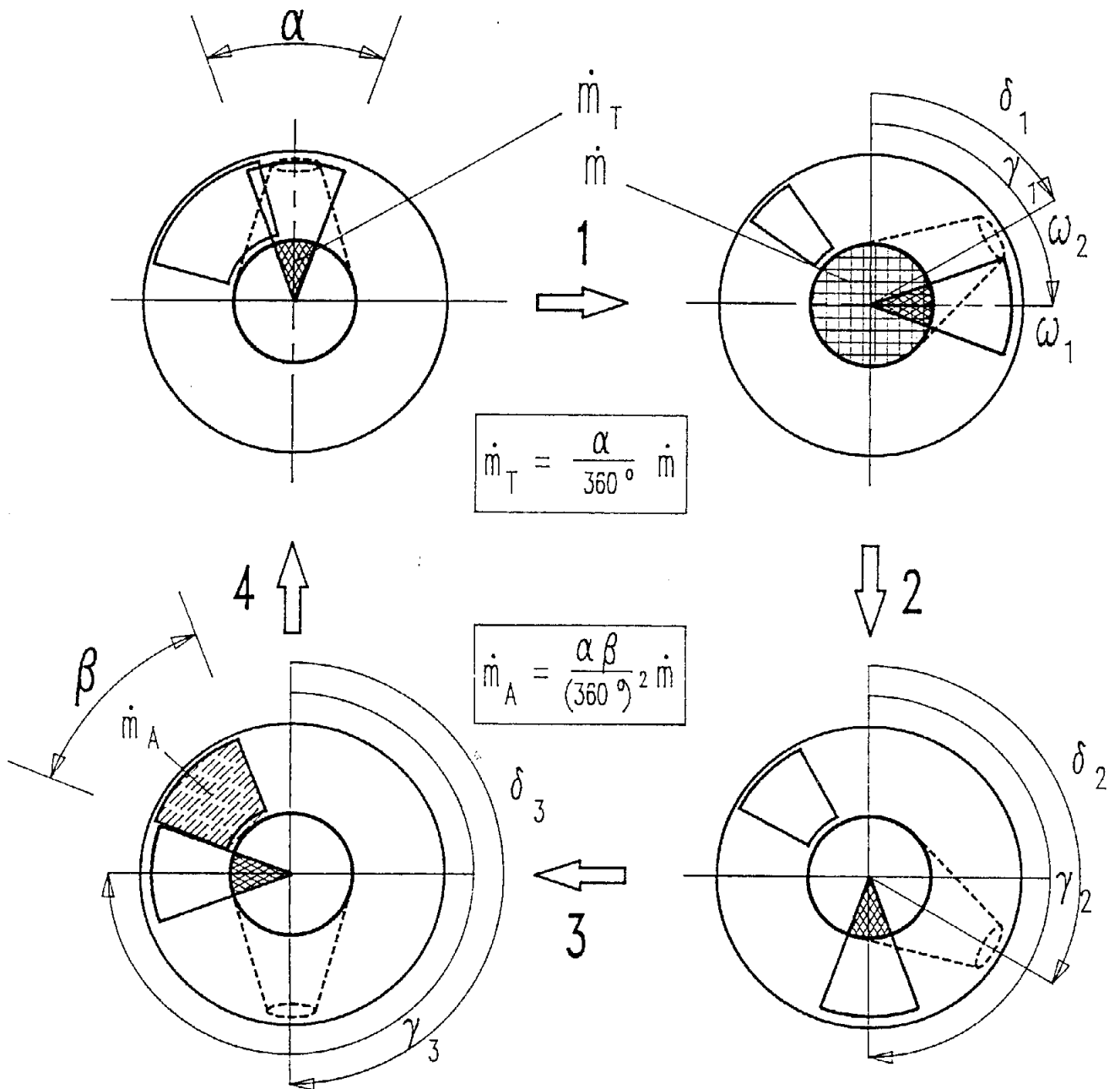
Figure 8: Phase sequence of a sampling integration from circular cross sections with two-stage sample splitting

α: Aperture angle of the sampling orifice (sampling and first splitting step)

β: Adjustable outlet angle of the transfer device (second splitting to sample for analysis)

Γ-δ: Dynamic angle between orifice and distributor tube

while the sample splitting device situated downstream must perform the remaining reduction representatively by an additional two to three orders of magnitude by means of an appropriate design.

This condition is realized in such a way that the continuous partial stream withdrawn through the aperture of the circular sector orifice is subdivided into a sequence of partial stream quantities, which finally yield the sample for analysis by means of a selected combination. By virtue of the extensive splitting into a multitude of individual samples and the systematic execution of the random sample collection, only very small systematic errors can be expected.

In figure 8, the phase sequence is illustrated for a sampling integration with two-stage sample splitting.

The apparatus for the new method is available in two design versions. With the first version, bulk powders are withdrawn from vertical chute arrangements. The second version involves withdrawal of dispersed products contained in fluid transport media. In this case, an equal velocity of the (isokinetic) vacuum extraction of the fluid stream must, in addition, be ensured during withdrawal of the partial stream, for an otherwise identical sequence of partial steps.

4.2.1 Rotating sampler and in-line sample splitter, ROPRON

The simplest case in which the sampling operation is performed as correctly as possible is probably that where particles separated from the flow medium are falling freely on the way to the next process step, for example, through a pipe.

With due consideration of the principles and specifications already developed, the rotating sampler and in-line sample splitter, ROPRON, has been designed for installation between two flanges of a pipeline with a specified clearance.
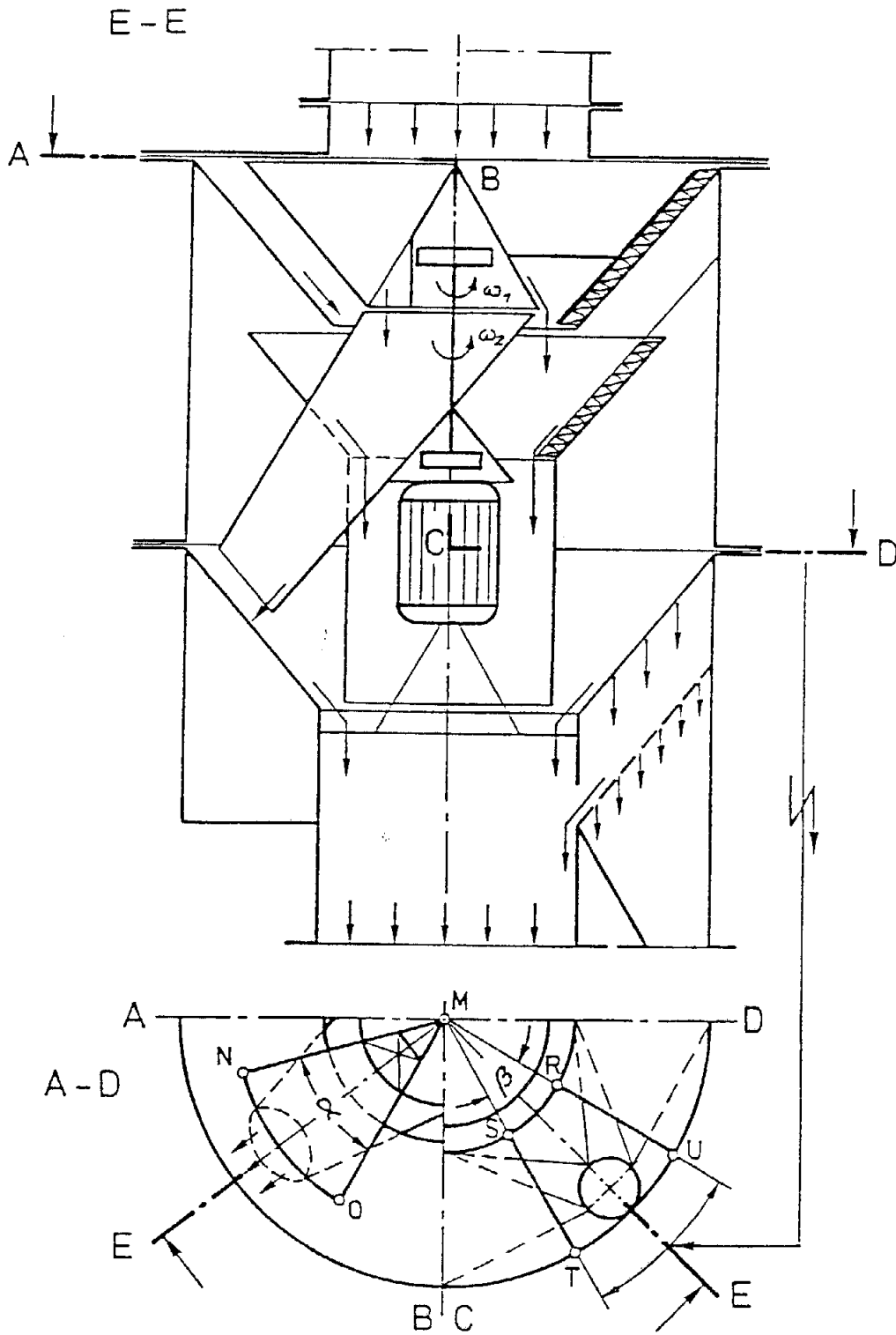
Figure 9: Sectional view for the installation and mounting of ROPRON

An adapter is provided between the upper pipe section upstream and the sampling orifice; by means of this adapter, the standard instrument with a diameter of 500 mm can be connected very simply with pipes of different diameter. The sector-shaped sampling orifice has been designed with a funnel shape in the direction of the gravitational force. The volume flow, $\dot{m}_H$, of the main stream falling in front of the sampling orifice is guided into the centre of fall, back and through the device, by an external, stationary collector cone.

The first subsample withdrawn, $\dot{m}_T$, is transferred to a distributor tube, which is situated under the central cone and can be driven. The drive unit for both components is located on the exterior wall of the housing and is not in contact with the product. By means of a reducing gear between the cone and distributor tube, the two components are driven at different angular velocities about the same axis of rotation.

At the outlet from the rotating distributor tube, the withdrawn subsample is transferred to the cone of the second in-line sample splitting stage. The mass flow rate for analysis, $\dot{m}_A$, is determined as a function of the adjustable outlet angle, ß, which can be set during the sampling operation.

The aperture angle for sampling, α, must be preset during designing in such a way that the variation,

$$0^{o} < ß < 90^{o}$$

allows compensation for the inevitable fluctuations in the mass flow rate of the main stream for ensuring a constant mass flow rate, $\dot{m}_A$, for analysis.

The performance of ROPRON is demonstrated by means of a selected example of on-line quality control realized during the production of polymers.
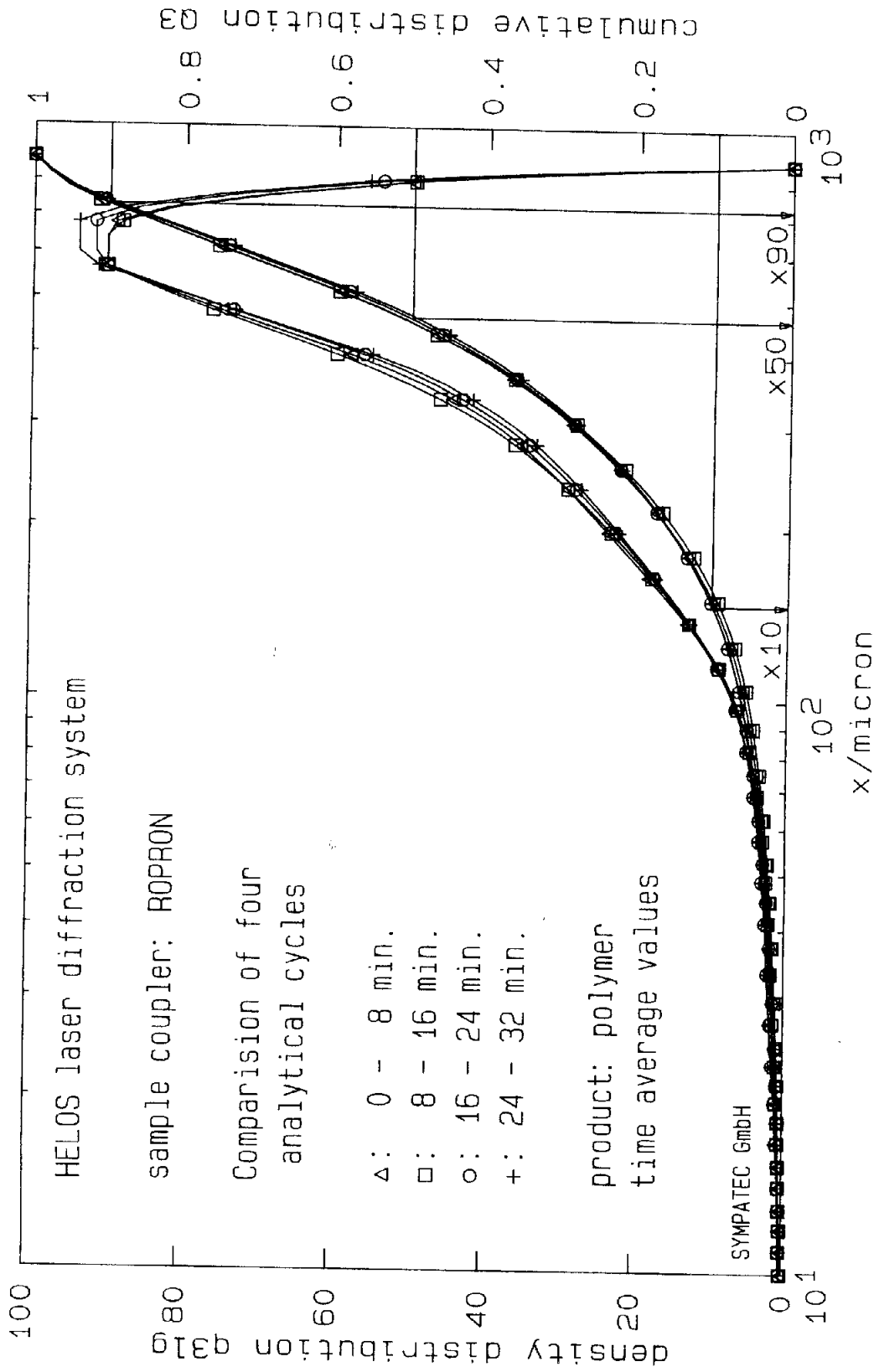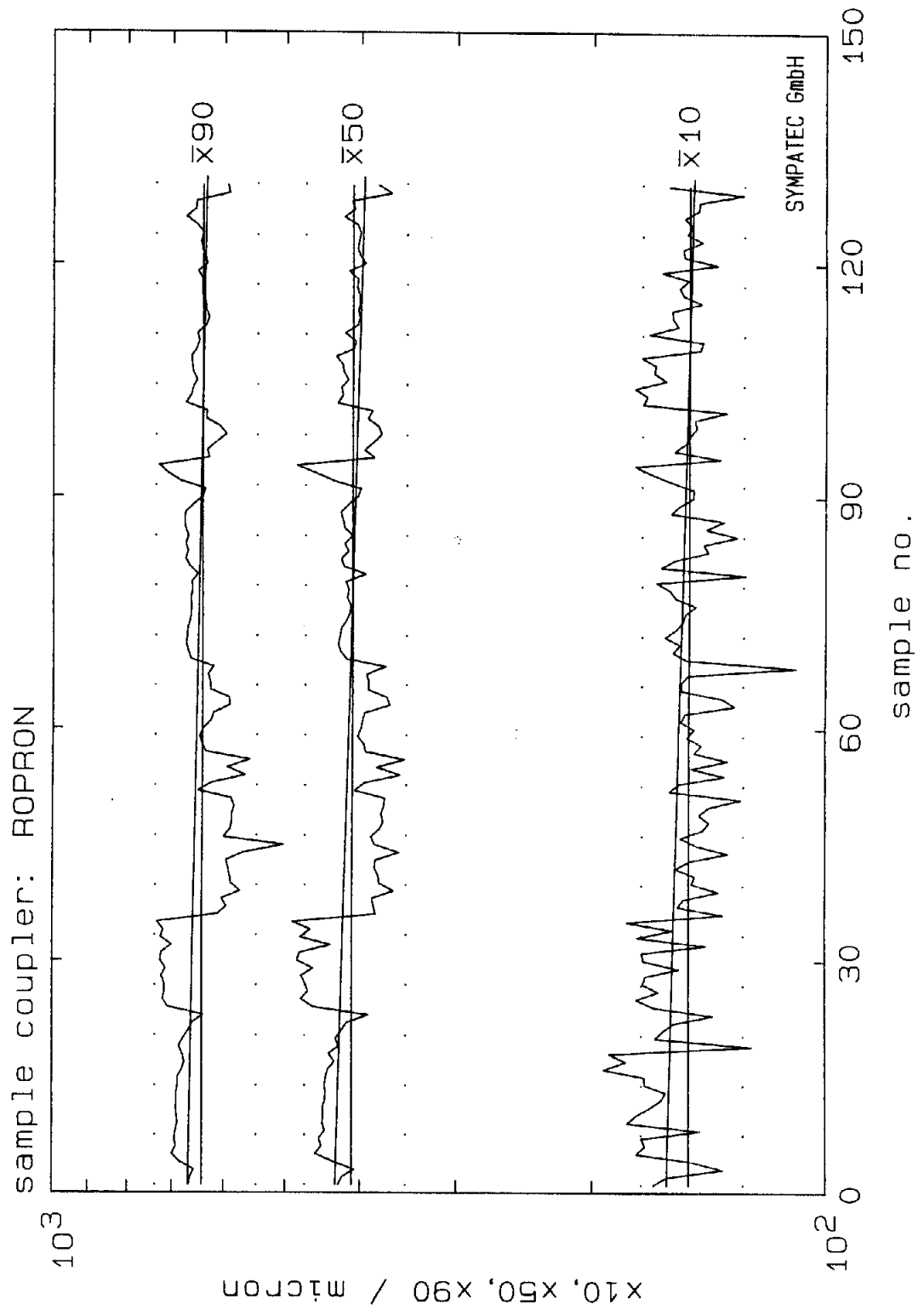
Figure 10: Comparison of four analytical cycles

Figure 11: Production control:
Parameter curves over eight shifts

In figure 10, cumulative and density distribution curves are plotted for four successive analytical cycles with a duration of eight minutes each. The selection of the analytical campaign takes into account a production status for which only extremely small fluctuations were expected from production, on the basis of experience. The results are average values for production over time and are based on complete measurements on the analytical samples, which were collected by ROPRON from the production pipeline over a period of eight minutes in this case. Practically no detectable influence is exerted by the sample coupler on the analytical result.

An impression from the production is provided in figure 11.

The parameters which were selected for documentation of the production sequence are indicated in figure 10. The parameters, x_{10}, x_{50}, and x_{90}, are plotted as functions of time for an analytical campaign over eight shifts with a total of 130 measurements.

The fluctuations of x_{50} and x_{90} exhibit an unambiguous synchronization, whereas the fine product components evidently behave independently. A remedial measure for this diagnosis with the use of on-line particle size analysis will undoubtedly not be feasible until additional information is obtained from production.

4.2.2 Isokinetic probe system, ISOS

A version which is more complicated, but in principle identical for sampling, is employed if the dispersed particles are contained in a fluid transport medium. During dry transport processes, such as pneumatic conveyance, the use of an isokinetic probe system as sample coupler is recommended for the purpose.

The rotating sampling head has the shape of a double cone for reasons of symmetrical flow perturbation in this case.
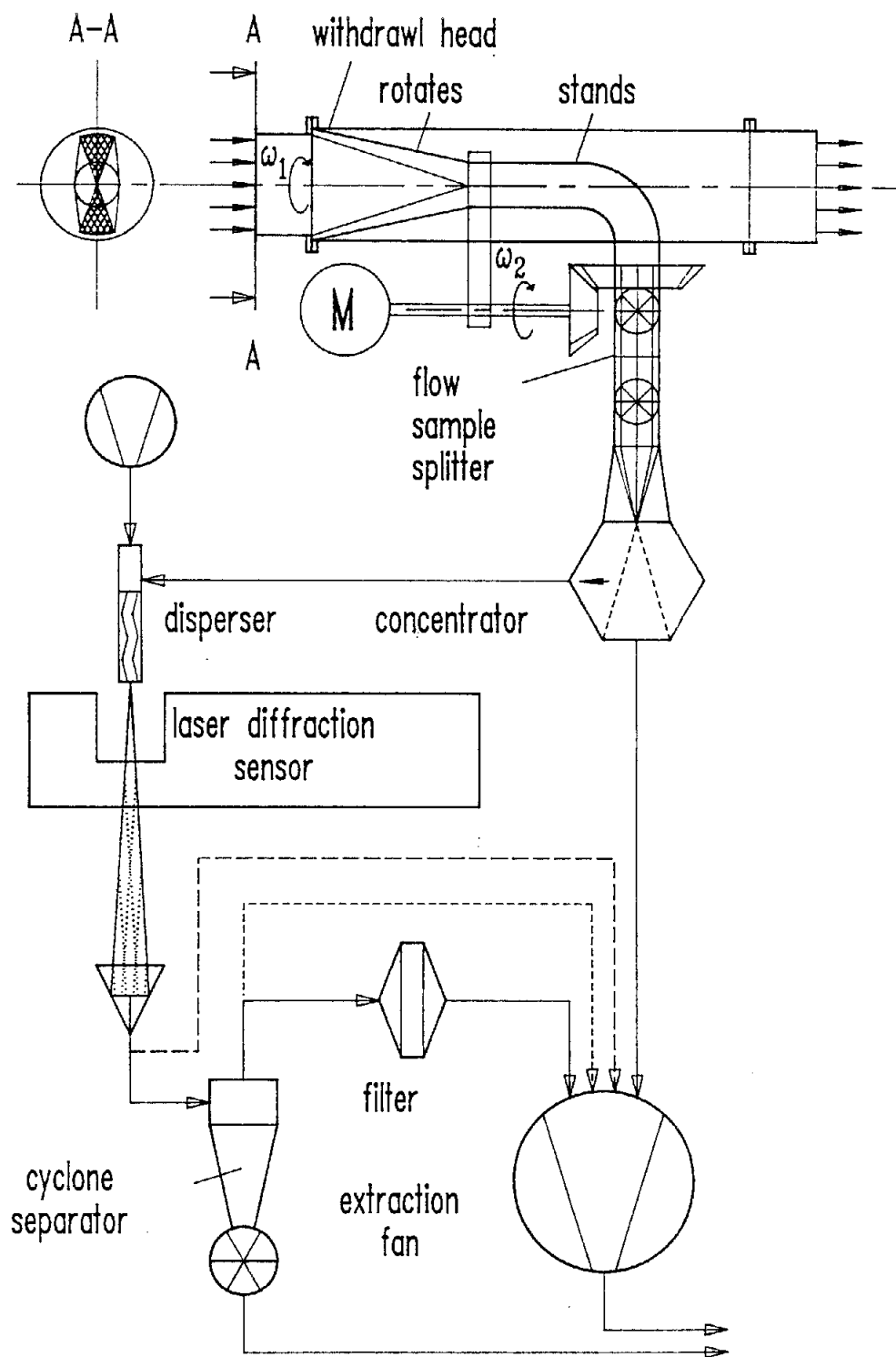
Figure 12: Isokinetic probe system, ISOS, as sample coupler for dry on-line analysis with laser diffraction

After the further coupling elements, a suction fan is installed downstream for regulating the isokinetic sampling conditions determined in the transport pipeline. After withdrawal and extraction of the subsample, the partial stream passes through an on-stream sample splitter and is subdivided in the concentrator. The partial stream designated for analysis is routed through the disperser and through the sensor in a free jet, and then recombined with the other partial stream before the suction fan after separation from the fluid phase, for example. As dictated by the process-technological boundary conditions, other versions are also plausible for the circuitry.

4.2.3 Sampling finger robot, SAFIR

SAFIR is a compact sample coupler for performing on-line analysis with suspensions.

With the use of SAFIR, samples are also taken from highly concentrated suspensions and prepared for the subsequent particle size analysis fully automatically under computer control.

For this purpose, the sample coupler is installed at the desired sampling site in the by-pass in the production process. The product stream is diverted, but not divided. The standardized by-pass routing of the undivided suspension stream ensures the withdrawal of a representative sample by means of an intermittent sampling finger. After withdrawal, the sample preparation and the analysis proceed fully automatically; after completion of a cycle, the instrument reverts to the stand-by status for sampling.

The sample coupler offers flexibility in selecting the measuring intervals by means of the cycle interval setting, which must be longer than five minutes. Matching to the suspension concentration in production is effected by means of the sampling frequency.
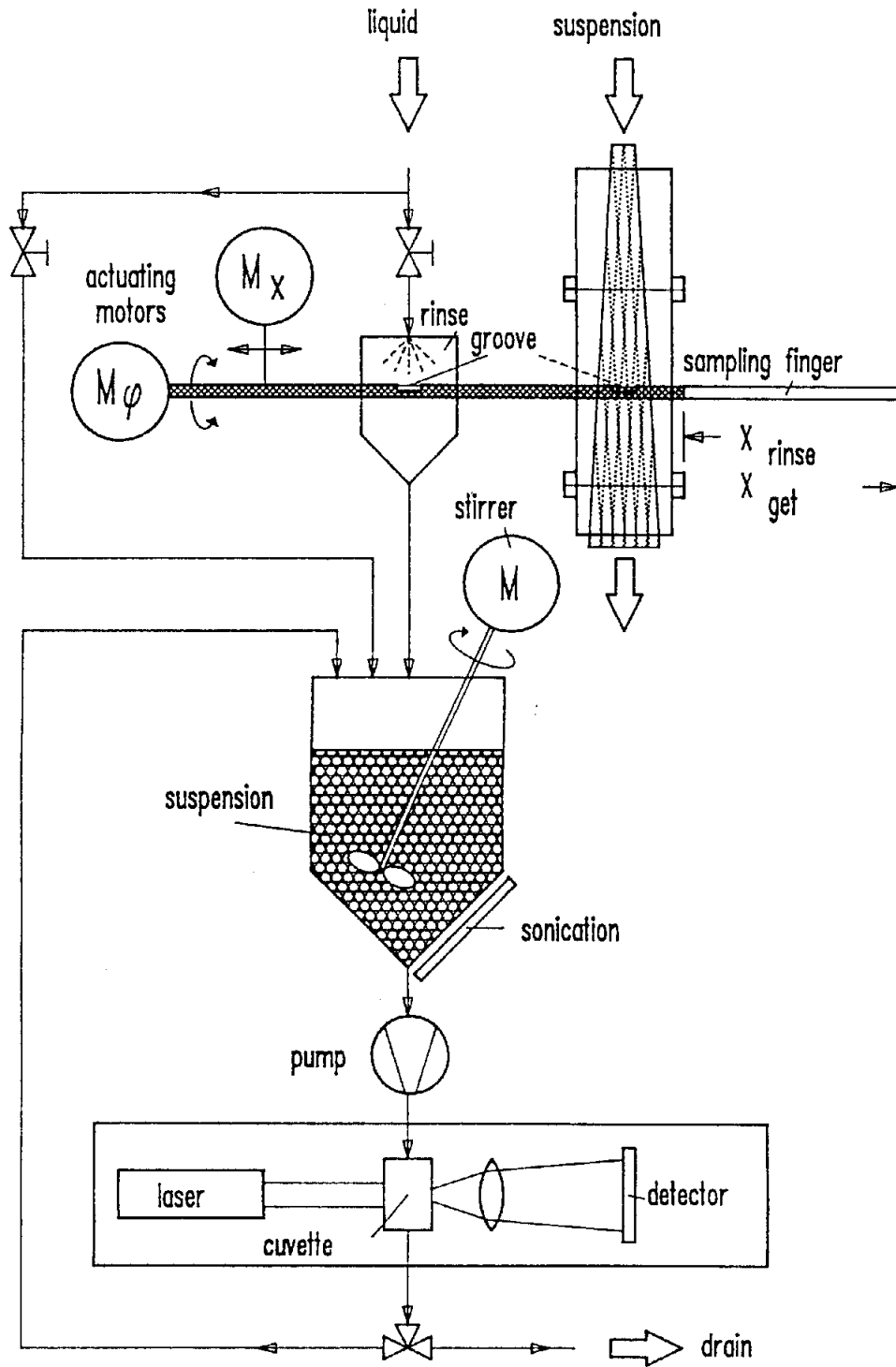
**Figure 13:** SAFIR/HELOS functional principle

The tasks for the user are reduced to the individual configuration of the product- and process-dependent sequence and are as a rule limited to the beginning and end of analytical campaigns and possibly control operations.

A flow diagramme illustrating the individual steps during an on-line suspension analysis with SAFIR and HELOS is presented in figure 14.

In the sample preparation section, the suspension vessel is first filled with clear liquid (for example, water). The zero measurement is then performed, as dictated by the analytical system. The system is now ready for sampling. For this purpose, the sampling finger is introduced axially into the suspension stream under investigation, and a representative sample is taken. After retraction of the sampler to its initial position, the sample is completely flushed into the suspension vessel and diluted to the required optical density. By means of a peristaltic pump, the suspension is supplied through the measuring cuvette to the analytical system and subsequently returned to the suspension vessel.

At the same time, it is dispersed and homogenized by means of ultrasonic waves and a stirrer. Prior to the measurement, the optical concentration is checked with the laser diffraction sensor. The suspension vessel is then filled stepwise with liquid until the optimal concentration has been established. If the optical concentration is not sufficiently high after the first withdrawal, the withdrawal operation is repeated until the desired optical concentration is exceeded.

The measurements are subsequently executed by the analytical system; the duration of the individual measurements is thereby variable, and their number can be selected. After evaluation of the measured results, they can be transferred, for example, to a host computer for further processing and appraisal.
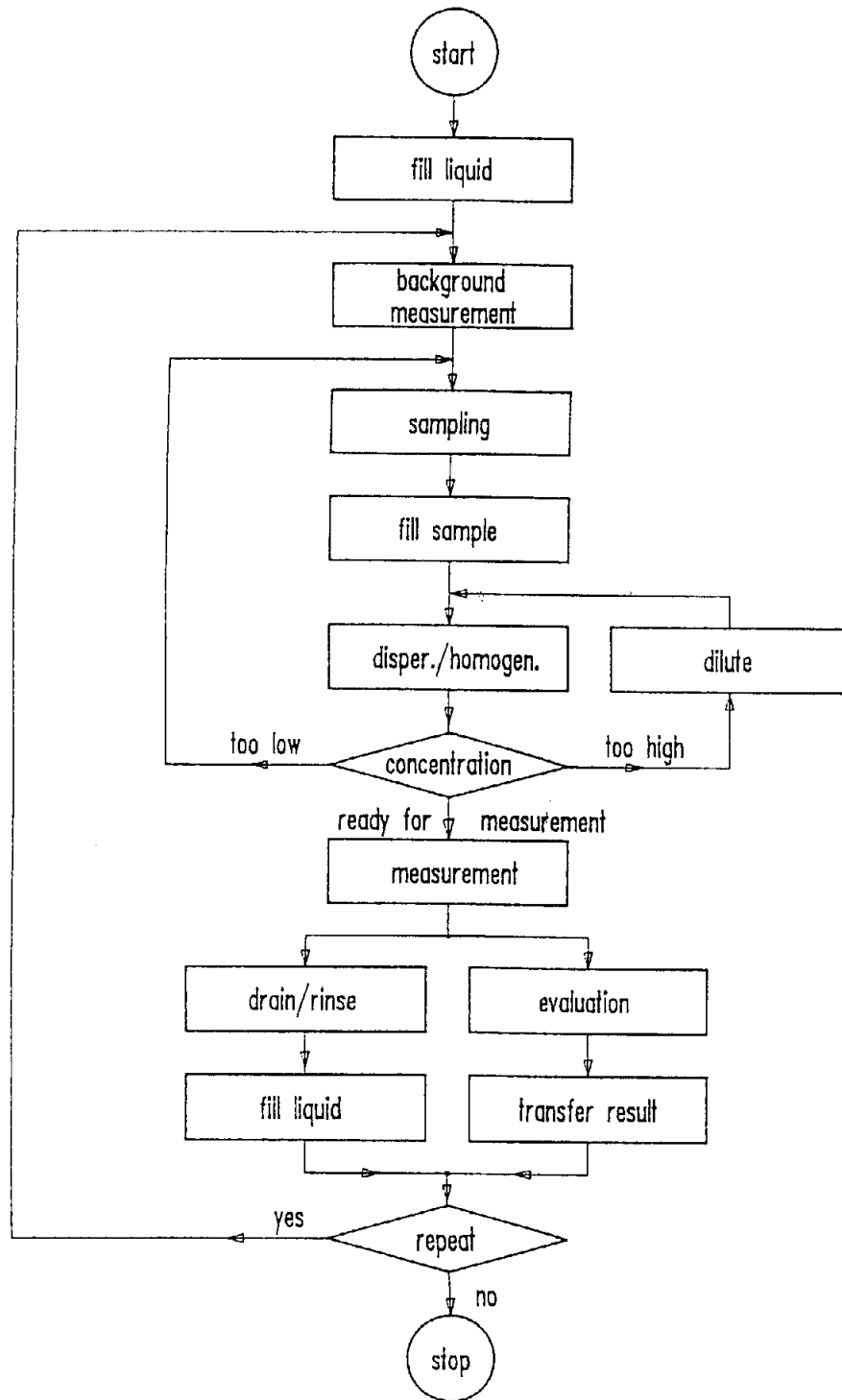
Figure 14: SAFIR: Substeps of an analytical cycle

At the end of a cycle, after conclusion of the final measurement, the system is emptied, purged, and refilled with liquid; these operations proceed in parallel with the evaluation. The system is now ready for executing the next sampling operation and initiating the following analytical cycle.

Finally, the performance capability of the sample coupler, SAFIR, is demonstrated with the use of an example from the analysis of highly concentrated polyamide.

In figure 15, the results of four multiple measurements are plotted for four consecutive samples. The samples were taken at random from the circulation system of a stirred batch vessel. The volume concentration exceeded 50 per cent, and homogeneous production conditions were simulated for the long-term experiment. The comparison indicates that practically no detectable influence is exerted by the sample coupler on the analytical result.

The experiment was designed as a sustained test with a duration of one week. The batch process was thereby continually stirred, but the internal product circulation system installed for sampling was restarted and restopped daily for a ten-hour analytical cycle.

In figure 16, the parameters, x_{10}, x_{50}, and x_{90}, are again plotted as functions of time for the one-week analytical campaign over six shifts of ten hours' duration each, with a total of 1300 measurements on about 500 samples.

The starting response on the first day is evident, and the x_{50} value exhibits a significant outlier. This outlier, as well as others for the x_{10} values are due exclusively to external interference in the system. These effects include, for example, opening and significant disturbance of the analytical instrument on the receiving side, or brief failure of the ultrasonic bath, as well as overproportional scatter in the concentration, if an
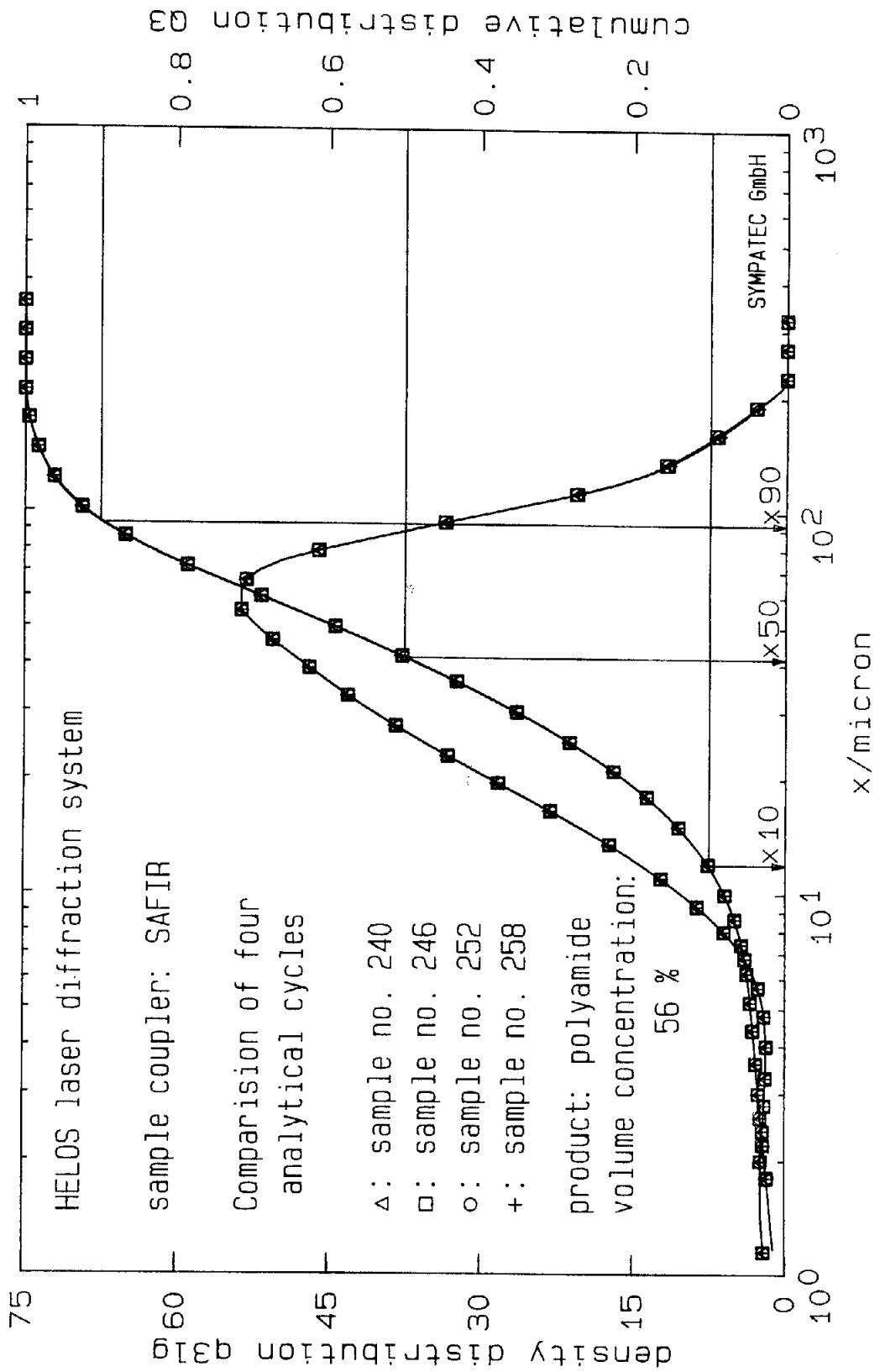
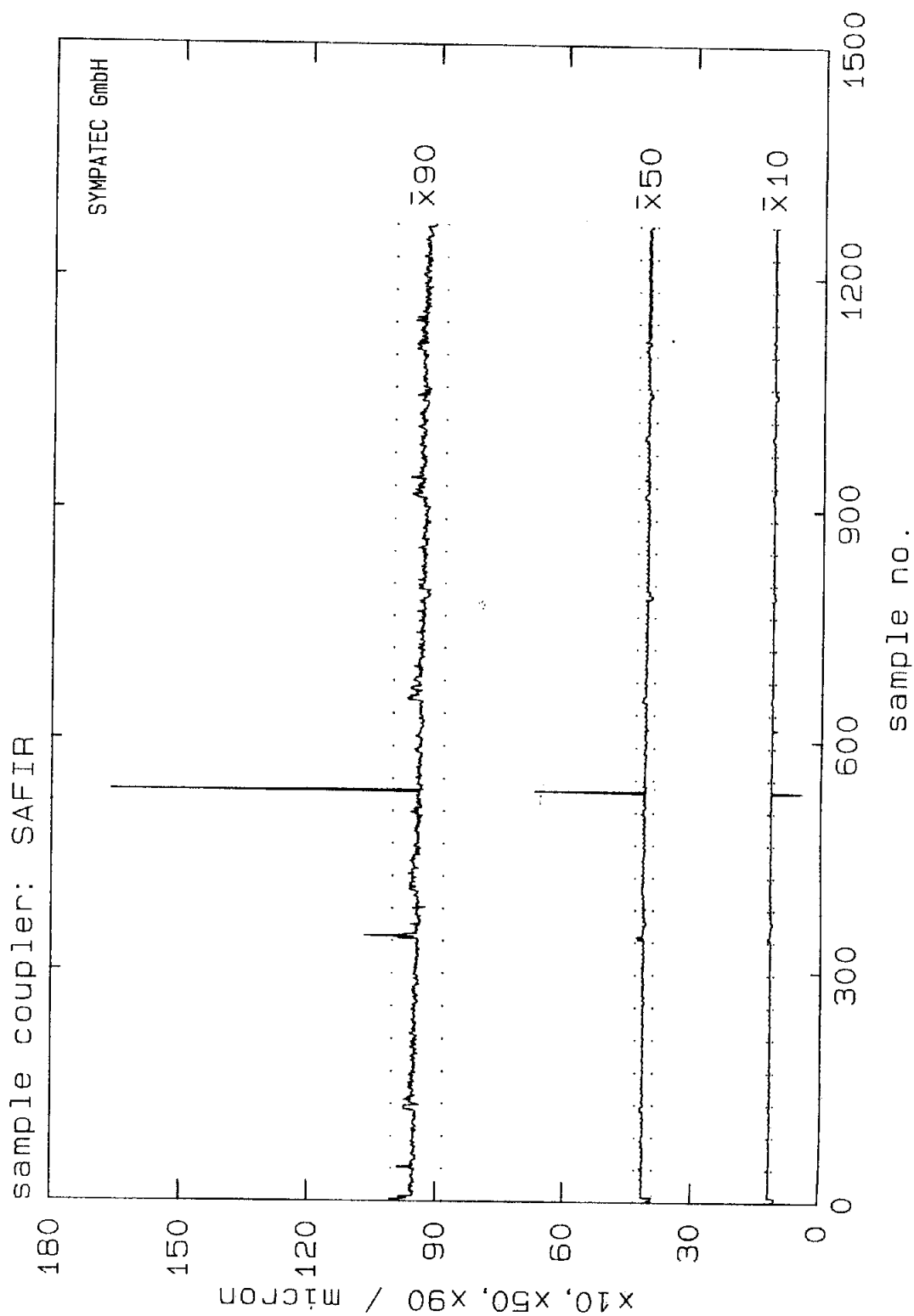**Figure 15:** Comparison of four analytical cycles

Figure 16: Response of parameters for a polyamide suspension over one week

excessive bandwidth had been defined or specified for the optically permissible operating ranges.

In the last figure, 17, an example is presented for the reproducibility of measurements supported by SAFIR. The scatter curves about the average Q_3 value are compared here. The two series of measurements shown were performed under different boundary conditions.

The first series (triangles) shows the result of six repetitive measurements on the same sample. The result indicates that the laser sensor always reproduces the particle size distribution decidedly better than a scatter less than ± 0.2 per cent in every size class, and preponderantly even better than $< \pm 0.1$ per cent.

The second series (squares) indicates the scatter for six different samples taken in succession in the same basic ensemble. The scatter curve is comparable; hence, an influence of the sampling operation is either undetectable or capable of isolation for an effect of mixing with the sensor and sample.

Although no ultimate experimental proof has been furnished, it can be concluded from the present results that SAFIR and HELOS provide a robust combination for on-line analysis, even for highly concentrated suspensions.
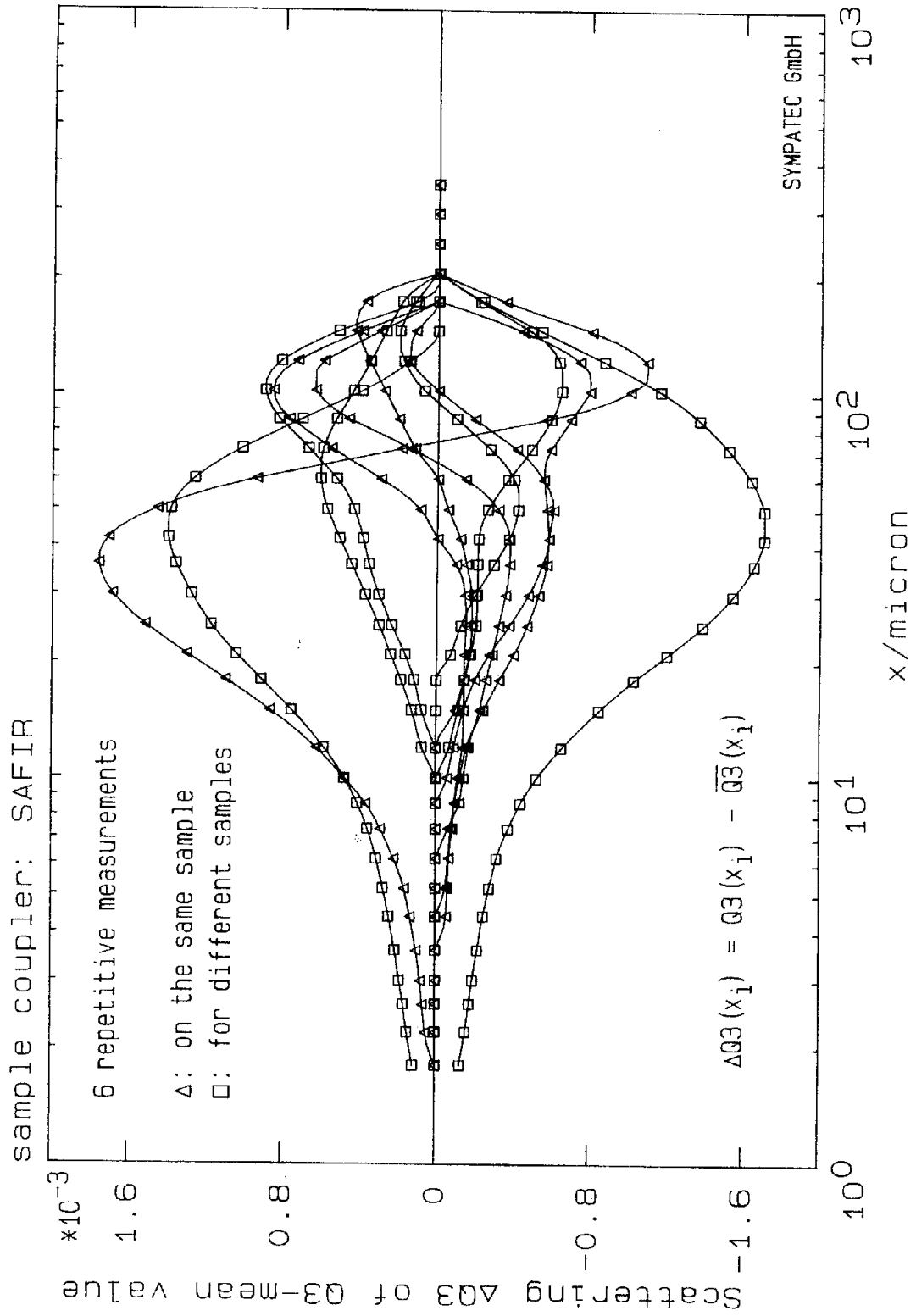
Figure 17: Reproducibility for sensor and sample coupler

5 Conclusions

The quality of the sample for analysis and the necessary use of the information then available will decisively influence the development for the application of on-line particle size analysis in the future.

A decisive requirement will be the ability of the interested potential user to envisage the realizability of the solution to his complicated tasks. In view of the wide variety of individual problems to be solved, this objective can be achieved only by means of systematic approaches. For this purpose, the sample couplers have been introduced as a new class of instruments on the basis of design considerations.

Their performance capability has been demonstrated on the basis of three examples presented. Coupling of the well-proven laser diffraction analysis with the sensor and dispersing unit with highly differing production processes can thus be accomplished by an extensively modular approach.

The procurement of information from production can thus be realized in a comparatively convenient manner. Appropriate tools are available for data processing. For the present, these must still be employed jointly by the user and supplier.

The incipient application is associated with profound systems analysis of the basic operations to be controlled; this will quickly reveal the progress which is attainable with on-line particle size analysis.