

## Laser-scattering – Basics

### The Milky Way - glowing gasses and dark dust

In the Twenties of the past century, the Swiss astronomer R.J. Tümler, discovered that far away star clusters appeared darker as based on their distance was to be expected. He figured that part of the starlight on its way to earth is lost. Few years later the American astronomer E.P. Hubble observed that the average number of visible galaxies in the direction of the centre of our milky way in the constellation Sagittarius, is clearly less, as when for example looking towards the direction of the Big Dipper. Besides brightly lit clouds of gas - predominantly consisting of hydrogen - in the so called galactic plane, also numerous dark areas are found, which almost completely block the light of objects situated behind these areas. The interstellar dust was discovered.

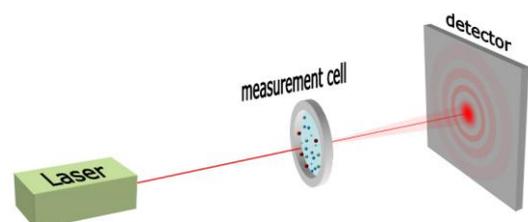


Interstellar dust consists mostly of very small particles - their typical diameter is between 0.1 and 1  $\mu\text{m}$  - which scatter and absorb the star light. Since these particles can't be examined with alternative procedures, like for example electron microscopy, was and still is the application of the light scattering theory for astronomers during the research of interstellar or interplanetary dust of great significance.

In a laboratory, quasi for earthly applications, the circumstances are simpler or one should even say the challenges are different ones. Here of course the optical composition of the entire system can be adjusted to the demands and most of the time more is known about the examined sample material as in case of particles from space. Starlight with its wide wave length spectrum can be replaced with monochromatic laser light and the chemical composition of the sample material is often very well known. Instead new difficulties occur, especially during the suitable preparation of the particle collective to be measured. But one issue after the other, let's start with the basic design of the suitable instrument for measuring the particle size distribution with the assistance of laser scattering.

### Basic design of a Laser Particle Sizer

Basically the design is always the same: A light beam, mostly supplied by a laser, shines through the sample to be measured and behind it, the intensity distribution caused by the scattering is picked up with a detector. Here already, it shall be mentioned, that the particle collective to be measured should be available sufficiently diluted and should not form clusters or even better said should not create agglomerates. Then the measured intensity distribution shows a system of numerous more or less concentric rings, which their spacing correlates with the particle size.



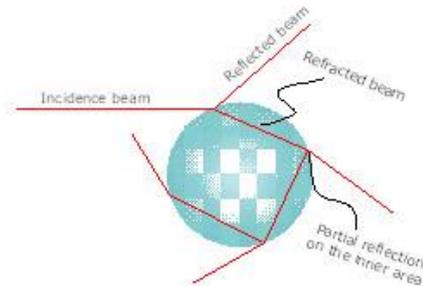
Large particles create close neighbouring rings, small particles create rings further apart. When now determining the distance of each ring, the particle size can be calculated from the results. Now before looking at the technical implementation of this simple principle, it makes sense to view the main features of the relevant physical processes.

**The physics: Scattering, Diffraction, Absorption, Extinction**

When illuminating a particle with light, different effects occur, which together lead to a reduction or extinction of the incident light. The extinction is basically the sum of **absorption** and scattering. Let’s initially view the absorption. Here part of the electromagnetic energy of the incidence light is absorbed by the particle and changed into another energy form, mostly in thermal energy. This energy is either through infrared radiance (thermal radiation) or through convection of the surrounding medium emitted, an effect which is without significance for dynamic laser scattering. The size of the absorption is for sufficiently large, non-transparent particles merely obtained from their geometric transverse section. “Sufficiently large” means in this context, their diameter is clearly above the wave length of the used light. With marginal particle sizes and with opaque particles, the circumstances are more complicated, the absorption coefficient of the material must be known in order to link the absorption and particle size. In the Mie-Theory, the absorption plays a major part. But more about that topic that later.

**Scattering**

Now let’s address scattering. Here, initially a distinction is drawn between basically two different forms of scattering: The inelastic scattering whereas the energy and therefore the wavelength of the light changes and the elastic scattering, where the wave length remains. For us, the latter is solely of interest, and the inelastic scattering shall not be discussed and with “**scattering**” it is always referred to the “elastic scattering”. Scattering classifies everything deflecting the incident light from its original direction. It can be divided in three parts, first: the reflection, second the refraction and third the diffraction.



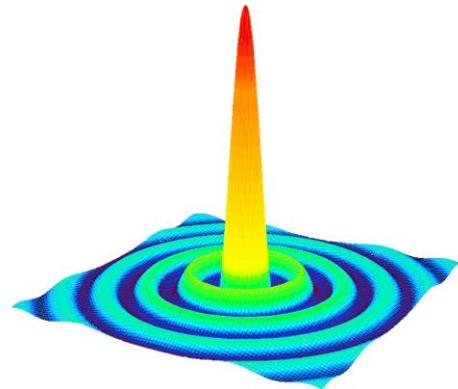
The **reflection** occurs mostly on the surface of the particles and along with the geometric optic is described according to the law “angle of incidence equals angle of reflection”. When viewing the angle dependent complete course of an intensity distribution caused by scattering, the reflexion on the surface of a sphere provides a very smooth share. Basically, reflection with transparent materials can also occur on inner boundary surface, which is especially important in regards with the refraction.

According to the refraction law of Snellius, during the refraction, the direction of a light beam changes directions during the transition between two materials with different indexes of refraction. For example, hits a light beam a drop of rain, so it is refracted towards the middle of the droplet, and in the further course, on the outer edge of the raindrop, it is continuously reflected back inside the raindrop again and again.

A part of the irradiation leaves with each reflexion the droplet. With this image for example, the creation of a rainbow can be explained, but also numerous structural details of particle intensity distributions are the observed on the particles during the laser scattering measurement.

**Diffraction**

In order to understand diffraction, one has to imagine the light beam as a wide wave front, which hits a particle and partially encircles it, similar to a water wave, hitting a pole or even a larger obstacle. Through the superimposition of various parts of the broken wave front (interference) behind the particle, the characteristic diffraction patters evolves, which its direct course is described with the **Fraunhofer-Theory** and is clearly defined by the diameter of the particles.



The illustration shown here here is the graphic depiction of the scattering amplitude of a sphere shaped particle which can be exactly described with the so called Bessel Function. Here the central diffraction maximum for only very small scattering angles is clearly recognizable, which show the highest intensity for the scattered light. Towards larger scattering angles - and therefore to larger distances of the detector centre of the corresponding measuring instrument – then follow alternatively dark and light rings, which their distance, like already mentioned above, directly co-relate with the particle diameter: The tighter the rings the larger the particles and vice versa.

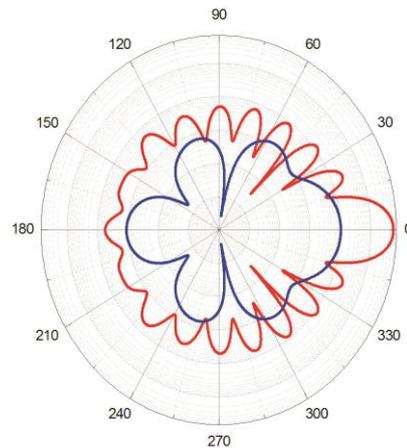
**Mie-Scattering**

Strictly speaking, the above mentioned only applies to sufficiently large enough particles, whereas „sufficiently large“ again means here just like with the absorption that their diameter is clearly above the wavelength of the used light. For particle diameters in the scale of the light wavelength, the already briefly mentioned above Mie theory is applied. The Mie theory is the complete solution of the Maxwell equations for the scattering of electromagnetic waves on spheric particles. Now what does this mean? Well, one can imagine that electromagnetic light wave couples onto the atoms and molecules in a particle and get these oscillating. These oscillations generate then in turn electromagnetic waves, light waves of the same wave length to be exact (like already mentioned, we are only discussing elastic scattering here), which can be radiated in all possible directions. The overlapping of the individual waves from the various areas of the particle then causes a formation of a characteristic intensity distribution, which different from the Fraunhofer-diffraction can be observed not only in the forward direction, but also in scattering angles larger than 90 degrees.

Based on the Maxwell equations, which describe the distribution of electromagnetic waves in general terms, examined Gustav Mie at the beginning of the 20<sup>th</sup> century, effects during the light scattering in colloidal metal solutions, especially the scattering of light on fine gold particles and developed for this as one of the first ones, a complete theory, which later was named after him.

### The Polar Diagram

With the aid of the polar diagram, the angle dependent intensity distribution of the scattered light can be clearly displayed. The diagram reads as follows: The numbers of the outer edge of the diagram represent the scattering angle. The distance between the centre of the diagram and the coloured distribution curve shows the intensity of the light scattered in that direction. Noted should be here, that the radial intensity axis is “logo rhythmically” the thin, grey, concentric circles are one factor ten apart each. Now comparing the blue with the red line, it is clearly seen, that for larger particles – red – the intensity for small scattering angles - 0° up to approximately 15° - is approximately 100 times stronger as in the reverse direction at close to 180°. For the blue curve, this difference is already clearly less. From this, it can be derived that for really small particle diameters, the intensity of the backwards scattered light is becoming important.



Scattering intensity of red laser light which is scattered once on gold particles with a diameter of 1.5 µm – red line – and once on gold particles with 0.5 µm diameter – blue line.

Analogous to the procedure during the Fraunhofer-scattering, now the intensity distribution can be again used for the calculation of the particle size. The difficulty with the intensity calculation according to Mie is though, that here different from the Fraunhofer-theory the knowledge of the material constants of the examined system are necessary. Needed precisely, are the real and imaginary share of the complex index of refraction (the index of refraction as well as the absorption co-efficient), for the sample material, as well as for the used dispersion medium and this respectively for each wave length of the used light – or with two different light wave lengths even all indices of both wave lengths. Despite extensive data bases, which offer at least the index of refraction of numerous materials, are for many sample systems like they occur in the daily lab life, the corresponding parameters not available and must initially be determined with elaborate analysis.

### The technology: Optical design

Now, after the important processes during the light scattering have been described at least some extent; the exact execution of the optical design of a laser particle sizer shall be explained. The above described basic alignment can be achieved with two different concepts. Besides the mentioned components (laser – measurement cell – detector) a converging lens must be integrated inside the optical path, which focuses the scattered light onto the detector.

Since the converging lens from the spatial distribution of the scattered light, at the location of the particle (in the measuring cell) generates its Fourier transform (on the detector), the converging lens is also regarded as the Fourier lens. The formation of this Fourier-lens makes the decisive difference between so called **conventional** design and the **reverse Fourier** design.

### Conventional Design

Let's start with the conventional design: Here a sufficiently broad, parallel laser beam is generated, in which then the measuring cell with the scattering particles is inserted. Between the measurement cell and the detector the Fourier lens is positioned. With this alignment the focal distance of the Fourier lens is determined, and a variation of it makes the exchange of the lens necessary. This must be adjusted with a high degree of accuracy, since especially with larger particles very small angles are measured and a tipping of the Fourier lens, directly has a very large influence on the result of the measurement. An additional disadvantage of this set up is the limited possibility, to measure large scattering angles. And these large scattering angles are – which we know – necessary for the measuring of really small particles.

### The Reverse Fourier Design

Therefore, approximately 25 years ago, as an alternative, the reverse Fourier design was introduced. The FRITSCH GmbH was the first company, which with the first model of the ANALYSETTE 22 type series, used a reverse Fourier optic for the particle size determination. The difference to the conventional design is that here the Fourier lens is situated in front of the measurement cell, so it is not traversed by a parallel, but instead by a convergent laser beam. The scattered light is therefore without additional optical elements focussed directly onto the detector. Despite this basically same set up of the individual components (laser – Fourier lens – measuring cell – detector) the designs of the reverse Fourier optic of the various models greatly differ in significant details.

With a very common approach small scattering angles – namely large particles – are covered with a main detector, whereas for the large scattering angles of the small particles, a lateral detector system is used. For very large scattering angles close to 180° (backward scattering), a second system must be integrated, which often consists of a blue light source – usually a LED – with a lens and a detector. The main disadvantage of this design is, that during each measurement the entire measuring range of the instrument will be covered (only the area of very small diameters can be specifically measured respectively omitted by switching on and off of the second light source). Why is this a disadvantage? The vast majority of the samples measured show a size distribution which only partially covers the entire measurement area of the used instrument. A large measurement area is therefore essentially interesting in order to analyse as many sample systems as possible. With the design of the reverse Fourier lens, in many or even in the most cases, an unnecessary measurement area is covered, which comes at a high cost: Reduced measuring accuracy, lesser particle size dissolution and reduced sensitivity. And the larger the entire measuring range of an instrument is the more drastic is this effect. How come?

In the most basic case, a sample consists of a strict mono disperse material, i.e. the intensity distribution shows a simple ring structure, whereas the particle size can be directly determined. The more exact that this intensity distribution can be measured, the more exact then is the obtainable result. This means, the accuracy of the measurement is directly dependent on the amount of the measuring channels, which are available for the current measuring interval. Now, during a measuring, if the maximum usable measuring area is always covered, the diffraction rings with sufficient intensity are - for example for a sample with large particles - always confined to the central area of the detector. The number of detector elements in this central area is naturally low in comparison, whereas the outer channels for such material are quasi unused.

To apply a comparative example: It is almost like measuring the voltage of a 1,5 V battery with a measuring instrument adjusted to a measurement range from 0 to 1000 V...

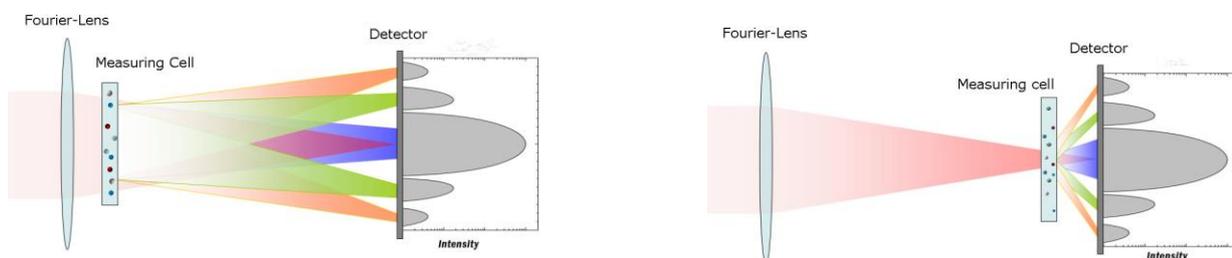
For the separation of two closely neighbouring particle sizes, results from an analogue argumentation, also the dependence of the dissolution of the effective amount of the utilized detector elements; In order to exactly measure fine differences in the intensity distribution, a large number of elements is absolutely necessary.

### The Fritsch-Patent

Now in order to avoid the disadvantage of an unnecessary large **measuring area**, the patented by FRITSCH principal of the movable measuring cell position is used with the ANALYSETTE 22 line. Here the position of the measuring cell between the Fourier lens and the detector is varied, whereas the covered measuring area is adjusted to the respective demands.

And it works like this: The left illustration shows the situation for large particles. With a measuring cell far away from the detector, the only slightly scattered light waves cover the entire detector and all channels are utilized during the measurement.

Is alternatively the measurement cell positioned close to detector (illustration on the left), so now the heavily scattered light waves of the small particles are measured with the full resolution of the detector. If necessary both cell positions are combined further, so that during a measurement, the entire possible measuring range of the instrument is covered, but now with double the amount of effective detector elements.



### The Math: Calculation of the particle size distribution

Like already mentioned in almost all applications relevant samples do not consist of particles with identical diameters. Rather a continuum of the particle size is found and therefore an overlapping of all corresponding scattered light distributions. Which the following illustration for example shows, a marginally structured measuring signal is obtained - compared with only one particle diameter - from which now the individual particle size diameters and their relative share from the sample shall be calculated.

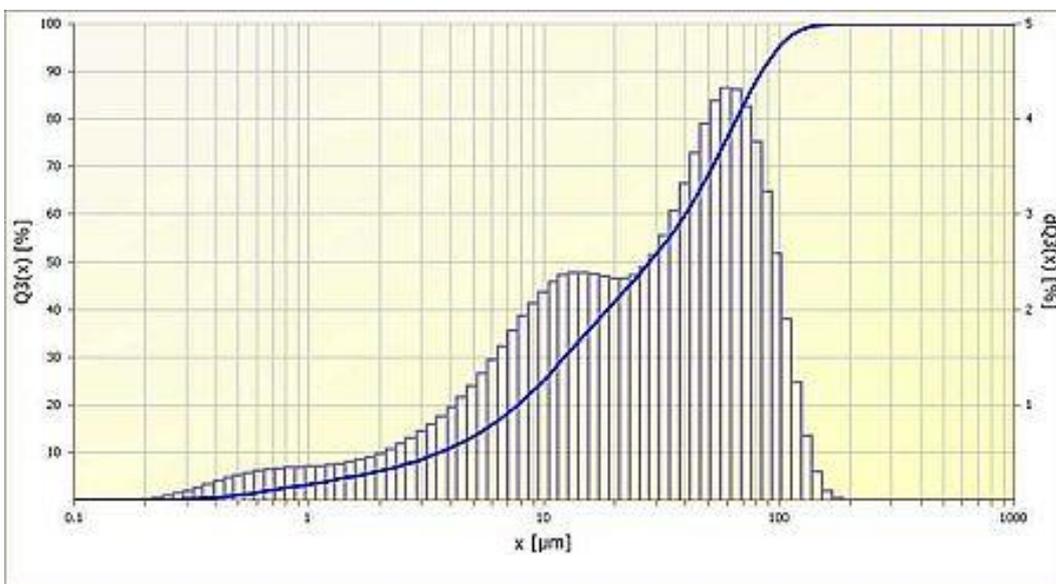
Initially the entire measuring range is divided into individual intervals and then a system of equations is created, which describes for each particle size interval the scattered light intensity for each of the available detector elements. The solution of this equation system is provided by the respective relative shares, i.e. the sought after particle size distribution. Incidentally this is the reason that the technology of the particle size determination has only been commercially available since the 80's. Prior to this, the processing power necessary to calculate the system of equations was not obtainable for a justifiable price.

Unfortunately, the equations systems to be calculated are instable. Instable means that the slightest deviations from the input values – the measuring data – could lead to drastic changes of the results. This behavior is not device-specific, but is rather based in the nature of the method. In order to handle these instabilities different mathematical methods exist, so that nevertheless, reproducible and exact results can be obtained. Here care is to be taken, that stabilizing of the equation systems is not too strong, since this results in an increased smoothing of the yield curve and possible details are absorbed.

**Results**

Laser scattering determines the relative volume distribution of the measured sample. This means, the result of a measuring via laser scattering tells you for example, how many percent of the complete sample volume are contained in particles smaller than a certain particle size. This reference number is usually called  $dQ3(x)$ .

Or you can view how many percent of the overall sample volume are contained in particles, which are present in a certain size interval. This reference number is then called  $dQ3(x)$ .



**Illustration:** Particle size distribution of fly ash measured with ANALYSETTE 22 . The continuous line is the so called sum curve  $Q3(x)$ , the bars represent the values of  $dQ3(x)$ .

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