



Bayerisches Landesamt für
Gesundheit und Lebensmittelsicherheit



LGL

Food safety and nanotechnology: Results
from LENA Project
Richard Winterhalter

Outline

- **Project LENA**
- **Nanoparticles in food and food supplements**
- **“Colloidal silver”**
- **Field-Flow-Fractionation**
- **Measurement of nanosilver in food supplements (“colloidal silver”)**
- **Summary**

Introduction

- **Application of nanotechnology and nanoparticles also in food production**
- **Possible exposition of consumers to nanoparticles?**
- **New challenge for food safety authorities**
- **Measurement methods for nanoparticles in food must be developed**

Project LENA (Food safety and nanotechnology)

1. Migration of nanoparticles from food packages into food

*Fraunhofer Institute for Process Engineering and Packaging (IVV),
Product Safety and Analytics, Freising. Roland Franz, Gerd Wolz, Diana Kemmer*

2. Analytics and characterisation of nanoparticles in food and food supplements

*Bavarian Health and Food Safety Authority, Institute for Occupational and Products Safety;
Environment related Health Protection (AP), Munich*

Goals

- Development of analytical methods for measurement of nanoparticles in food and food supplements (SiO₂, TiO₂, Ag)
- Appropriate sample preparation (homogenisation methods)
- What happens to nanoparticles during digestion?
Agglomeration/Deagglomeration

Nanoparticles in Food and Food Supplements

Natural Nanoparticles

- Micelles
- Liposomes
- Proteins
- Polysaccharides

Example: Milk

- Casein-micelle (20 – 300 nm)
- Fat micelles (1 – 2 μm)

Nanoparticles in Food and Food Supplements

Synthetic (engineered) Nanoparticles

- Food additives SiO₂ (E 551), TiO₂ (E 171)
- Organic nanoparticles (micelles, liposomes)
- Food supplements advertised with „nano“
- Colloidal silver as „natural antibiotic“

Nanoparticles in Food and Food Supplements

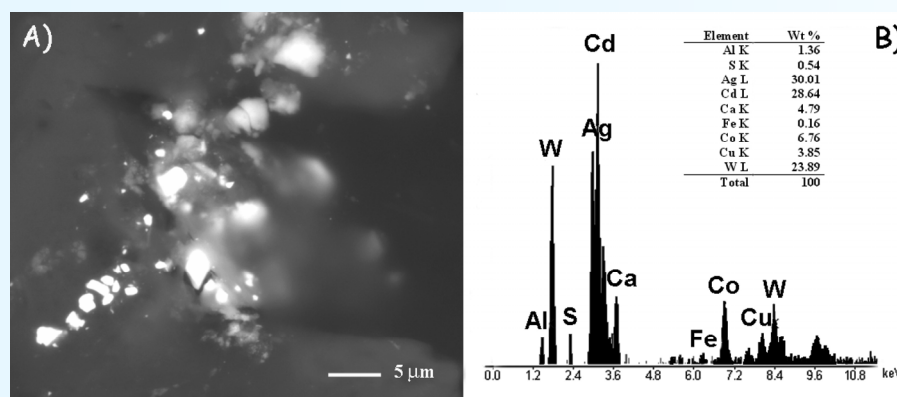
Migration from food contact materials

- nano-clay, nano-cellulose, TiN (approved explicitly as nano-TiN), SiO₂, TiO₂, MgO, ZnO, Ag
- used in polymers as gas barrier, for improved thermal and mechanical stability, for UV-protection, as antimicrobial agent
- faster processing of PET bottles (TiN)

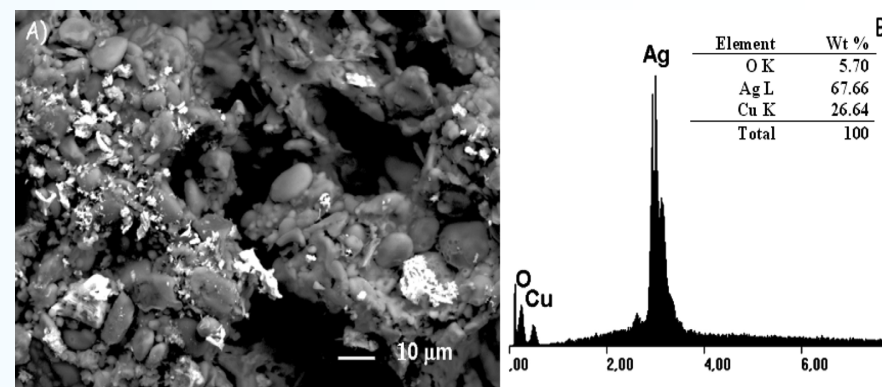
Nanoparticles in Food and Food Supplements

Metallic micro- and nanoparticles

- metallic debris from milling
- environmental contamination during crop cultivation
- 44% of the samples (n=135) contained micro-and nanoparticles



ESEM image (A) of debris in a sample of bread with its EDS spectrum



ESEM picture of home-made bread (A) with silver micro and nanodebris (B)

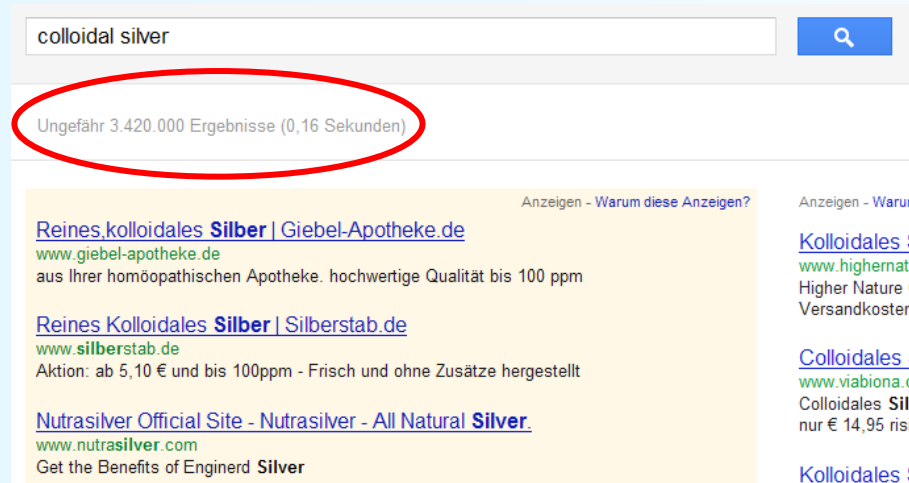
Source:

Investigation of the Presence of Inorganic Micro- and Nanosized Contaminants in Bread and Biscuits by Environmental Scanning Electron Microscopy. A.M. Gatti, D. Tossini, A. Gambarelli, S. Montanari, and F. Capitani, *Critical Reviews in Food Science and Nutrition*, 49:275–282 (2009)

Nanosilver in Food and Food Supplements

- **Approved food colour for sweets (silver coating) E 174**
silver shining effect, cannot be nano-Ag → brown colour
- **Migration from nano-Ag containing food contact materials**
- **Colloidal silver (“food supplement”)**

Colloidal Silver (nanosilver, mesosilver)



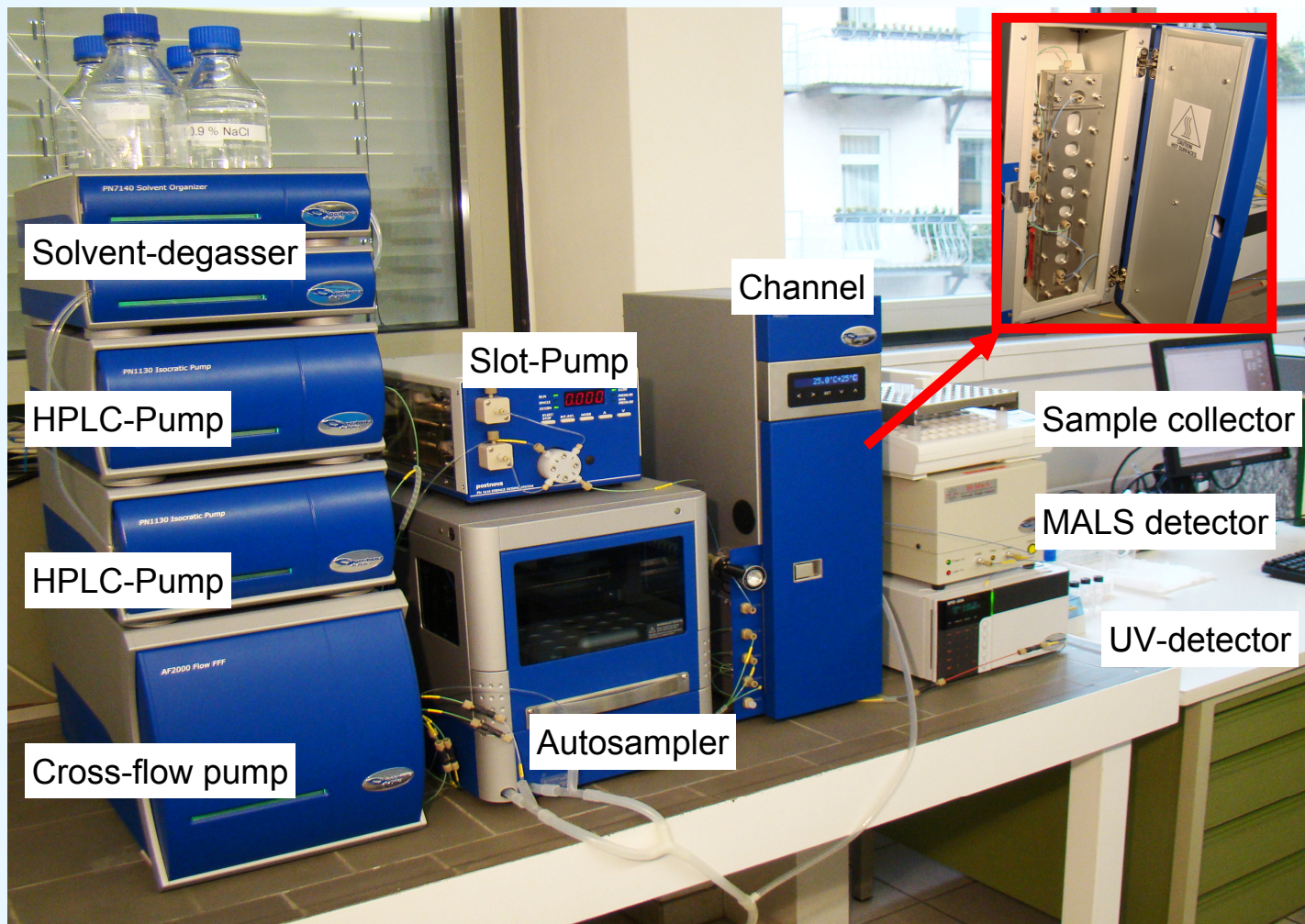
The screenshot shows a search engine interface with the search term 'colloidal silver' entered in the search bar. Below the search bar, the text 'Ungefähr 3.420.000 Ergebnisse (0,16 Sekunden)' is circled in red. The search results are displayed in a grid format, with three columns of results. The first column contains three results from 'Giebel-Apotheke.de', 'Silberstab.de', and 'Nutrasilver.com'. The second and third columns contain partial results from 'highernatur.com' and 'viabiona.com'.

“Health benefits” of Colloidal Silver

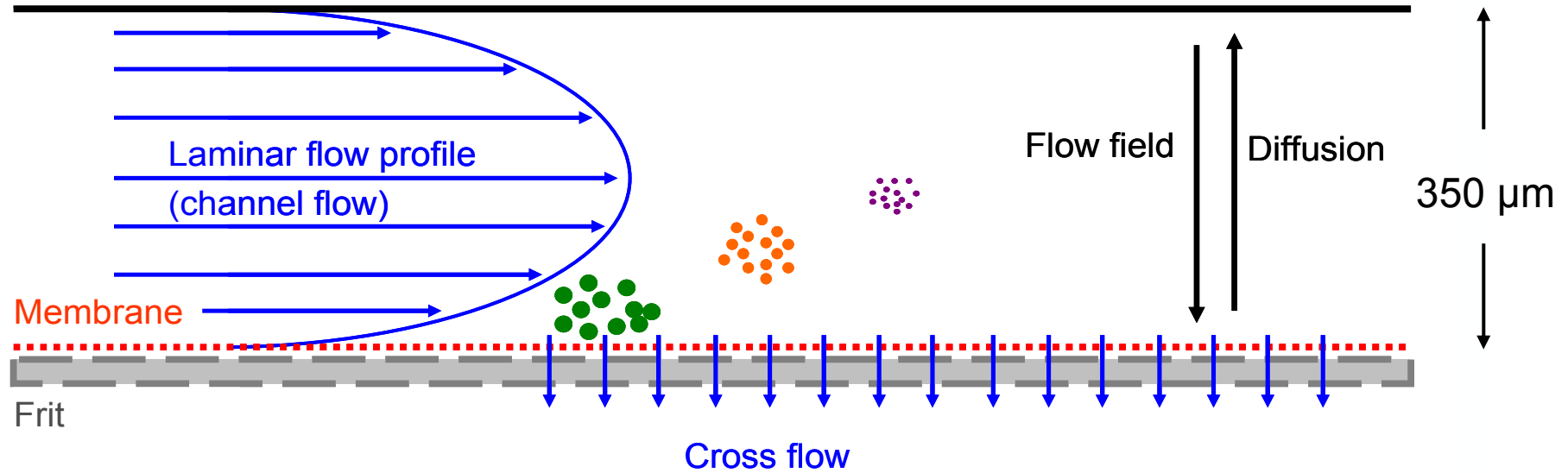
“nano silver as a dietary supplement:

- Natural antibacterial, antiviral, antifungal, & antimicrobial effects
- Strengthening of the body's immune system
- elimination of bad bacteria without harm to good bacteria**
- While most antibiotics are effective against about half-dozen disease causing organisms, silver is effective against over 650 organisms”

Asymmetric-Flow-Field-Flow-Fractionation (AF⁴)



Theory of AF⁴



$$t_r \approx d w^2 \frac{\dot{V}_x}{\dot{V}_{Ch}}$$

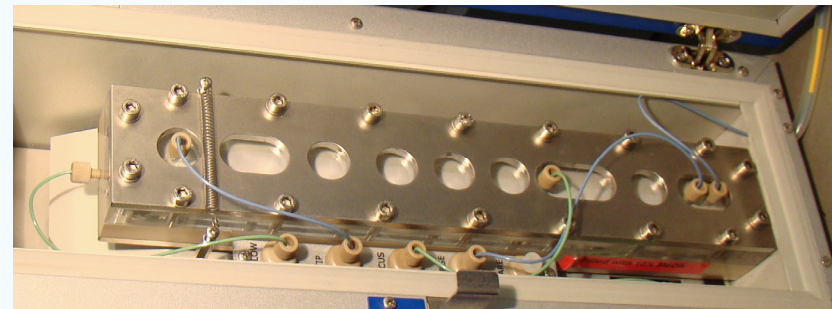
t_r : Retention Time

d : Particle Diameter

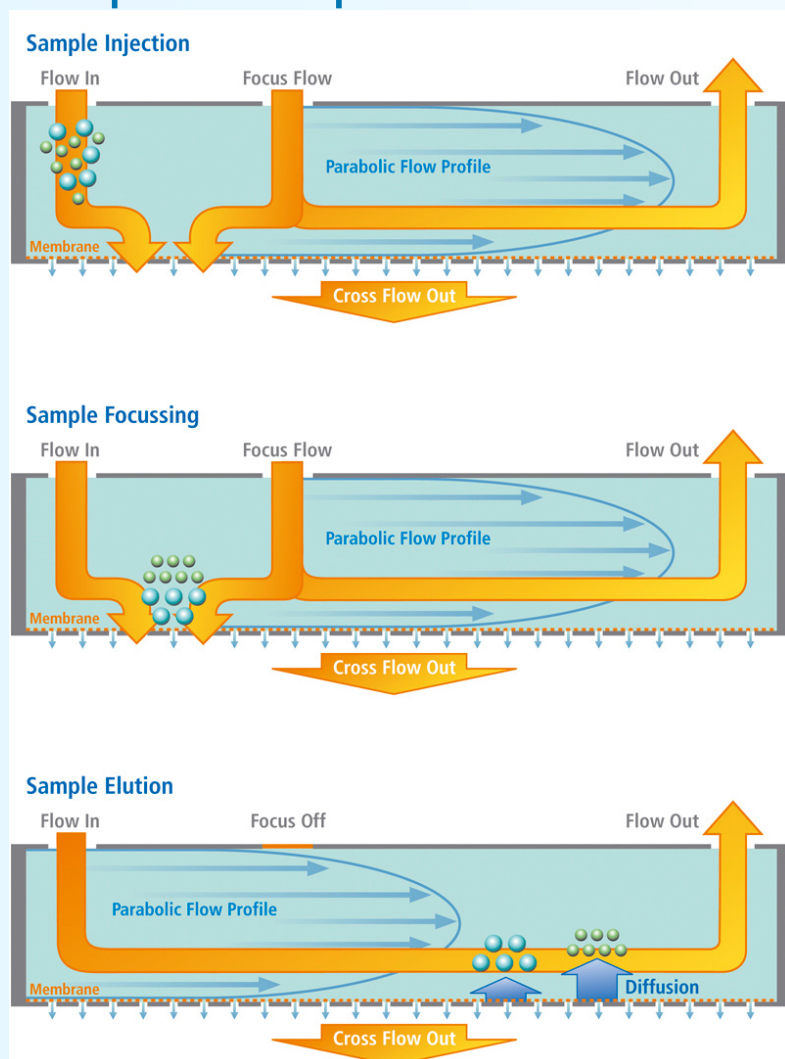
w : Channel thickness

\dot{V}_x : Cross Flow

\dot{V}_{Ch} : Channel Flow



Steps of separation



Source: Postnova Analytics

Eluents/solvents:

- pure water
- aqueous solutions (buffers, detergents)
- organic solvents (e.g. Ethanol, Methanol)

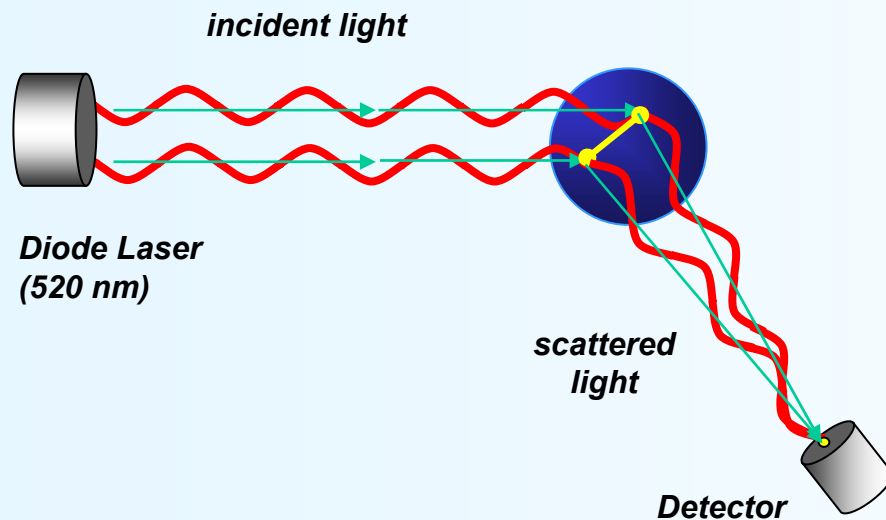
Detection of particles

- UV-Detector (280 nm): concentration
- MALS-Detector (520 nm): particle diameter

Multi Angle Light Scattering:

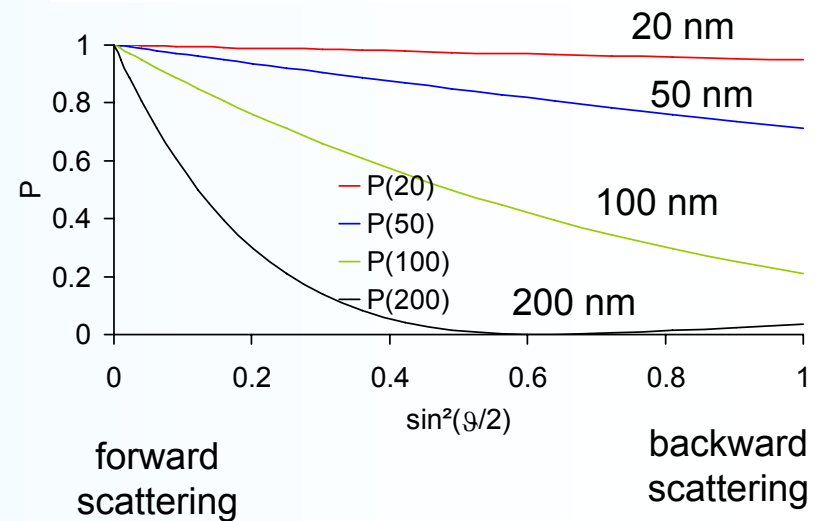
measurement of scattered light at various angles:

35°, 50°, 75°, 90°, 105°, 130°, 145°

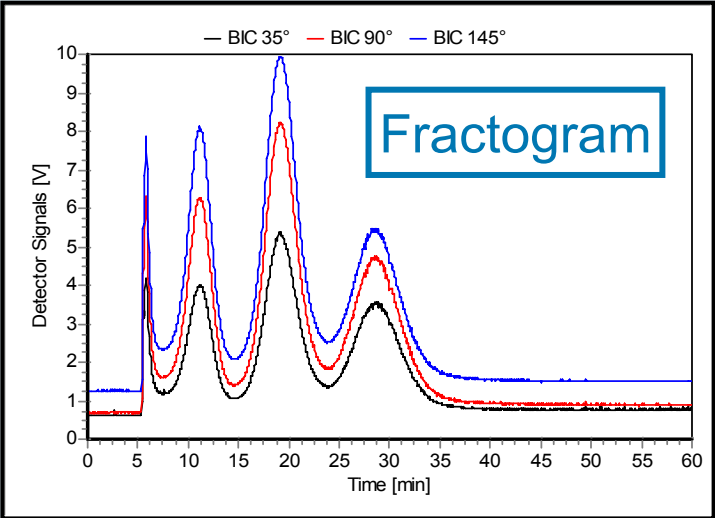


Source: Postnova Analytics

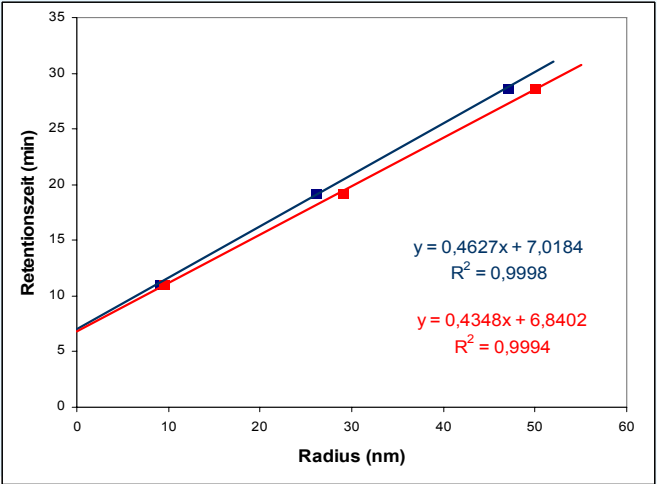
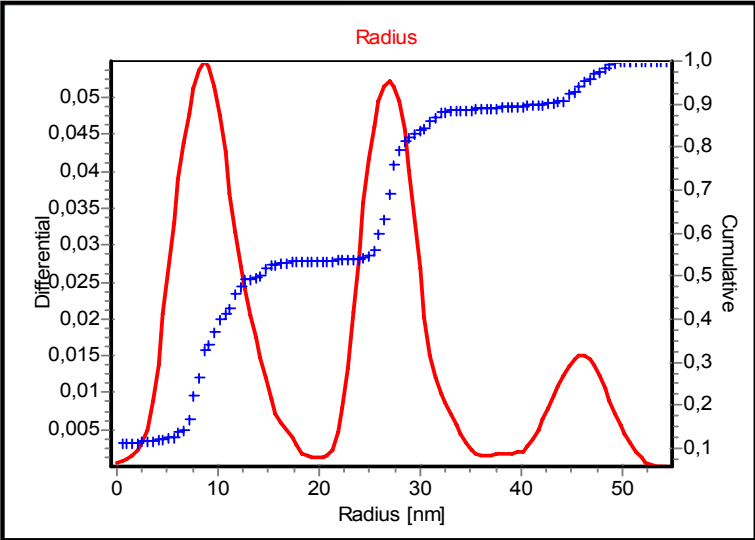
angular dependent scattering function of spherical nanoparticles



Polystyrene particles (radius 9,5 nm, 29 nm and 50 nm)



Size distribution

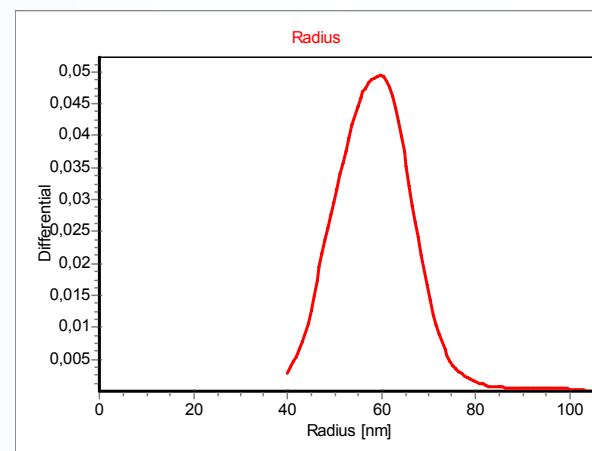
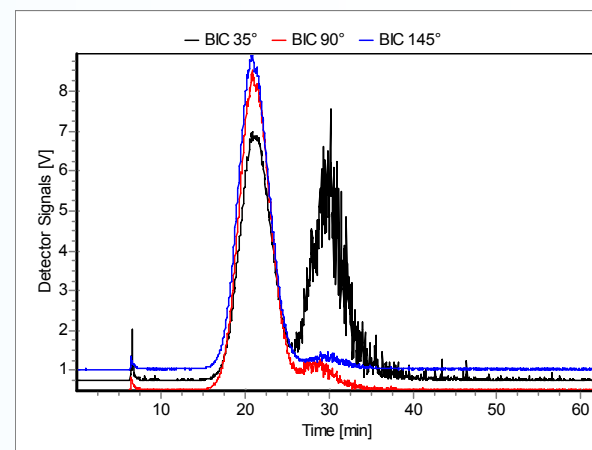


Linear relationship particle radius and retention time
 blue: radius from MALS detector
 red: according to manufacturer

Reproducibility of AF⁴ method

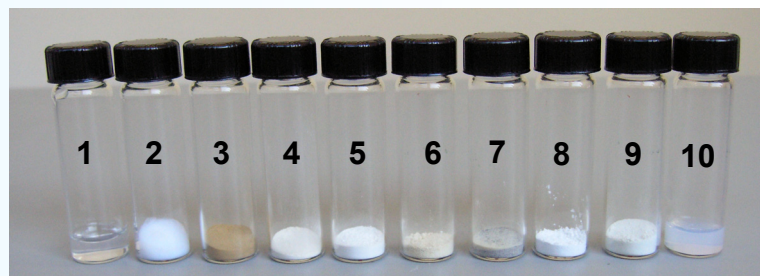
Ag-NP in consumer product (spray) solvent 15% MeOH

	Injection time (min)	Cross flow (mL/min)	Mean radius (nm)
Nano-Ag_2511_0	5	2.0	59.4
Nano-Ag_2511_1	5	2.0	63.7
Nano-Ag_2511_2	4	2.0	66.8
Nano-Ag_2511_3	4	2.5	66.0
Nano-Ag_2511_4	5	2.0	63.5
Nano-Ag_2511_5	6	2.0	64.5
Nano-Ag_2511_6	7	2.0	71.2
Average			65.0
Standard deviation			3.6



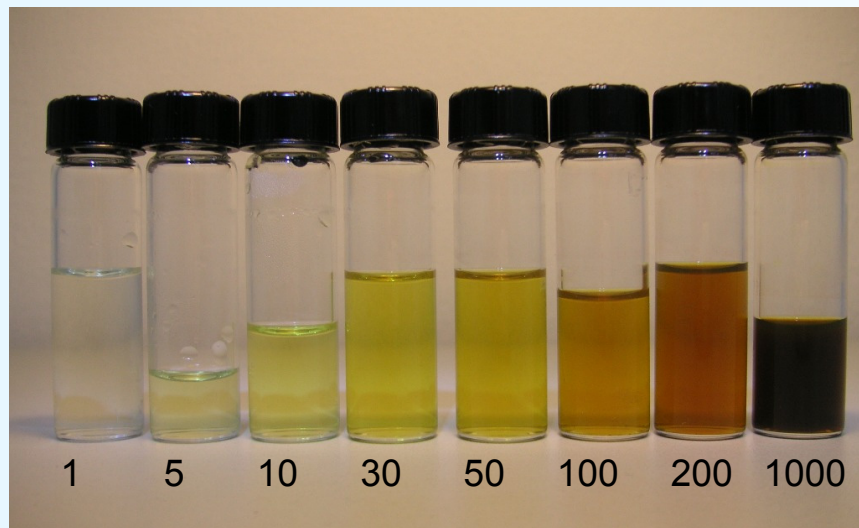
Nanoparticles in SiO₂-containing food supplements

Conventional supplements and „nano“-supplements measured with AF4 after ultrasonic homogenisation

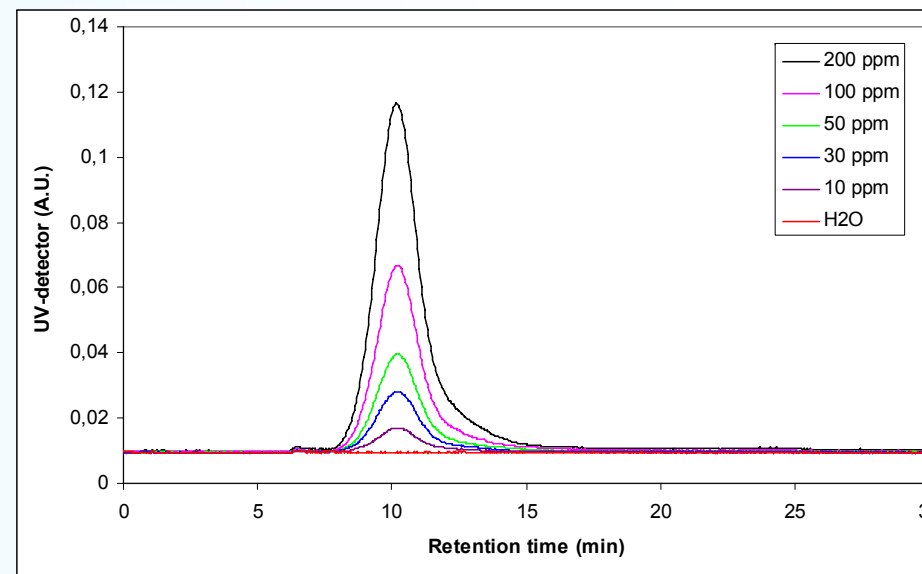


no.	Product	Solvent	Max. of size distribution (Diameter in nm)	Range of size distribution (Diameter in nm)
1	Levasil 300 hydrophilic silica sol	0,9% NaCl	20	10 – 70
2	Aerosil 300 hydrophilic fumed silica	0,2% NovaChem	200	80 – 400
3	Mineral powder	0,2% NovaChem	70	10 – 330
4	Silica powder	0,2% NovaChem	80	54 – 580
5	Silica powder with Calcium	0,2% NovaChem	220	150 – 550
6	Silica powder with vitamins	0,2% NovaChem	100	70 – 590
7	“Nano“-Silica powder	0,2% NovaChem	86	66 – 220
8	“Nano“-Silica powder	0,2% NovaChem	130	70 – 570
9	“Nano“-Silica powder	5 mM Na ₄ P ₂ O ₇	100	60 – 300
10	“Nano“-Silica sol	5 mM Na ₄ P ₂ O ₇	120	60 – 300

OECD nanosilver standard NM-300

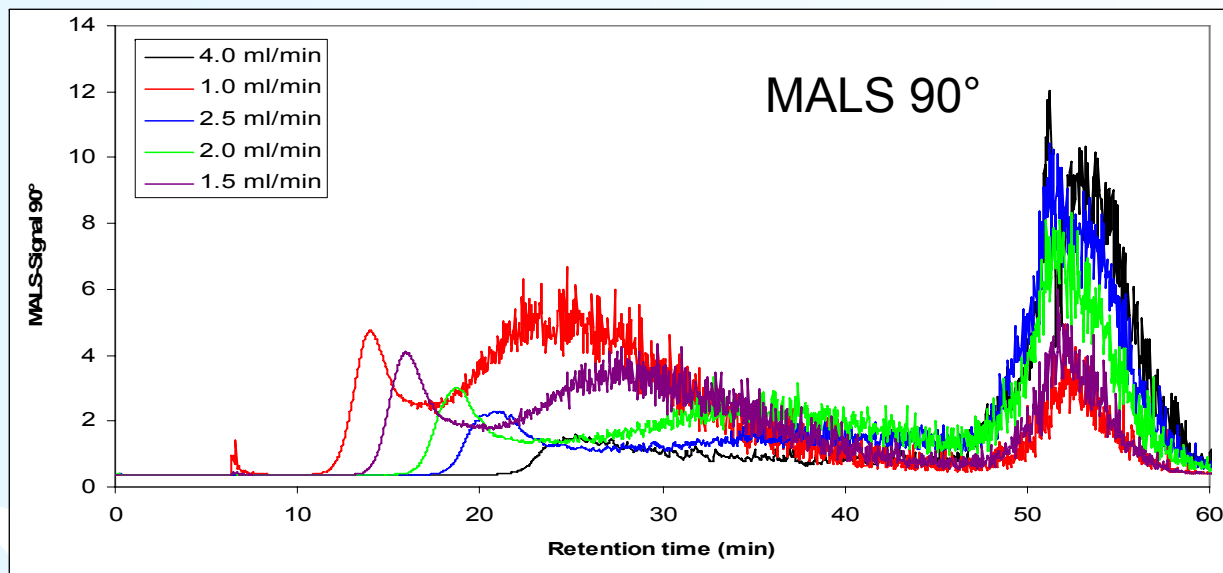
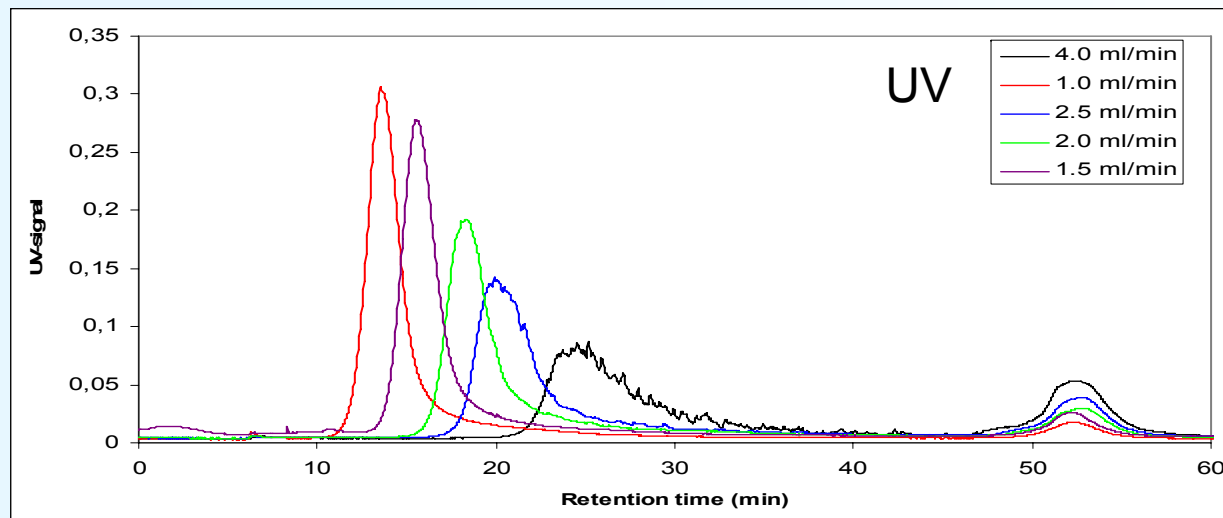


UV-signal at different concentrations in water

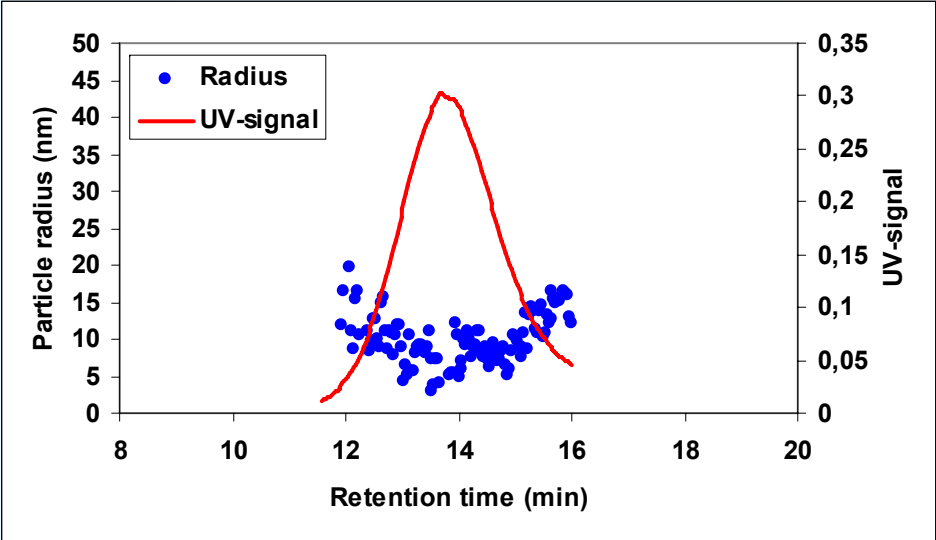


OECD nanosilver standard NM-300

Method development:
different cross flow rates



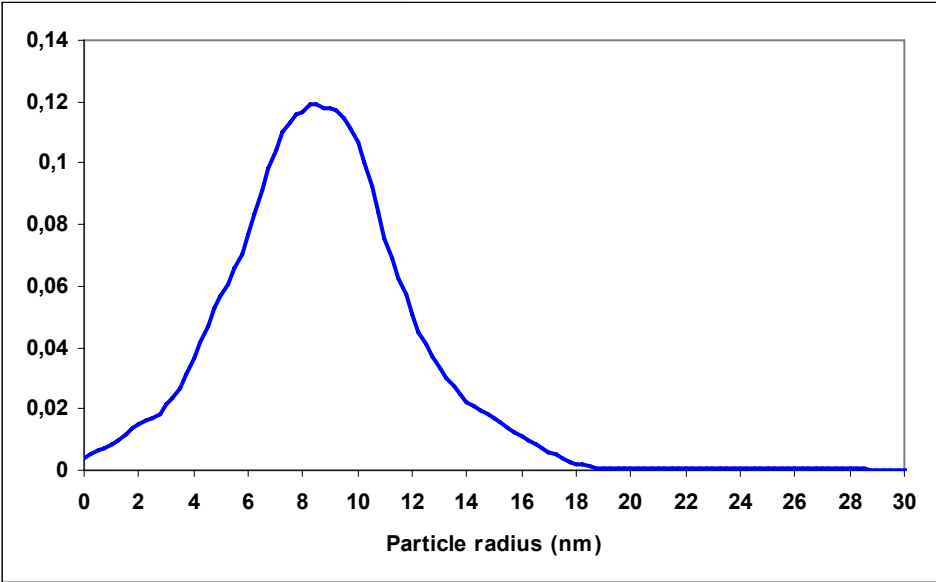
OECD nanosilver standard NM-300



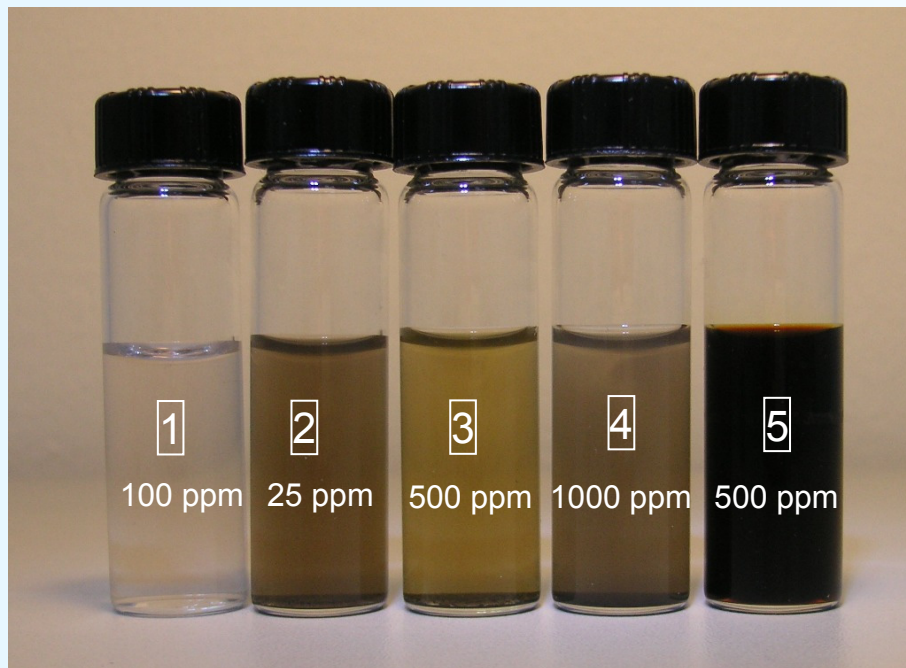
Fractogram

Size distribution

Particles radius (AF⁴): 8.5 nm
Reference value (TEM): 7.5 nm

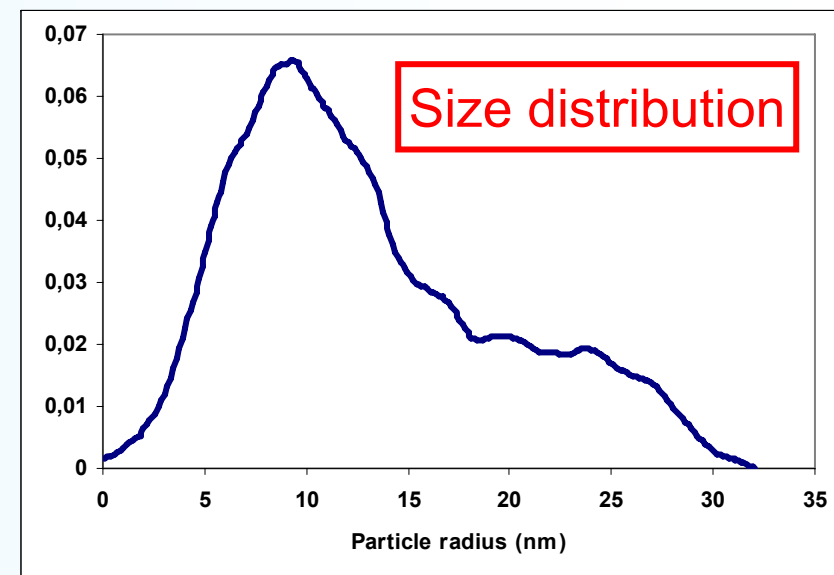
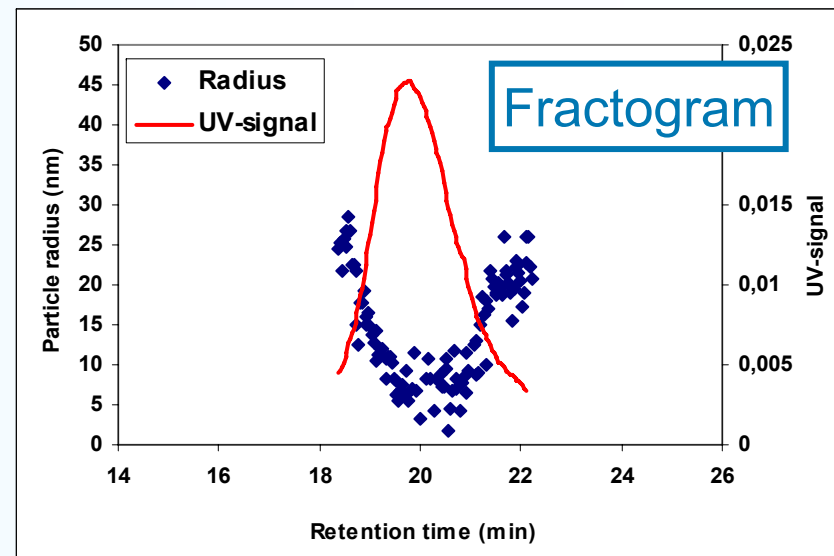


Colloidal silver samples



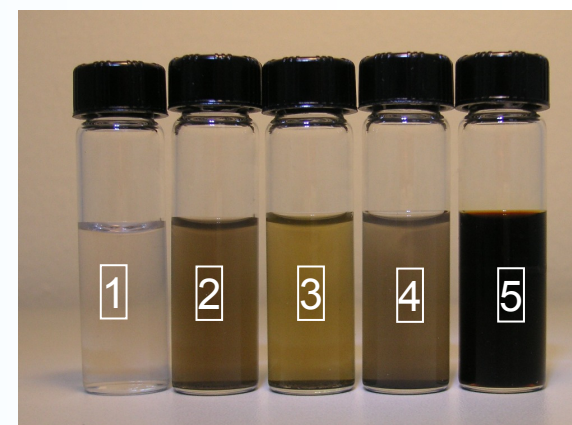
Solvent/Eluent: water

Sample No. 2



Colloidal silver samples

	particle diameter (nm)	measured concentration (ppm)	concentration according to manufacturer (ppm)
No. 1	130	2	100
No. 2	20	10	25
No. 3	30	11	500
No. 4	24	6	1000
No. 5	loss of NP to membrane		500



Summary

- **Several sources of nanoparticles in food and food supplements**
- **Project LENA: 1. NP-migration from food packages and 2. Measurement of NP in food and food supplements**
- **Analytical method AF⁴ applicable for NP-characterisation**
- **Method development necessary: cross flow rates, solvents (buffers, detergent etc.), sample preparation**
- **First results from measurement of Ag-NP in “colloidal silver”**

Acknowledgement

- The project LENA (Lebensmittelsicherheit und Nanotechnologie) was funded by the Bavarian State Ministry for Environment and Health



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