On the Production of Radioactive Labeled Nanoparticles Using a Cyclotron for Oil Consumption Measurements

ZYKLOTRON

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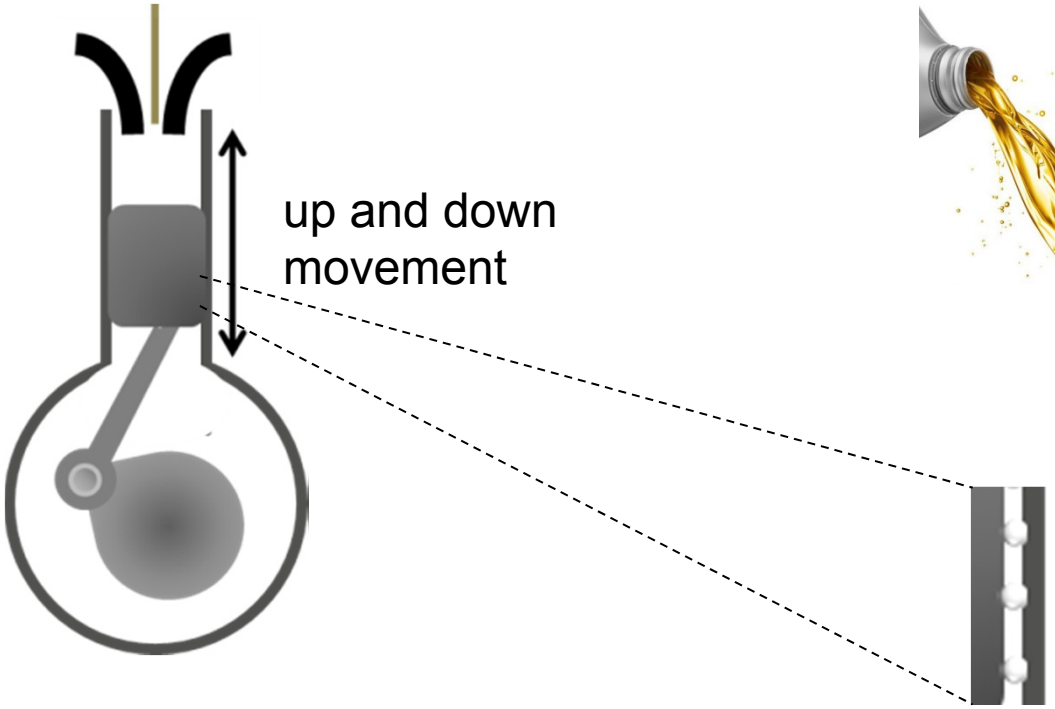
Zürich, 12.09.2016

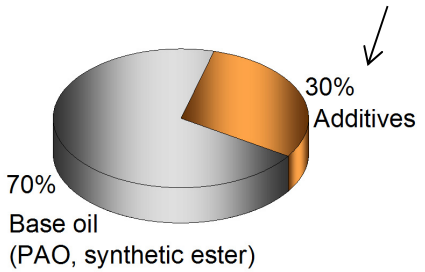
Motivation

Combustion engines



Engine oil

e.g. nanoparticles



Friction → Reduction of life time
of mashine components
Wear → Power losses

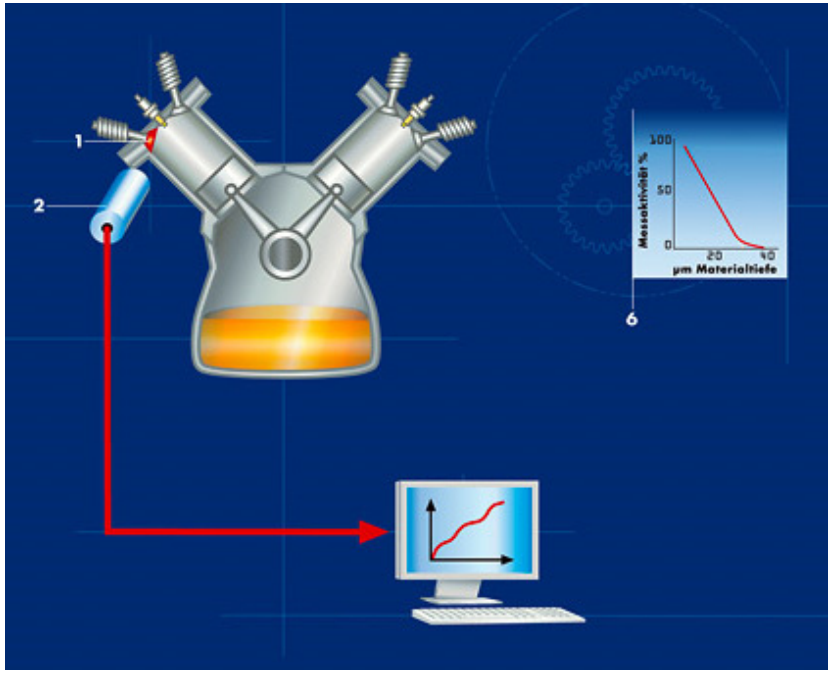
→ Friction and wear
reduction by engine oil

Motivation

Established techniques at Zyklotron AG

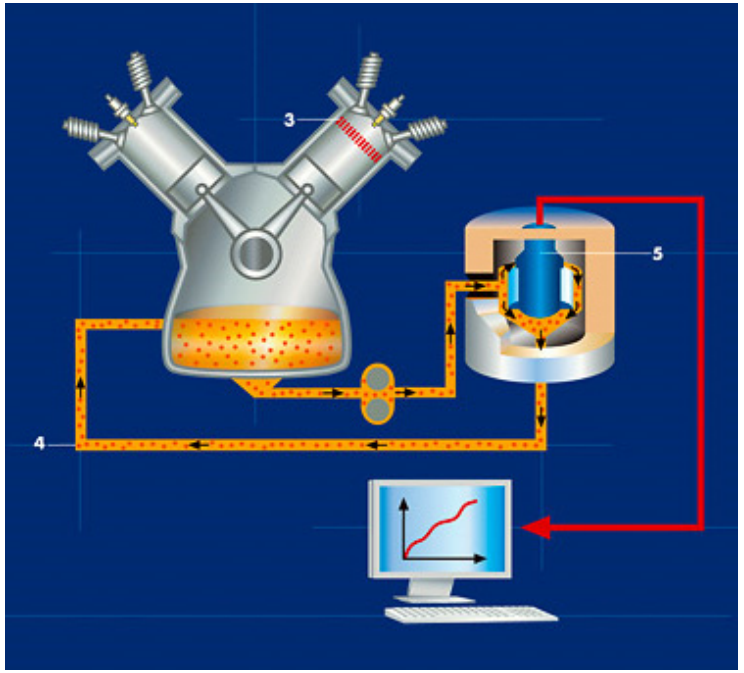
RTM measurement (Radionuclide Technique in Mechanical Engineering)

A) Thin layer difference method



Zyklotron AG, Karlsruhe.

B) Concentration measuring method



Zyklotron AG, Karlsruhe.

Motivation

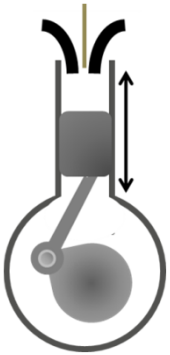
Drawback

Emission norms are tightend

Control and measurement of oil consumption crucial!

What should be investigated?

Engine test bench



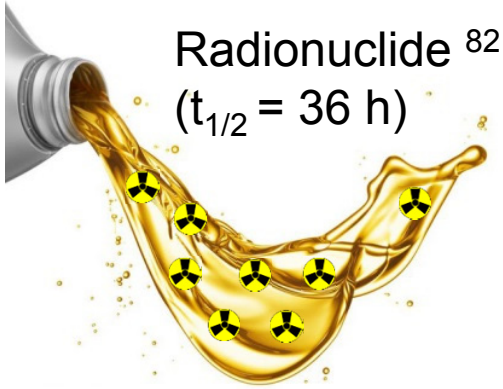
Determination of oil residuals in

- Particle filter
- Environment

→ Optimization/evaluation of suitability of engine oils and engines

How to determine the oil consumption?

Previous research



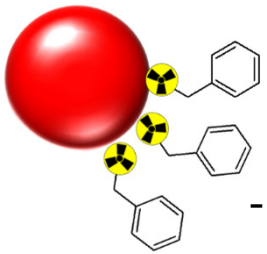
Radionuclide ^{82}Br
($t_{1/2}$ = 36 h)

H. Zellbeck et al., Tribotest **2000**, 6(3).

Idea

Expected advances:

- High nanoparticle dispersibility in all oil fractions
- No precipitation of radioisotopes



Radionuclide [^{123}I] Benzyl Iodide
($t_{1/2}$ = 13.5 h)

- High affinity of Iodide to gold
- Dispersibility of nanoparticles in oil

V. Merk, C. Rehbock, F. Becker, U. Hagemann, H. Nienhaus, S. Barcikowski, Langmuir **2014**, *30* (15)

A. Kleinrahm, F. Oberdorfer, H. Schweickert, B. Gökce, S. Jendrzej, S. Barcikowski,
Patent, *Nanopartikel-basierte radioaktive Tracer in Schmierstoffen,* **2016**, No. 102016206725.7.

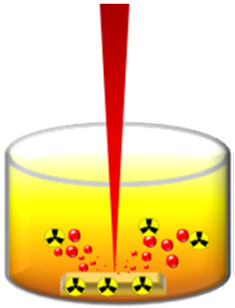
Disadvantages:

- Reduced dispersibility of halides in engine oil
- Precipitation of halides by reaction with additives
  $Zn^{2+} + X^- \rightarrow ZnX_2$

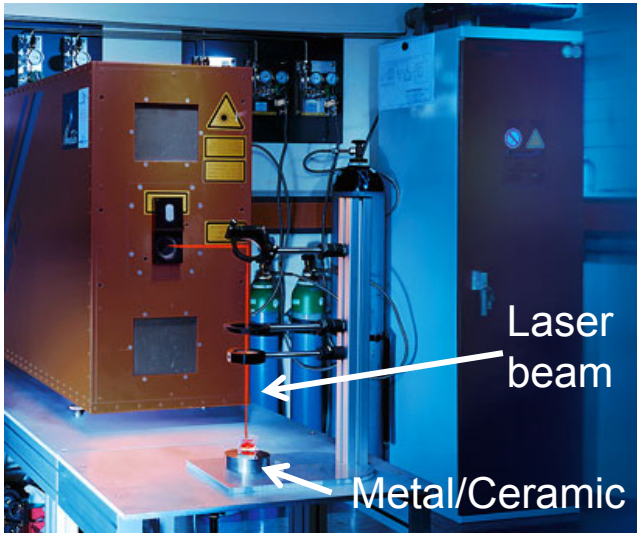
Radioactive labeling

In situ

Combination of thin layer difference method and laser ablation



High specific activity of 50 MBq/mL

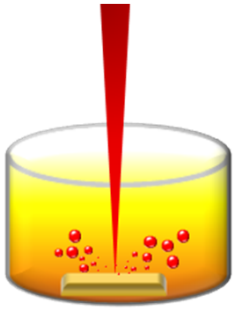


Zyklotron AG, Karlsruhe.

→ Not established method

Ex situ

Seperate synthesis of nanoparticles and radioisotopes



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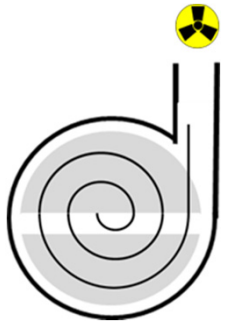
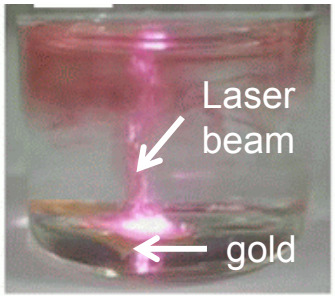
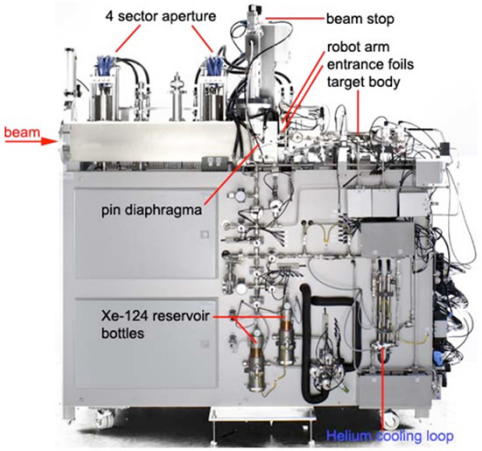


UDE, Essen. Zyklotron AG, Karlsruhe.



UDE, Essen.

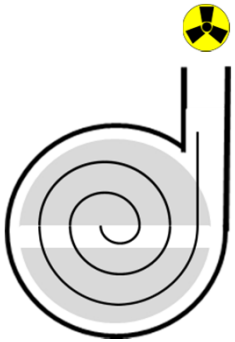


Zyklotron AG, Karlsruhe.

A. Kleinrahm, F. Oberdorfer, H. Schweickert, B. Gökce, S. Jendrzej, S. Barcikowski, **Patent**, *Nanopartikel-basierte radioaktive Tracer in Schmierstoffen,* **2016**, No. 102016206725.7.

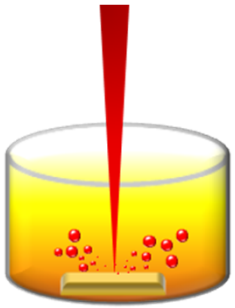
Process steps

Production of radioisotopes in a cyclotron



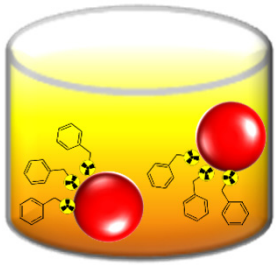
Zyklotron AG, Karlsruhe.

Synthesis of nanoparticles

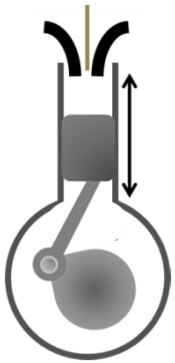


UDE, Essen.

Labelling of nanoparticles in oil



Engine test

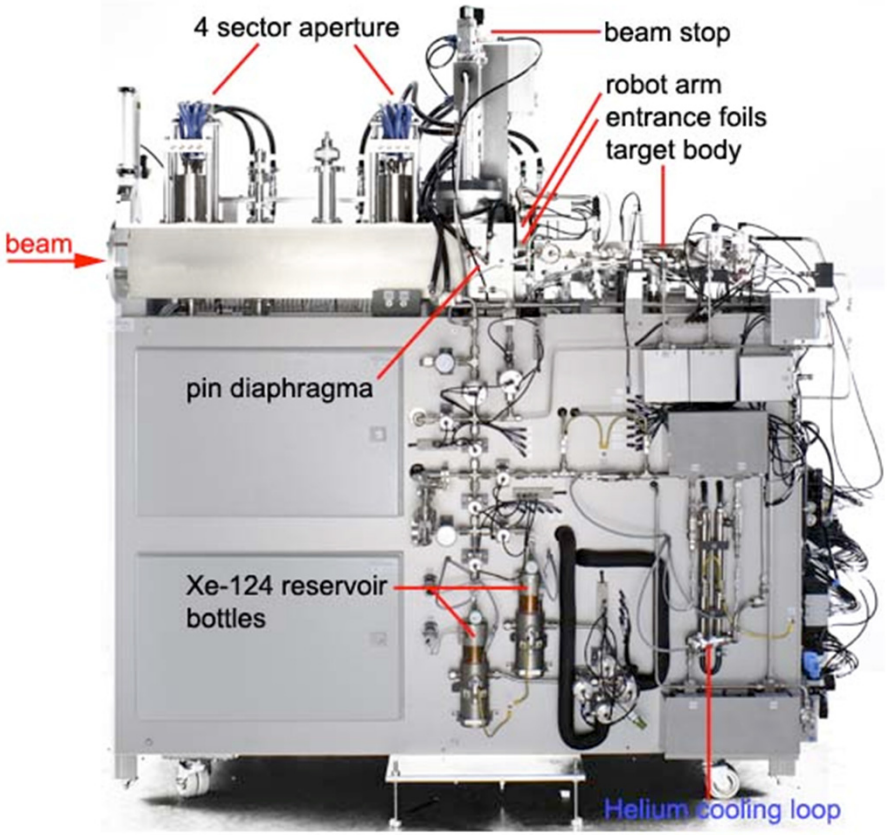


A. Kleinrahm, F. Oberdorfer, H. Schweickert, B. Gökce, S. Jendrzej, S. Barcikowski, **Patent**, *Nanopartikel-basierte radioaktive Tracer in Schmierstoffen,* **2016**, No. 102016206725.7.

Production of radioisotopes at a cyclotron

Production of ^{123}I at a cyclotron

KIPROS 120
(Karlsruher Iodine-123 Production System)



Zyklotron AG, Karlsruhe.

Proton irradiation of Xe target

Target thickness:	20 MeV
Current:	200 µA
Pressure	3 bar cold
	10-12 bar @ 120
Seals:	Metal, FKM, EPDM
Yield:	6-8 mCi/µAh
$t_{(irradiadion)}$	6 h

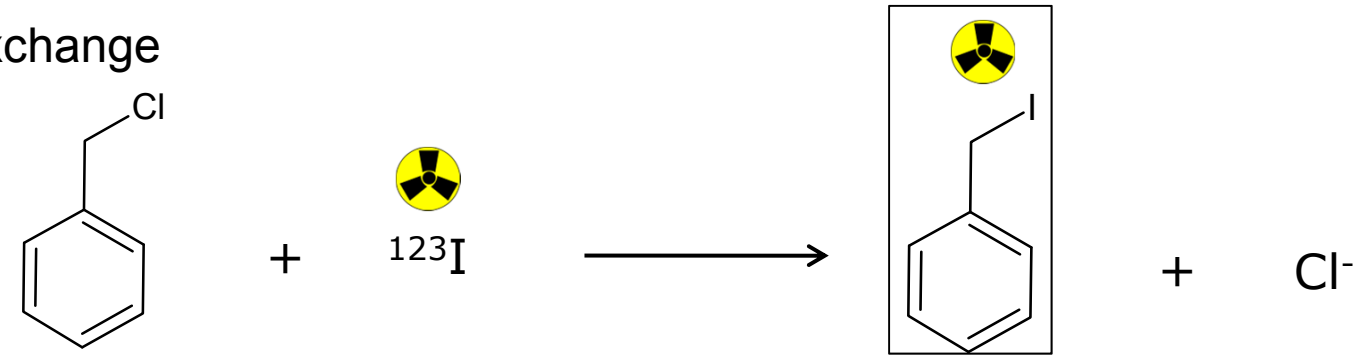
Production of radioisotopes at a cyclotron

Specifications for I-123

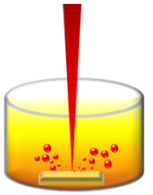
Radionuclide purity at calibration time ^{123}I:	> 99.65 %
Radionuclide impurities at calibration time (Sum of ^{120}I, ^{121}I, ^{124}I, ^{125}I, ^{121}Te):	≤ 0.35 %
Specific activity at calibration time:	≥ 30,000 MBq/mL
Radiochemical purity:	≥ 95 % Iodide
Constitution:	Dissolved in 0.02 mol/L (± 10 %) NaOH

Synthesis of [^{123}I] Benzyl Iodide

Anion exchange

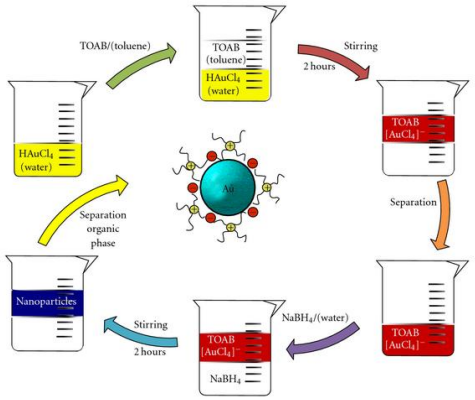


Synthesis of nanoparticles



1) Brust-Schiffrin method

Gold nanoparticle synthesis in toluene



M. Brust, M. Walker, D. Bethell, D. Schiffrin, R. Whyman, J. Chem. Soc., Chem. Commun. **1994**, *7*.

subsequent mixing with oil

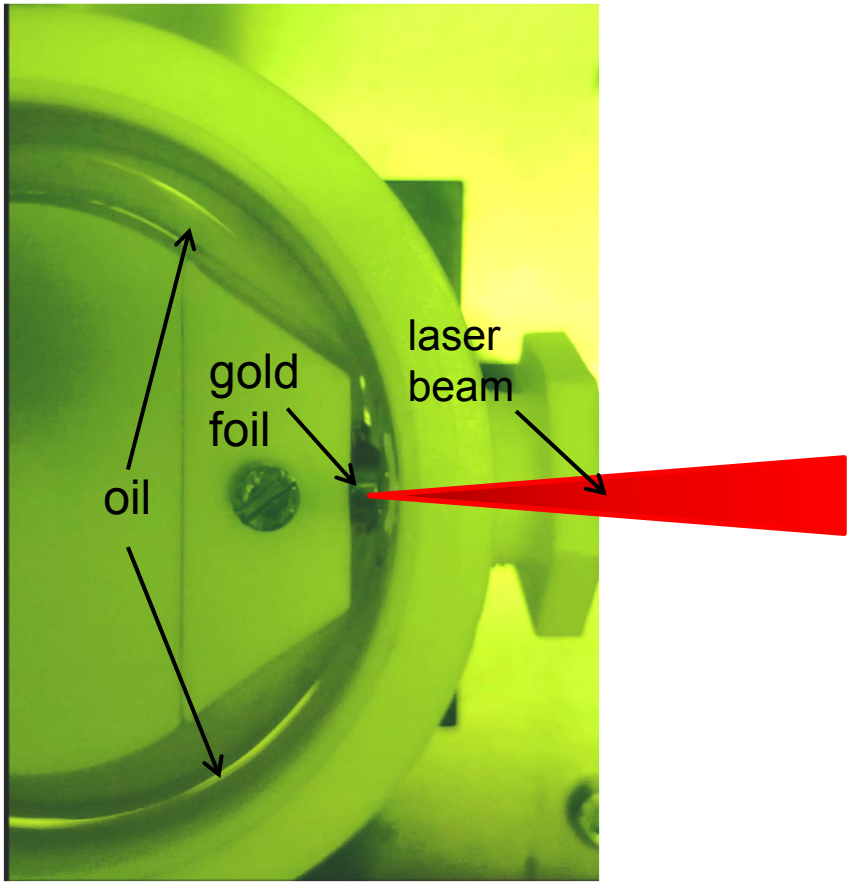
2) Dispersion of powder into oil

Drawbacks:

- Complex synthesis
- Nanoparticle agglomeration

3) Pulsed laser ablation in liquids

Directe gold nanoparticle synthesis in oil



A. Kleinrahm, F. Oberdorfer, H. Schweickert, B. Gökce, S. Jendrzej, S. Barcikowski, **Patent**, *Nanopartikel-basierte radioaktive Tracer in Schmierstoffen,* **2016**, No. 102016206725.7.

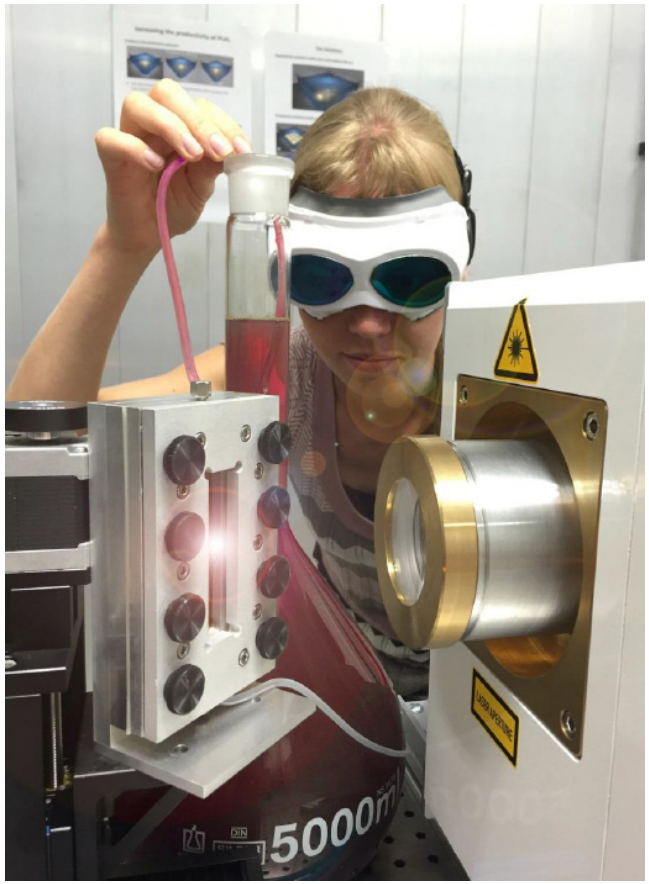
Up scaling of pulsed laser ablation method

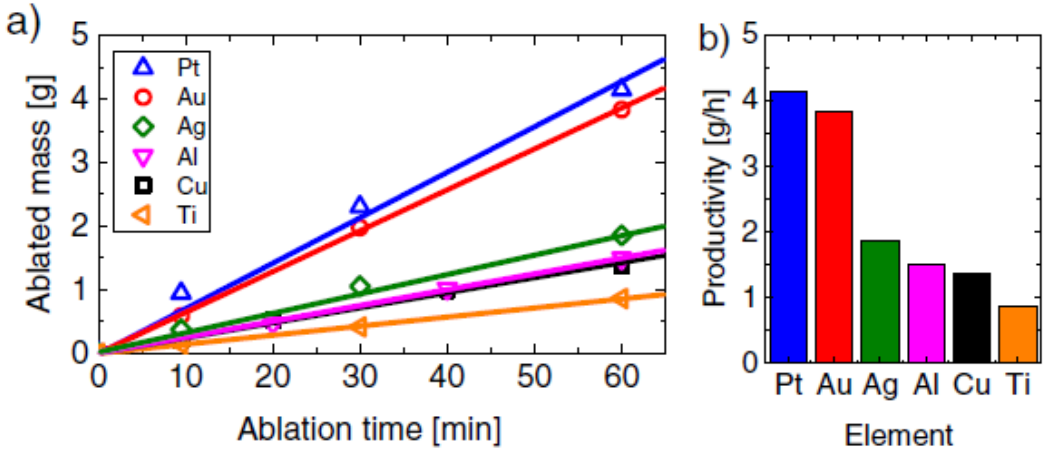
5 L Gold colloid in water

→ 1 h of efficient work time

→ 4 g Gold nanoparticles

High-power laser: 500 Watt, 3 ps, 10 MHz





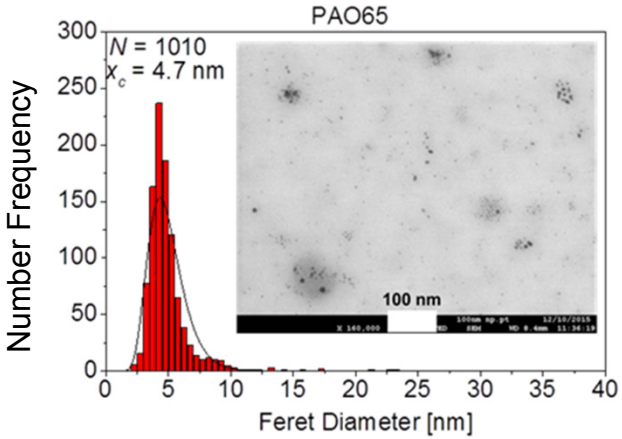
R. Streubel, S. Barcikowski, G. Gökce, Optics Letters **2016**, 41.

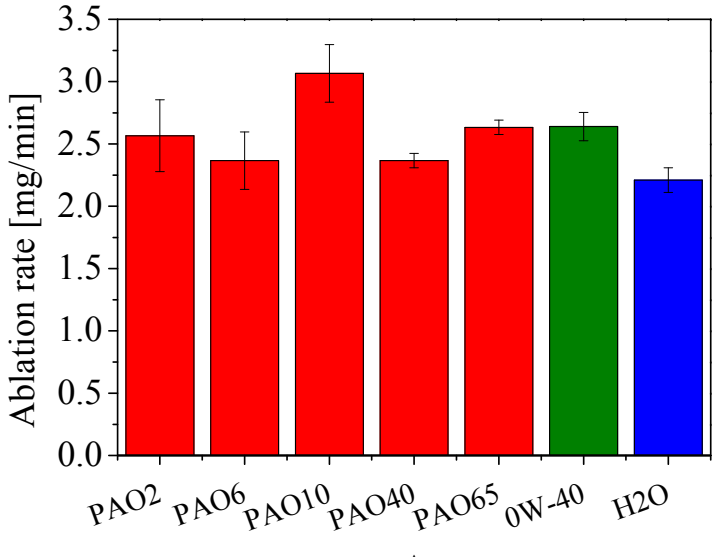
Economic nanoparticle synthesis for engine tests

Performance of 1 engine test:

5-20 L engine oil

15 pg ^{123}I (4.5 MBq)





0.2 µL of colloid (50 µg/mL) are required for accumulation of 15 pg ^{123}I

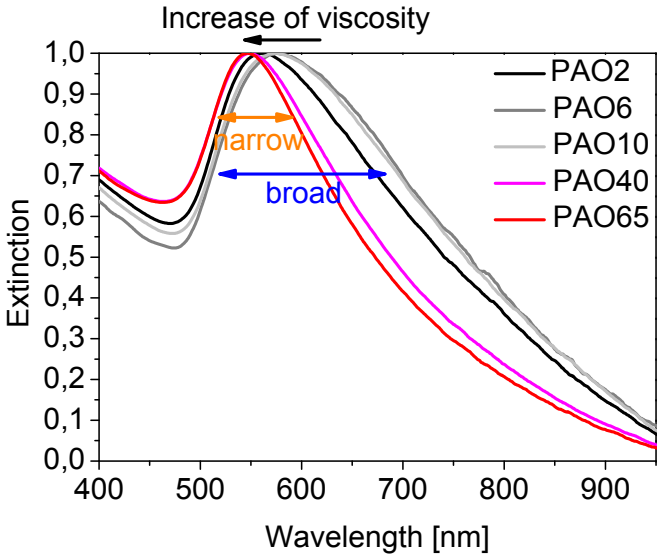
→ 1 min laser ablation in oil could be enough for 200,000 engine tests

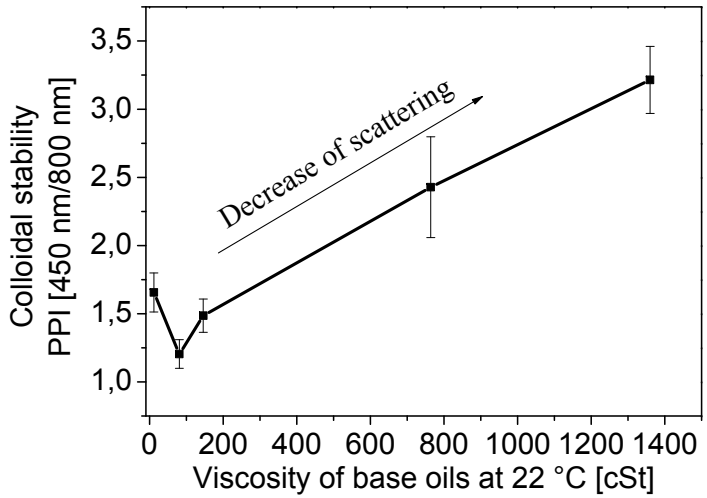
Highly economic synthesis

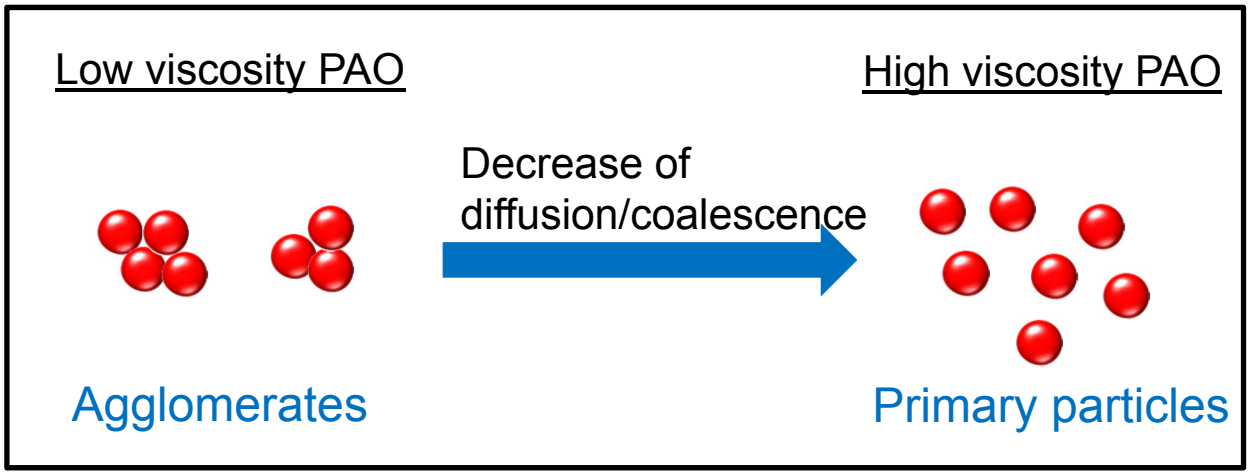
A. Kleinrahm, F. Oberdorfer, H. Schweickert, B. Gökce, S. Jendrzej, S. Barcikowski, **Patent**, *Nanopartikel-basierte radioaktive Tracer in Schmierstoffen,* **2016**, No. 102016206725.7.

Optical properties of gold in base oils

Optical properties:





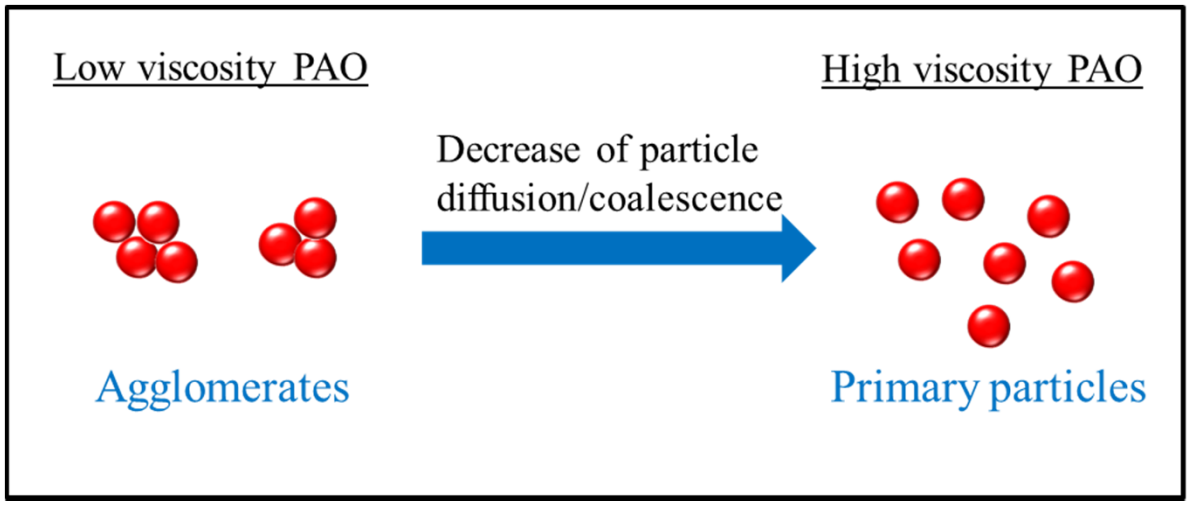


Stokes Einstein equation

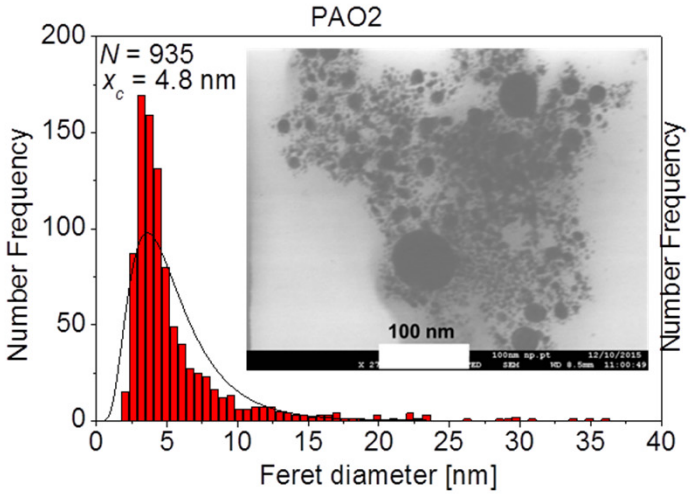
$$D = \frac{k_B T}{6\eta r\pi}$$

A. Kleinrahm, F. Oberdorfer, H. Schweickert, B. Gökce, S. Jendrzej, S. Barcikowski, **Patent**, *Nanopartikel-basierte radioaktive Tracer in Schmierstoffen,* **2016**, No. 102016206725.7.

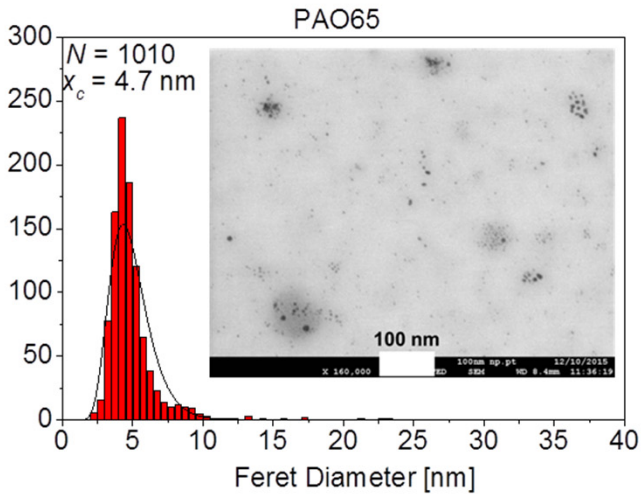
Size distribution of gold in base oils



Au in PAO2



Au in PAO65



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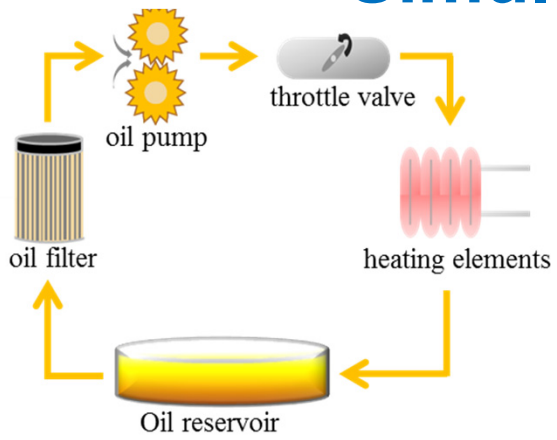
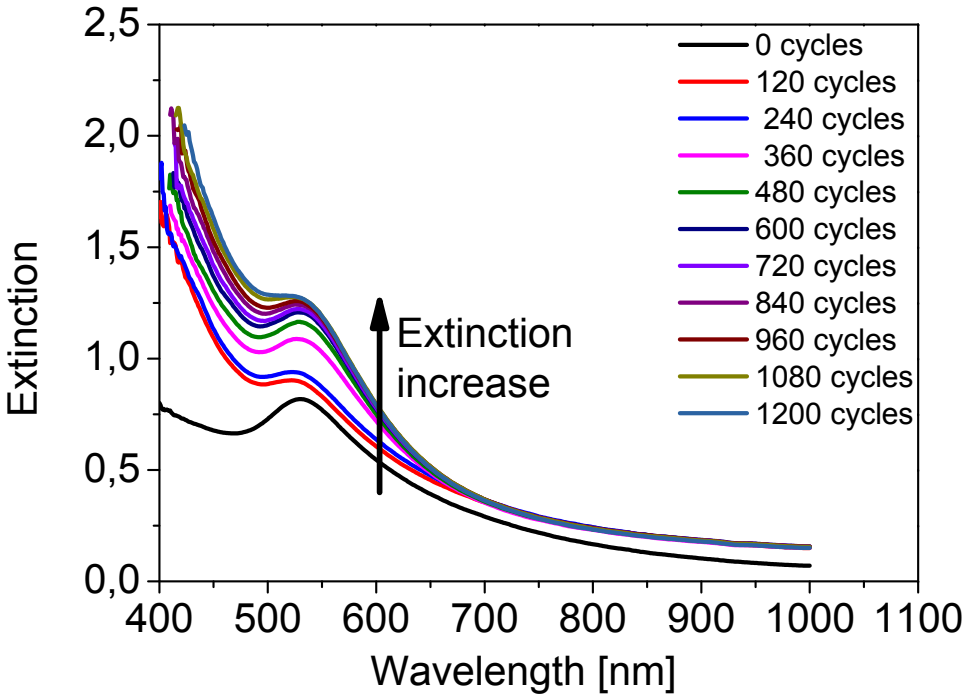
Simulation of first engine tests



Au nanoparticles in full synthetic engine oil (0W-40)

Au concentration: 100 mg/L
Oil is compressed to 6 bar in the measurement chamber
Oil temperature: approx. 150 °C
Circulation duration: 2 h
8 oil cycles/min



Low viscosity engine oil

Protective shell by additives

Primary particles

Thank you for your attention !

Questions?

GDCh
GESELLSCHAFT
DEUTSCHER CHEMIKER

We gratefully acknowledge the financial contribution by the GDCh