# The Biochemical Process of Lubricant Film Formation in Joint Replacement

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**State doctoral examination**

Brno 13.11. 2020

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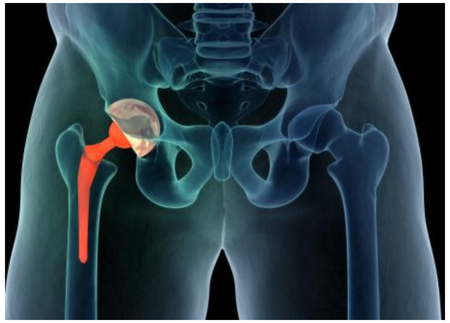
# Content

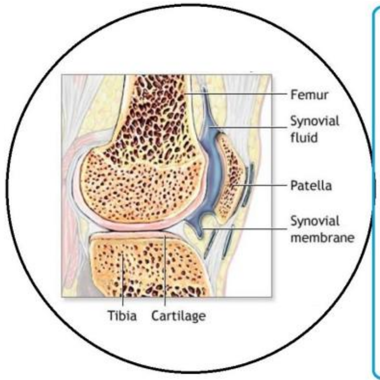
- Motivation
- Introduction to the problem
- Summary of the current state of knowledge
- Analysis and evaluation of the knowledge
- Defining the goals of the dissertation
- Scientific questions and working hypothesis
- Materials and Methods
- Current state of dissertation
- Overview of achieved results
- Conclusions

# Motivation

**Synovial fluid film formation is a complex procedure**



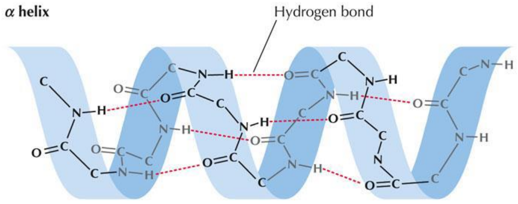
**Chemical adsorption of the of lubricant film on implant material**



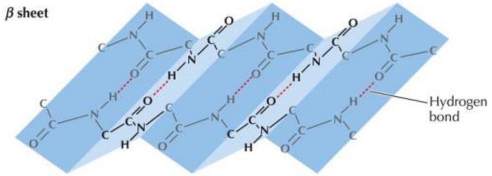

**The chemical composition of synovial fluid film**

**Individual fluid components reacting with implant materials**

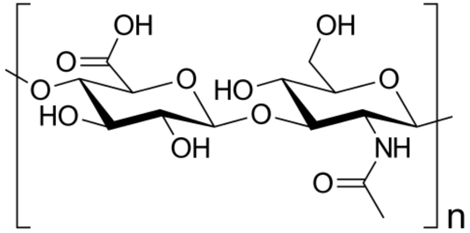
**Albumin**



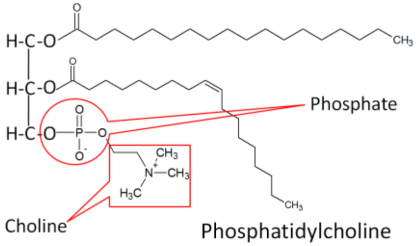

**γ-Globulin**




**Hyaluronic Acid**



**Phospholipid**



# Introduction to the problem

50 years — 30 years — 20 years

## CoCrMo Alloy Hip Implant

**CoCrMo Chemical Composition**

- Chromium, Cr 27–30%
- Molybdenum, Mo 5–7%
- Iron, Fe <0.75%
- Nickel, Ni <1%
- Carbon, C <0.35%
- Silicone, Si <1%
- Manganese, Mn <1%
- Tungsten, W <0.2%
- Sulfur, S <0.02%
- Nitrogen, N <0.25%
- Aluminium, Al <0.3%
- Titanium, Ti <0.1%
- Boron, B <0.01 %
- Phosphorus, P <0.02%
- Cobalt, Co *Balanced Amount*

(ISO 5832-4)

## BIOLOX®forte Hip Implant

**BIOLOX®forte Chemical Composition**

- Alumina, $Al_2O_3$ **Ultra pure**
- Magnesium oxide, MgO *(Trace amount)*

(ISO 6474)

## BIOLOX®delta Hip Implant

**BIOLOX®delta Chemical Composition**

- Alumina, $Al_2O_3$ 75%
- Zirconia, $ZrO_2$ 24%
- Strontium oxide, SrO
- Yttrium oxide, $Y_2O_3$
- Chromium oxide, $Cr_2O_3$

→ *(Trace amount)* (Strontium oxide, Yttrium oxide, Chromium oxide)

(ISO 6474-2)

# Introduction to the problem

50 years — 30 years — 20 years

CoCrMo Alloy Hip Implant

BIOLOX®forte Hip Implant

BIOLOX®delta Hip Implant

Lubrication mechanisms → Tribological performance → Service-life of the implant

- Ion release
- Corrosion & Wear debris
- Micro-cracking
- Phase transformation

# Summary of the current state of knowledge

**Lubrication mechanism of joint replacement**

- **Film formation and thickness analysis**
- **Material analysis of joint implants**
- **Joint implants correlation with frictional properties**
- **Spectroscopic analysis of synovial joint**

# Summary of the current state of knowledge

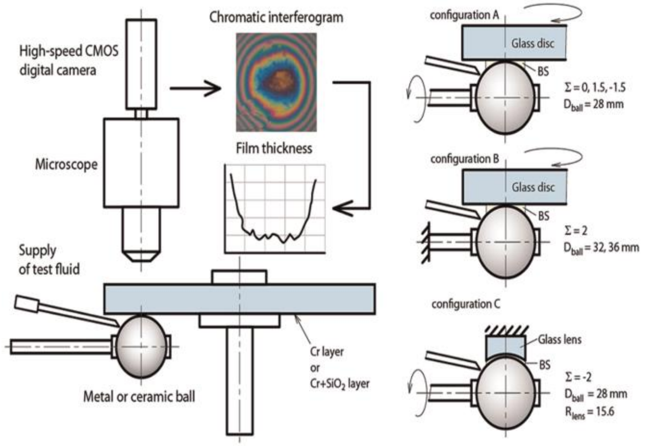
**Film formation and thickness analysis**

**2014**

**2015**

**Vrbka et al.** In situ measurements of thin films in bovine serum lubricated contacts using optical interferometry

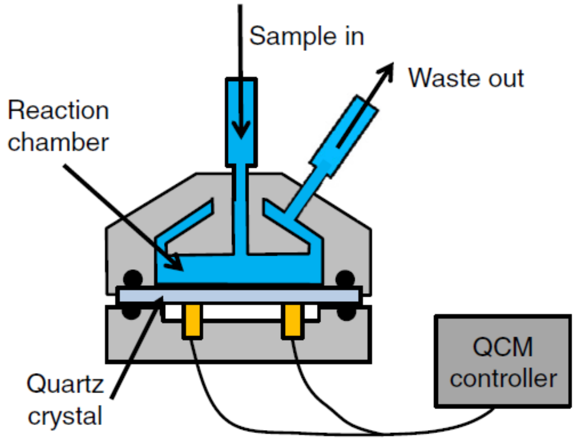
- Film thickness measurement as a function of time
- Optical interferometry method usage based on phase shifting interferometry
- Conformity of contacting surfaces and kinematic conditions observation




*Optical test rig experimental approach*

**Parkes et al.** Synovial fluid lubrication: the effect of protein interactions on adsorbed and lubricating films

- Film formation impact with different pH
- Film thickness with different compositions of synovial fluids
- Optical interferometry usage to determine the effect of protein content on lubricant film thickness.
- Adsorbed film analysis by Quartz Crystal Microbalance




*Quartz Crystal Microbalance with flow cell*

# Summary of the current state of knowledge

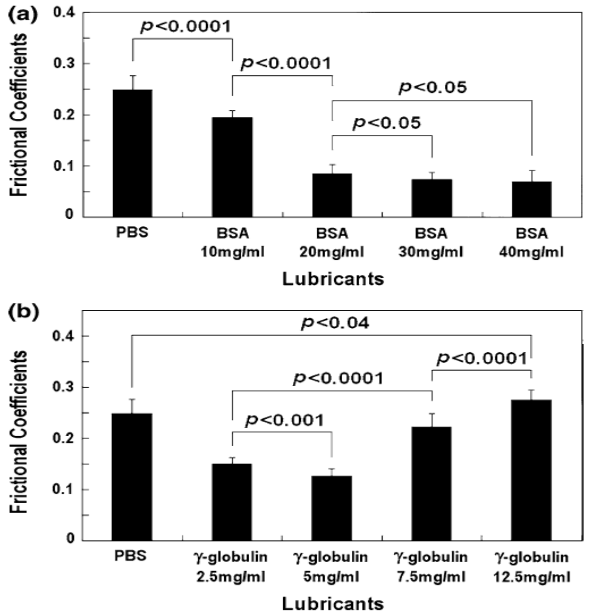
**Joint implants correlation with frictional properties**

**2012**

**2015**

**Duong et al.** Effect of protein concentrations of bovine serum albumin and γ-globulin on the frictional response of a cobalt-chromium femoral head

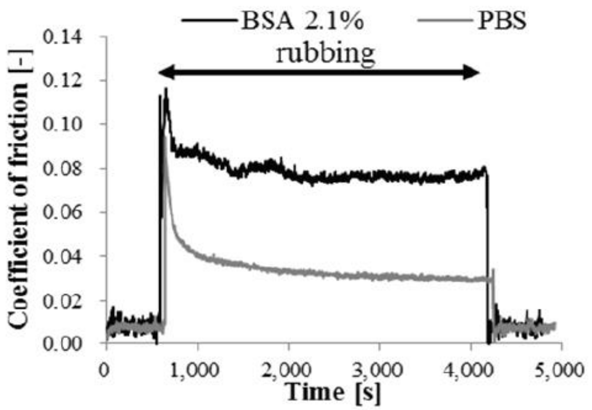
- Concentration levels dependency of BSA and γ-globulin on the lubricating ability
- AFM utilization for applied normal force and surface roughness to analyze microscopic frictional measurements.
- Friction coefficients with boundary lubricants calculation for CoCr femoral head .




*AFM frictional coefficients of the CoCr femoral head measured*

**Kazuhiro et al.** Behavior of adsorbed albumin film on CoCrMo alloy under in-situ observation

- Adsorption and frictional property in rubbing condition.
- Reciprocating pin-on-disk tribo-meter with electrochemical method
- Investigation of *in-situ*, real time information on adsorption and desorption of proteins.




*The effect of friction transition under OCP condition*

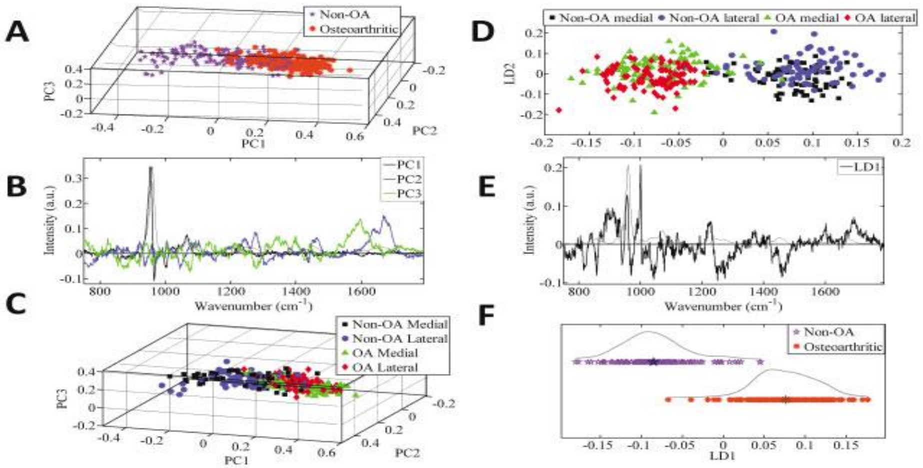
# Summary of the current state of knowledge

**Spectroscopic analysis of synovial joint**

**2014**

**Kerns et al.** Evidence from Raman spectroscopy of a putative link between inherent bone matrix chemistry and degenerative joint disease

- Molecular structures of tibial plateaus of healthy joints and joints with total replacements due to osteoarthritis
- Raman spectroscopy for comparing differences
- Comparison of medial and adjacent compartments of subchondral bones with different load baring sites

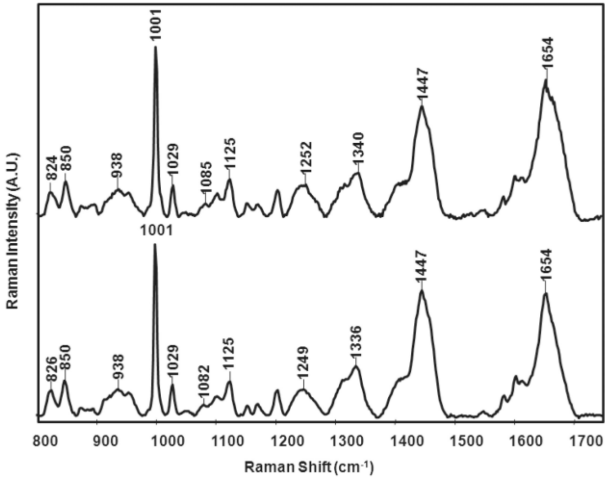



*Principal components analysis (PCA) of the Raman spectra. A–C, Plot of PCA scores for the non-osteoarthritis (non-OA) tibial specimens compared to the OA tibial specimens D–F, Plot of PCA–linear discriminant analysis (PCA-LDA) scores for the non-OA and OA medial and lateral compartments*

**2009**

**Esmonde-White et al.** Raman spectroscopy of synovial fluid as a tool for diagnosing osteoarthritis

- Biochemical compositions difference of healthy joint synovial fluids and synovial fluids of OA patients
- Pre-operative conventional postero-antero radiographs to assess symptoms
- Drop deposition/Raman Spectroscopy protocol utilization




*Raman Spectra of human SF dried drops*



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# Summary of the current state of knowledge

**Material analysis of joint implants**

**2012**

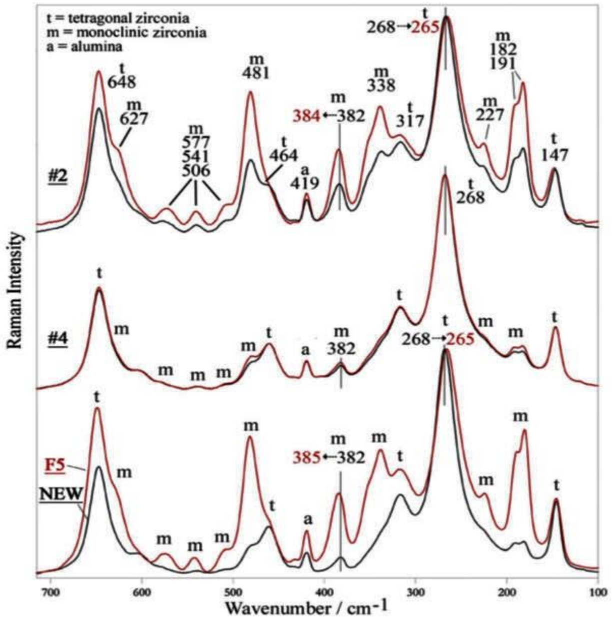
**2017**

**Taddei et al.** Raman and fluorescence investigations on retrieved Biolox® delta femoral heads

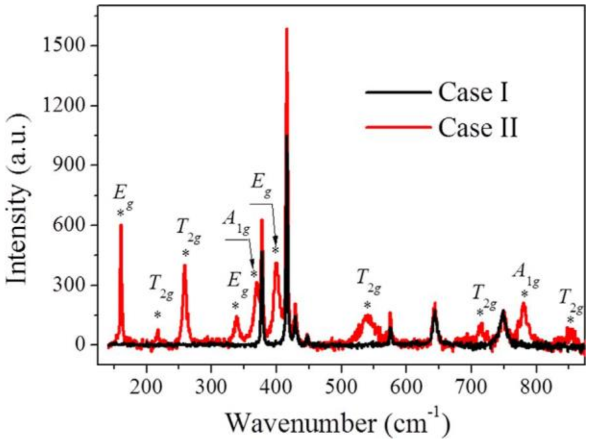
- The molecular level characterization of BIOLOX®delta retrievals
- Fluorescence and Raman spectroscopic technique applied
- Material properties alteration of BIOLOX®delta femoral heads observation.

**Zhu et al.** Tensor-resolved Raman spectroscopic analysis of wear-induced residual stress fields in long-term alumina hip-joint retrievals

- Polarized raman analysis of wear-induced (residual) stress fields
- Evolution of tensor-resolved residual stress motifs in the three-dimensional space observed
- Optical morphologies of the samples determination by back-scattered confocal laser microscope




*Average micro-Raman spectra of BIOLOX®delta femoral heads*




*Raman spectra collected on the alumina heads*

# Analysis and evaluation of the knowledge

## Film formation on implant material:

- Adsorption and desorption of protein
- Film thickness in different pH and concentration
- Frictional coefficient and shear force
- Boundary lubrication and rheology
- Frictional coefficient and chemical change
- Combination of biotribology and tribochemistry

## Biochemical analysis of synovial fluid:

- Composition and concentration of synovial fluid components of osteoarthritis patients
- Spectroscopic analysis of the healthy and osteoarthritis specimens of synovial fluids
- Molecular structures healthy joints and joints with total replacements with osteoarthritis
- Phase transformation of ceramic implants
- Biochemical composition of film formation on implant materials
- Chemical structural change of synovial fluid components after joint replacements

# Defining the aims of the dissertation

**Main Aim:**

The research aims to clarify the chemistry of film formation on hip implant material surfaces with synovial fluids components.

**Partial Aims:**

- Design the methodology of Raman spectroscopic technique for the analysis of lubricant film formation.
- Observation of the chemical structural changes of synovial fluid components and implant materials.
- Measurement of coefficient of friction for contact pairs including synovial fluid lubricants.

# Scientific questions and working hypothesis

## Scientific questions:

**From chemical perspective:**

- Which components of synovial fluids are adsorbing chemically while lubricant film formation on hip implant material surfaces within artificial joint replacement?
- What kind of chemical structural changes are taking place within the constituents of synovial fluid in hip prosthesis?

**From tribological perspective:**

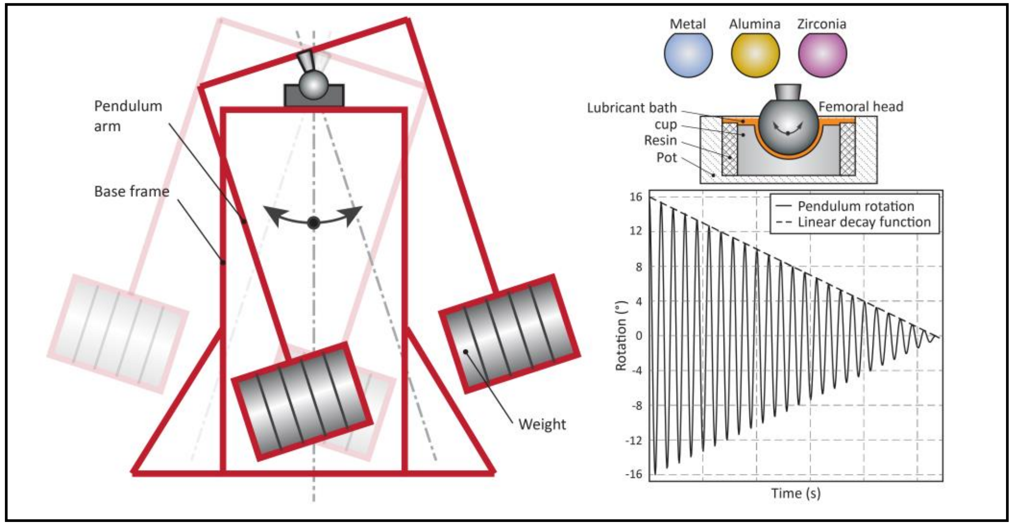
- How frictional coefficients are differing with this chemical change in the hip joint replacement?

## Working Hypothesis:

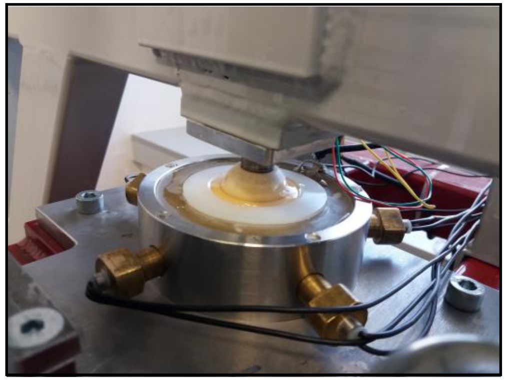
- On the surface of implant material, proteins of the synovial fluid are adsorbed chemically, rather than HA and phospholipids.
- CoCr implant head could act as heterogeneous catalyst to form synovial fluid film within joint replacement.
- The friction coefficient of the contact pairs is probably increased when chemical reaction occurring within implant materials and the lubricants.

# Materials and Methods

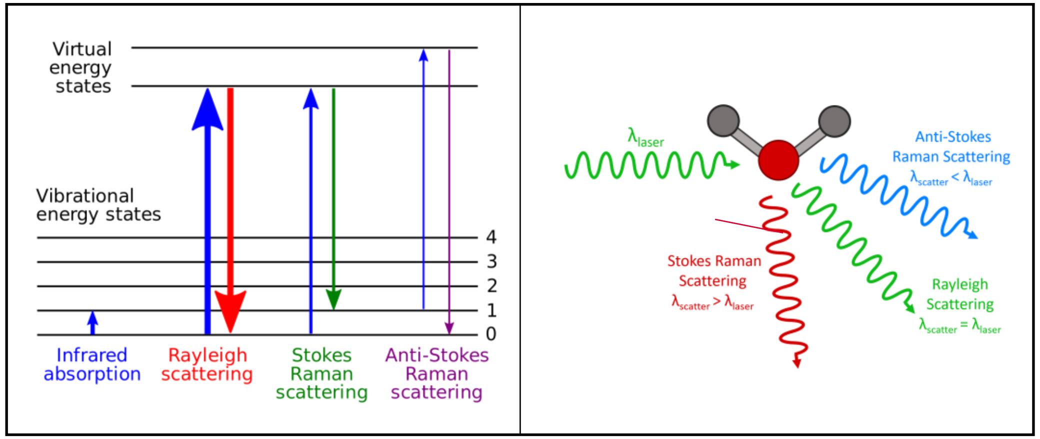
**Tribological test condition:**
- Time 5 minutes
- Load 15 kg
- Temperature: 37 ºC




***Schematic diagram of Pendulum hip simulator***



**Raman analysis condition:**
- Laser 532 nm Green
- Laser power 1 mW
- Exposure time 100s




***Raman Spectroscopic technique***

# Materials and Methods

**Materials for the experiment:**

- **Ball on cup configuration**
- **Lubricants:** *Albumin, γ –globulin, hyaluronic acid and Three types of Model Synovial fluids*

| Test Fluid | Albumin (mg/ml) | γ-globulin (mg/ml) | Hyaluronic Acid (mg/ml) | Phospholipid (mg/ml) |
|---|---|---|---|---|
| Albumin | 28 | | | |
| γ-globulin | | 11 | | |
| Hyaluronic Acid | | | 2 | |
| Healthy Joint (SF1) | 20 | 3.6 | 2.5 | 0.15 |
| After Total Joint Replacement (SF2) | 26.3 | 8.2 | 0.87 | 0.35 |
| Joint with Osteoarthritis (SF3) | 24.9 | 6.1 | 1.49 | 0.34 |

***Synovial fluid lubricants***

***Different types of hip implant balls and cups***

# Materials and Methods

**Experimental Process:**

**Tribological test**

*The analysis of developing method of lubricant film formation in hip replacement, by using Pendulum hip simulator*

**Friction coefficient measurement**

*Measurement of coefficient of friction for three different contact pairs within all the synovial fluid lubricants*

*Preserved for 24 hours in **4 ºC***

**Raman spectroscopic analysis**

*Raman spectroscopic measurement for the lubricants and the implant surface (After and Before the experiment process of The tribological performance of contact pair)*

**Data analysis**

*Analysis of Raman spectra to obtain chemical structure of film and chemical change in lubricants*

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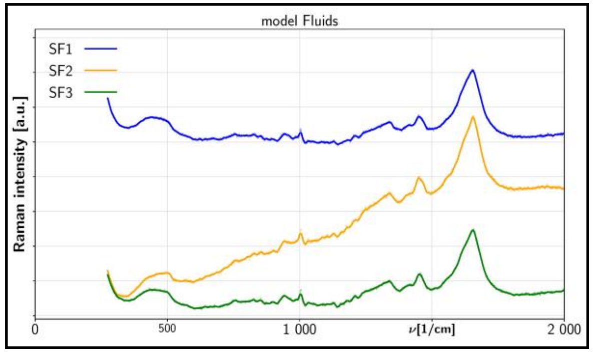
*Observation of correlation within Raman data and coefficient of friction data obtained*

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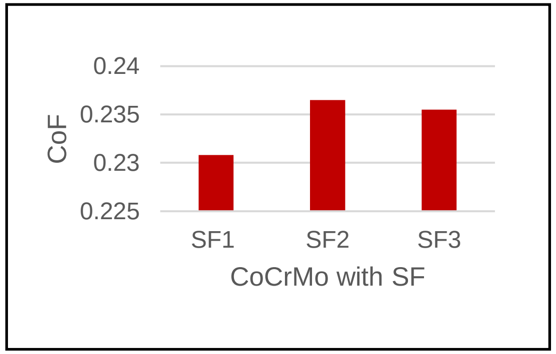
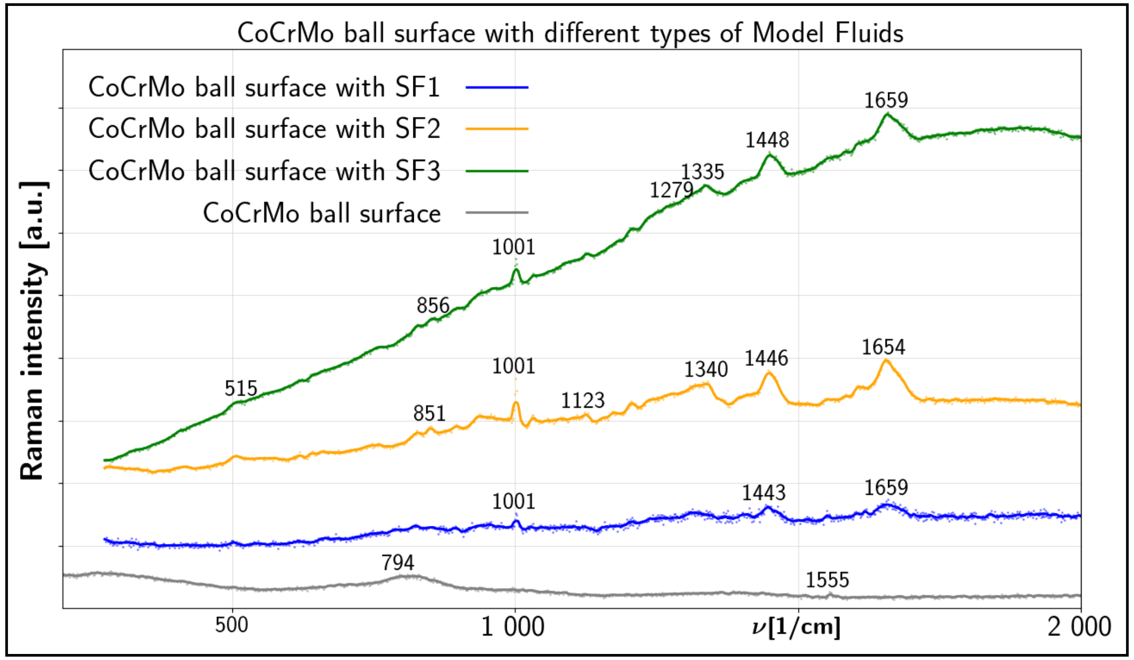



→ ?

# Current state of dissertation

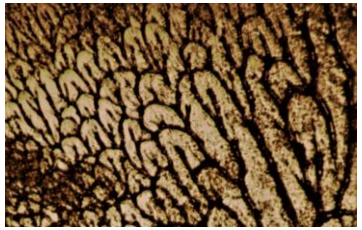



*Raman data of model Synovial Fluid Films on CoCrMo Ball Surface*

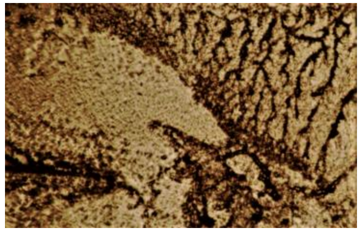
| Types of Model Synovial Fluids | |
|---|---|
| SF1 | Healthy Joint |
| SF2 | After Total Joint Replacement |
| SF3 | Joint with Osteoarthritis |

| Raman Range ($cm^{-1}$) | Chemical Structure | |
|---|---|---|
| 1660-1645 | C=O stretch (C-N, C-N-H) | α- helix Amide I |
| 1473-1446 | $CH_3$, $CH_2$ deformations | n-Alkanes |
| 1300-1265 | C-H, N-H deformation | α- helix Amide III |
| 1411-1174 | $CH_2$-$CH_3$ wagging | |
| 1150-1010 | C-C, C-OH, C-N stretch, C-O-C glycosidic linkage | Protein backbone. |
| 1001 | C-C in-phase symmetric motion | Ring breathing |
| 900-800 | C-C Skeletal Stretch | n-Alkanes |
| 500-460 | C-C Skeletal Stretch -$CH(CH_3)_2$, | Branched alkanes |
| 1555, 794 | CoCrMo Surface without lubricants | |

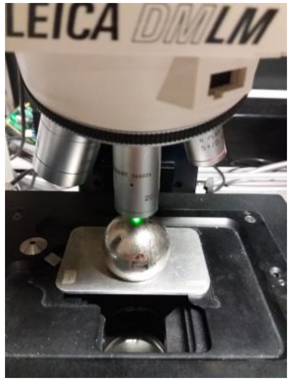
*CoCrMo Ball SF1 on surface*



*CoCrMo Ball SF2 on surface*

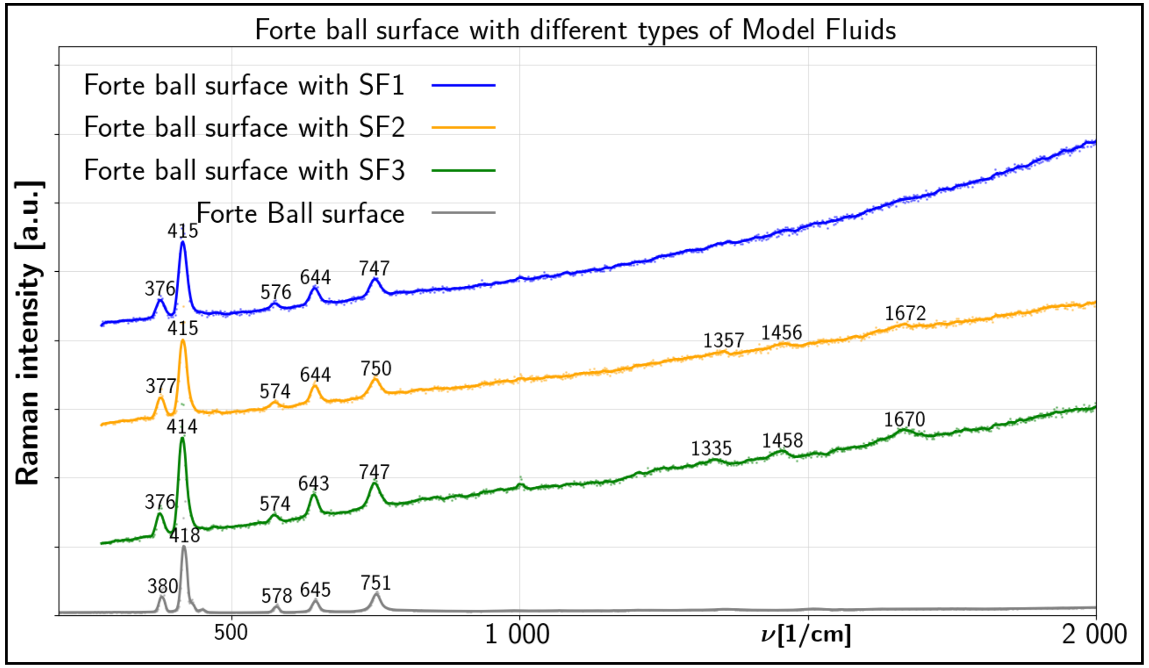


*CoCrMo Ball SF3 on surface*




*Raman Spectroscopic measurements for CoCrMo implant surfaces with SF Lubricant*

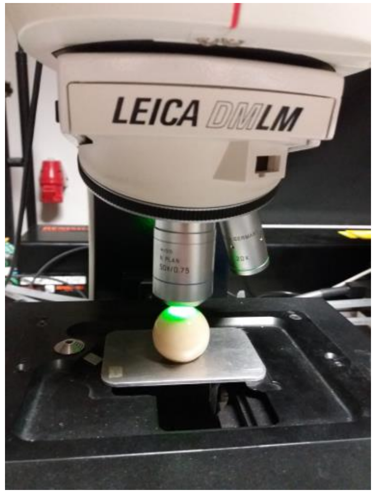
# Current state of dissertation



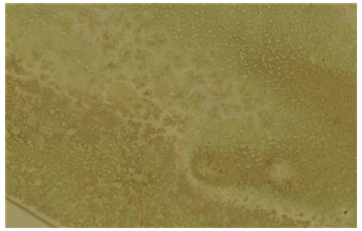

***Raman data of model synovial fluid films on BIOLOX®forte ball surface***

| Types of Model Synovial Fluids | |
|---|---|
| SF1 | Healthy Joint |
| SF2 | After Total Joint Replacement |
| SF3 | Joint with Osteoarthritis |

| Raman Range (cm$^{-1}$) | Chemical Structure | |
|---|---|---|
| 1680-1665 | C=O stretch (C-N, C-N-H) | β sheet Amide I |
| 1473-1446 | $CH_3$, $CH_2$ deformations | n-Alkanes |
| 1411-1174 | $CH_2$-$CH_3$ wagging | |
| 414-421 | Alumina | |
| Rest | Marker bands of implant material | |




***Raman Spectroscopic measurements for BIOLOX®forte implant surfaces with SF Lubricant***

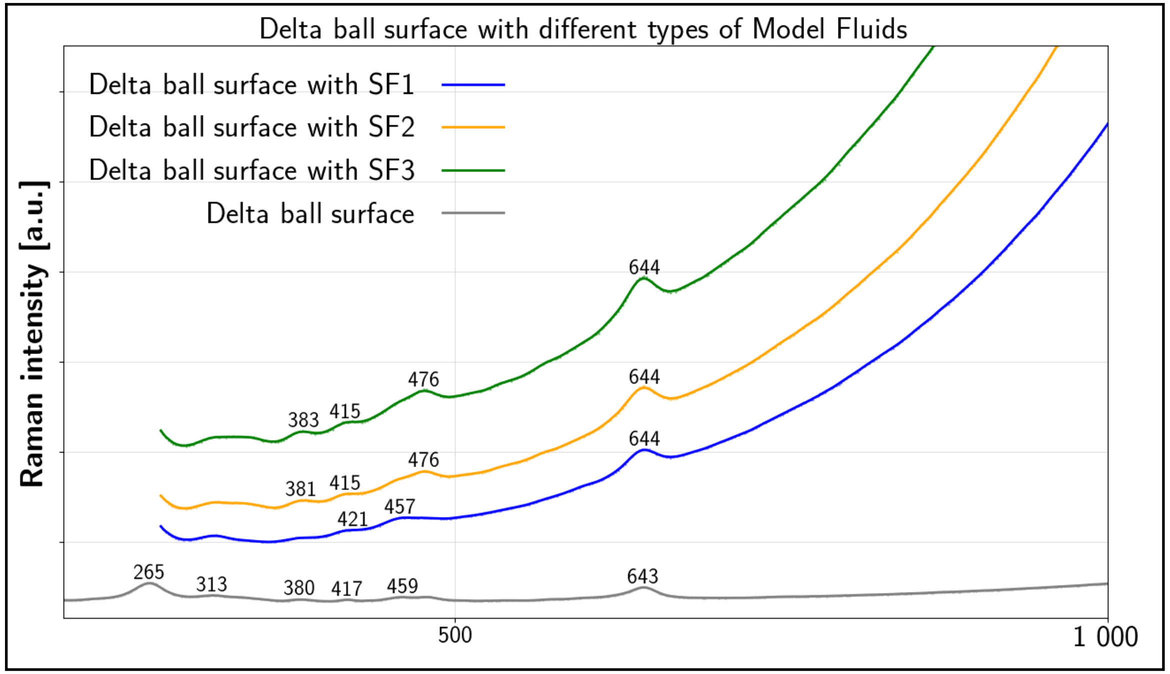


***BIOLOX®forte Ball SF1 on surface***

***BIOLOX®forte Ball SF2 on surface***

***BIOLOX®forte Ball SF3 on surface***

# Current state of dissertation

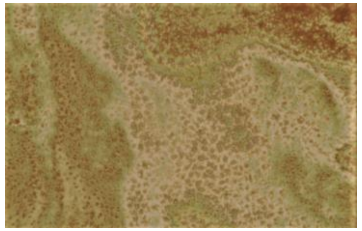



***Raman data of model synovial fluid films on BIOLOX®delta ball surface***

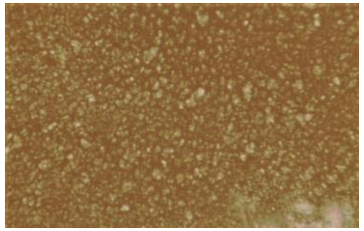
| Types of Model Synovial Fluids | |
|---|---|
| SF1 | Healthy Joint |
| SF2 | After Total Joint Replacement |
| SF3 | Joint with Osteoarthritis |

| Raman Range ($cm^{-1}$) | Chemical Structure |
|---|---|
| 414-421 | Alumina |
| Rest | Marker bands of implant material |

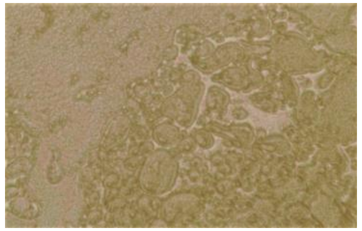
***Raman Spectroscopic measurements for SF Lubricant***



***BIOLOX®delta Ball SF1 on surface***

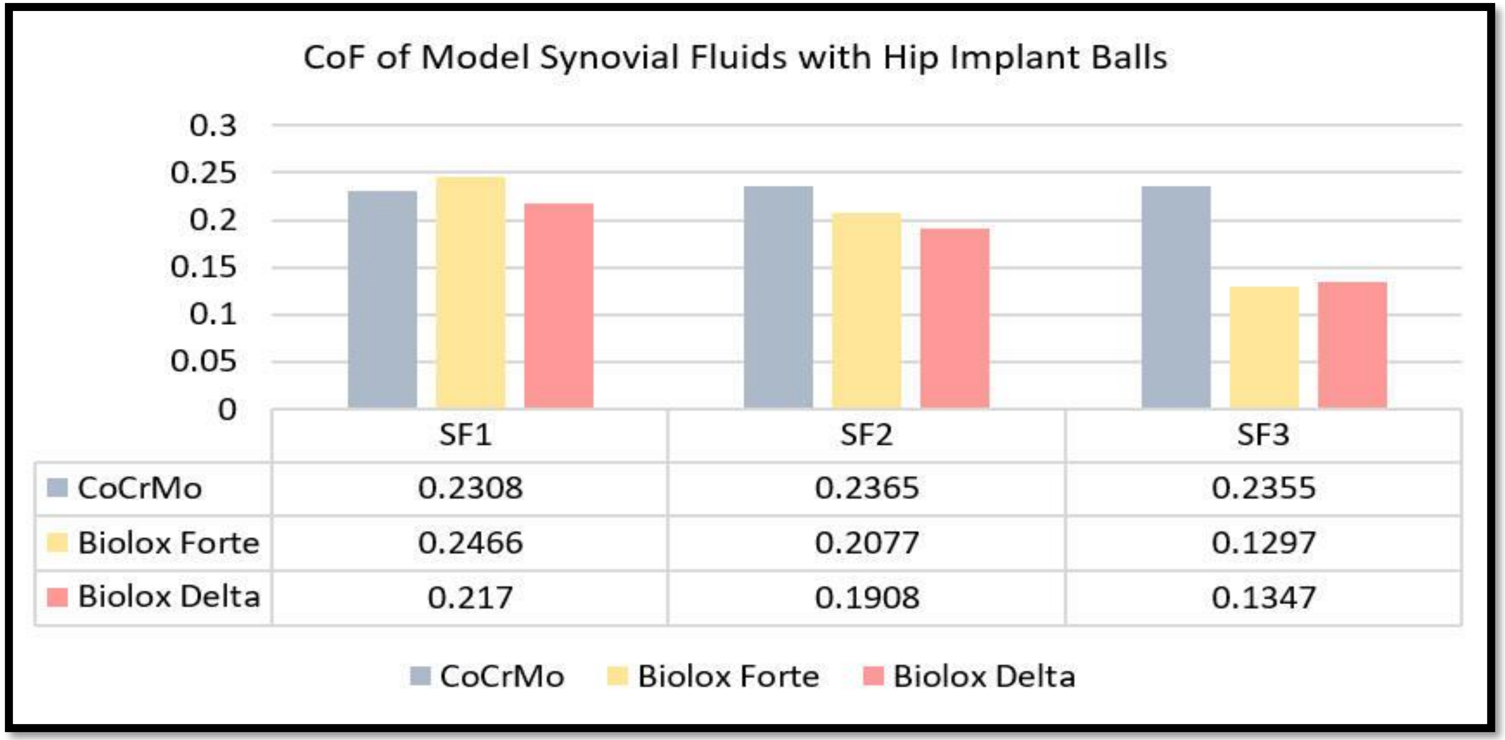


***BIOLOX®delta Ball SF2 on surface***



**BIOLOX®delta Ball SF3 on surface**

# Current state of dissertation




| | SF1 | SF2 | SF3 |
|---|---|---|---|
| CoCrMo | 0.2308 | 0.2365 | 0.2355 |
| Biolox Forte | 0.2466 | 0.2077 | 0.1297 |
| Biolox Delta | 0.217 | 0.1908 | 0.1347 |

***Coefficient of Friction of Model Synovial Fluids with different Hip Implant Balls***

| Types of Model Synovial Fluids | |
|---|---|
| SF1 | Healthy Joint |
| SF2 | After Total Joint Replacement |
| SF3 | Joint with Osteoarthritis |

***Ball-on-cup Configuration within hip joint simulator***

# Overview of achieved results

- Summary of the current state of knowledge
- Arrangement of experimental apparatus
- Preparation of model fluid lubricants
- Methodology of experiment
- Analysis of Raman spectroscopic measurement
- Coefficient of friction measurement of various implants with lubricants
- Influence of chemical reaction on friction in contact
- Interpretation and comparison of the hypothesis and acquired result
- Summary of achieved results

# Conclusions

**Year 2018**

- Methodology development and validation
- Primary results presentation (Engineering Mechanics Conference 2018)
- Analysis of Raman spectroscopic experiment

**Year 2019**

- Study of the coefficient of friction measurement in different contact pairs
- Raman Analysis of HA presentation (STLE Conference 2019)
- Publication on evaluation and method validation - article in an impact journal
- Assessment of Raman spectroscopy and friction with model synovial fluids

**Year 2020**

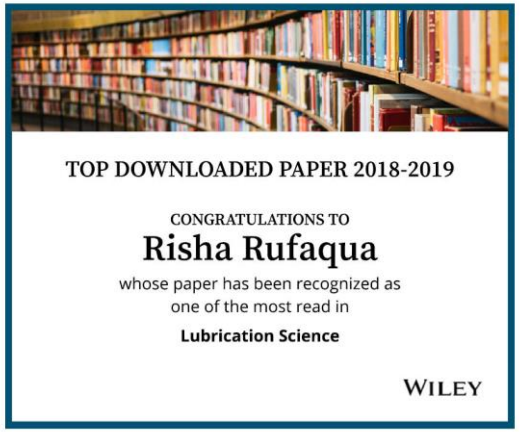
- Publication of results
- Writing dissertation

# Overview of Publications

## Article

Rufaqua, Risha, Martin Vrbka, Dipankar Choudhury, Dušan Hemzal, Ivan Křupka, and Martin Hartl. "A systematic review on correlation between biochemical and mechanical processes of lubricant film formation in joint replacement of the last 10 years." *Lubrication Science* 31, no. 3 (2019): 85-101.

($J_{imp}$–*IF 1,812)*




## Conference paper

Rufaqua, Risha, Martin Vrbka, Dipankar Choudhury, Dušan Hemzal, Ivan Křupka, and Martin Hartl. "The biochemical process of lubricant film formation in joint replacement." (2018).

## Results presentation in Conferences

- **24th International Conference**
  **Engineering Mechanics 2018**
  **Svratka, Czech Republic, (14 -17 May 2018)**
  Rufaqua, R., Vrbka, M., Choudhury, D., Hemzal, D., Křupka, I., and Hartl, M.
  The biochemical process of lubricant film formation in joint replacement

- **74th STLE meeting and exhibition 2019**
  **Nashville, Tennessee USA (19 - 23 May 2019)**
  Rufaqua, R., Vrbka, M., Choudhury, D., Hemzal, D., Rebenda, D., Křupka, I., and Hartl, M.
  Raman spectroscopic analysis of the biochemical reaction of hyaluronic acid in joint replacement

# Cooperation with other Institutions

✓Renishaw Invia setup
✓Raman Spectroscopic Measurement
✓Preparation of Liquid Capillaries

Mgr. Dusan Hemzal, Ph.D.
Department of condensed Matter Physics,
Faculty of Science,
Masaryk University, Brno, Czech Republic.

✓Observation of Analysis
✓Expert Consultancy

Ing. Dipankar Choudhury, Ph.D.
Nano Mechanics and Tribology Laboratory
Department of Mechanical Engineering
University of Arkansas, Fayetteville, AR, USA.

# Thank you for your attention

**Risha Rufaqua**

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