CALCIUM PHOSPHATES (CaP) OCCURRENCE AND PROPERTIES

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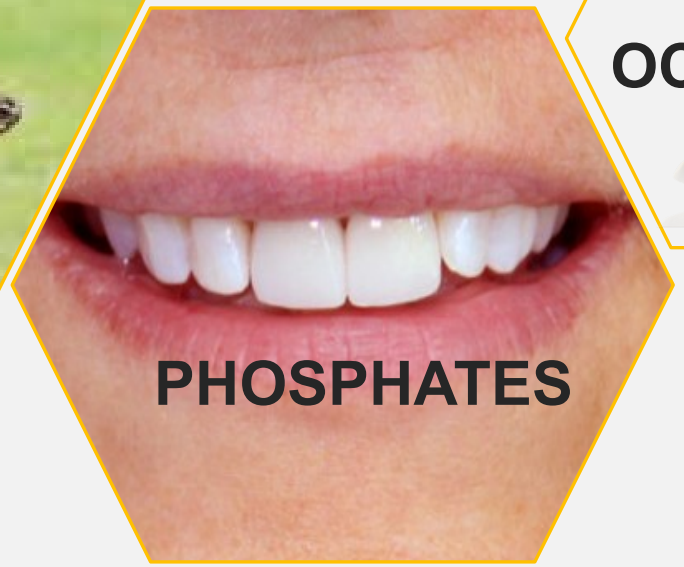
BDS, MSc, PhD (Orthodontics)

CALCIUM

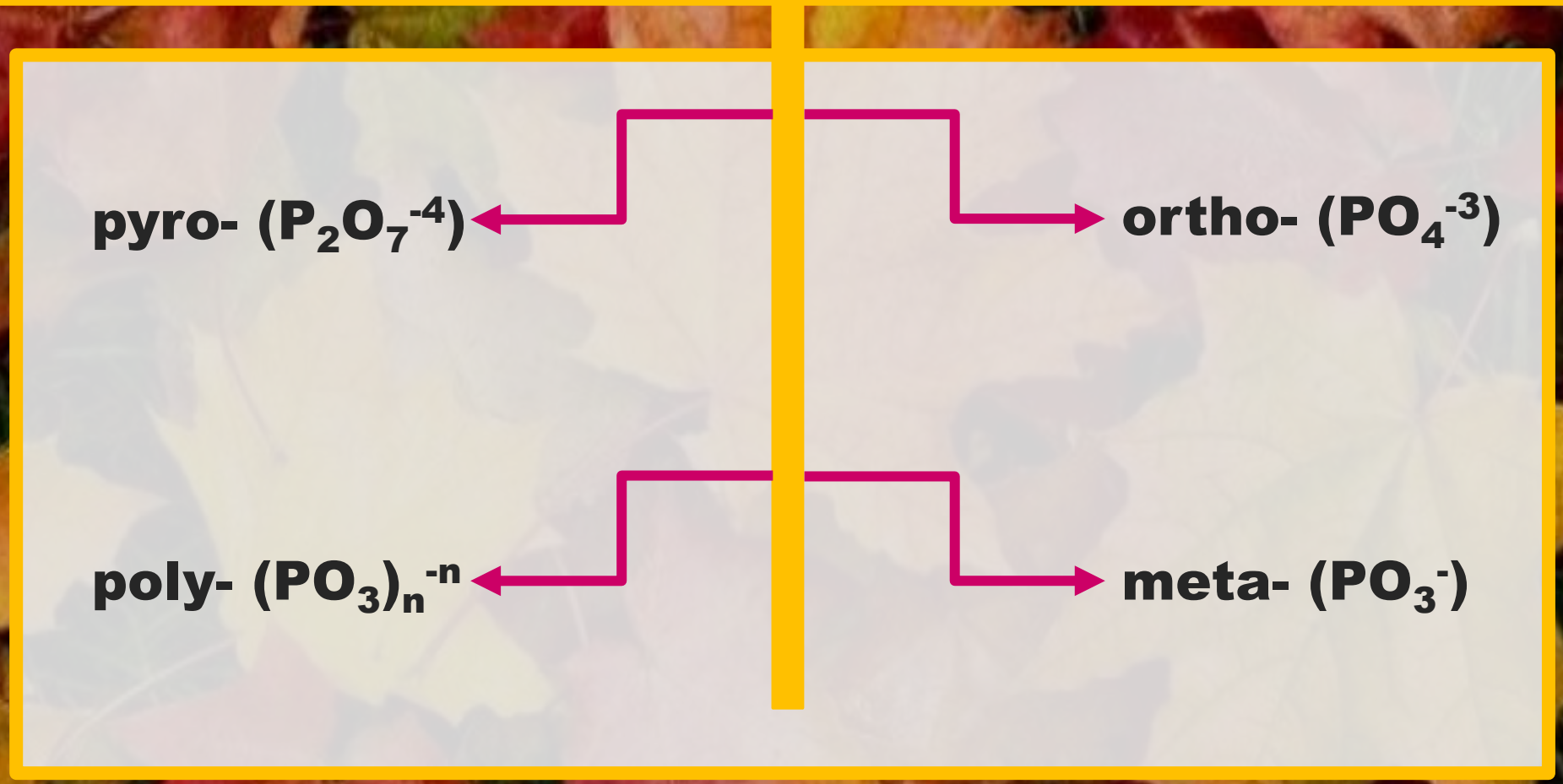


PHOSPHATES

OCCURRENCE

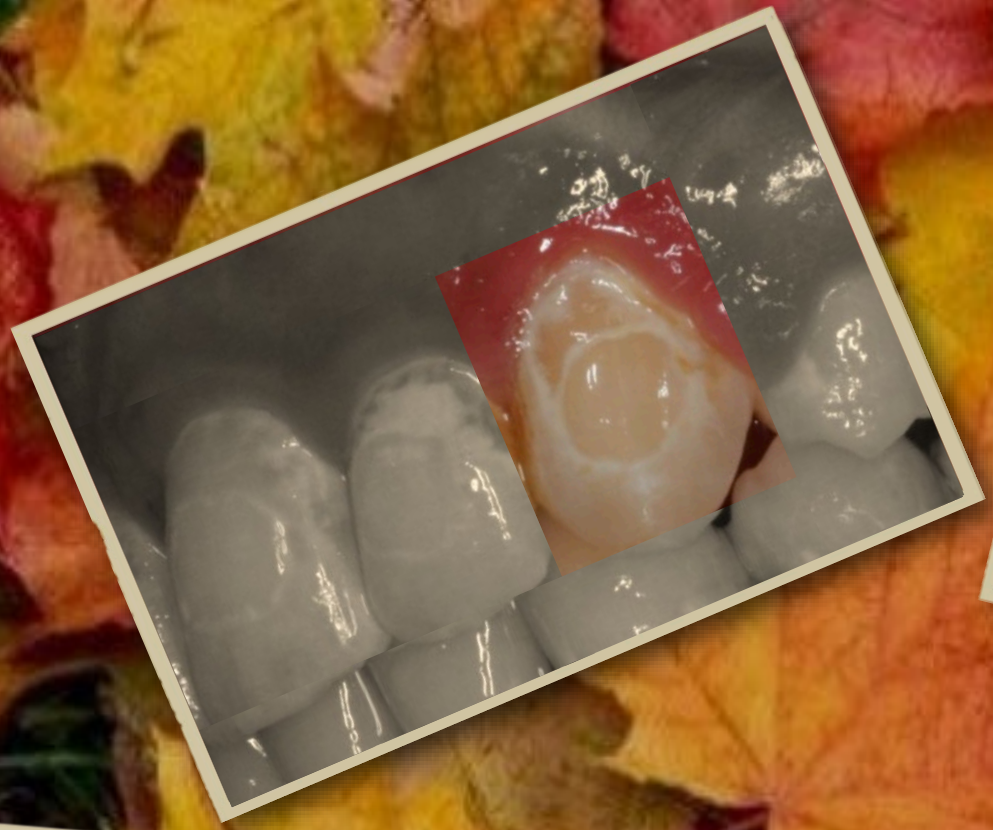
This type of material is of special significance for human beings because they represent the inorganic part of major normal (bones, teeth and antlers) and pathological (i.e., those appearing due to various diseases) calcified tissues of mammals. For example, atherosclerosis, and dental caries

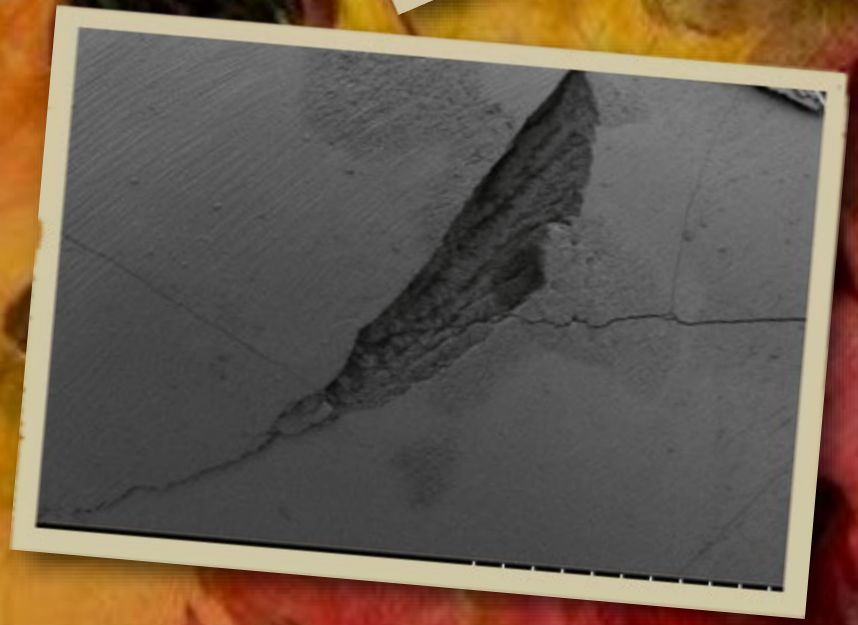
Calcium phosphate (CaP) is the mutual name of minerals family that contains the calcium cations (Ca^{+2}) together with different ionic phosphorous



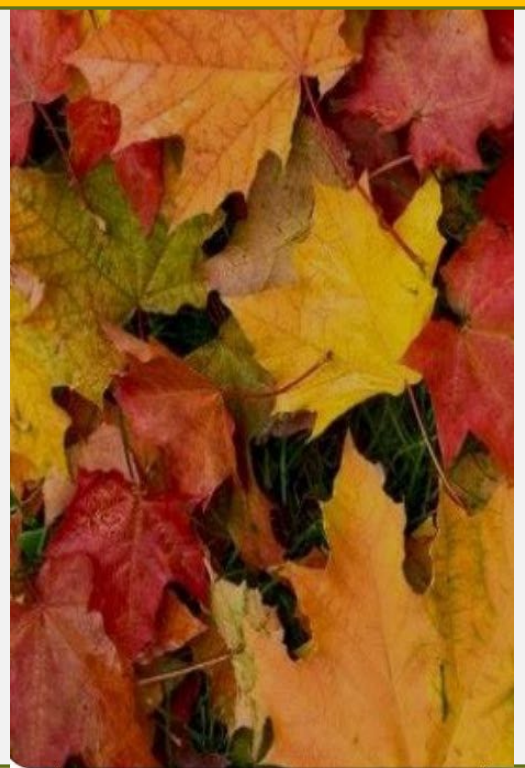
Ca/P molar ratio	Compounds and their typical abbreviations	Chemical formula	Solubility product at 25°C, -log(Ks)	Solubility at 25°C, g/L	pH stability range in aqueous solutions at 25°C
0.5	Monocalcium phosphate monohydrate (MCPM)		1.14	~ 18	0.0 - 2.0
0.5	Monocalcium phosphate anhydrous (MCPA)			~ 17	[c]
1.0	Dicalcium phosphate dihydrate (DCPD), mineral brushite			~0.088	2.0 - 6.0
1.0	Dicalcium phosphate anhydrous (DCPA), mineral monetite			~0.048	[c]
1.33	Octacalcium phosphate (OCP)			~0.0081	5.5 - 7.0
1.5	α -Tricalcium phosphate (α-TCP)			~0.0025	[a]
1.5	β -Tricalcium phosphate (β-TCP)			~0.0005	[a]
1.2 - 2.2	Amorphous calcium phosphates (ACP)	Ca_xH		[b]	~ 5 - 12 [d]
1.5 - 1.67	Calcium-deficient hydroxyapatite (CDHA)	$Ca10-_x$		~0.0094	6.5 - 9.5
1.67	Hydroxyapatite (HA)	C		~0.0003	9.5 - 12
1.67	Fluorapatite (FA)	C	.0	~0.0002	7 - 12
1.67	Oxyapatite (OA)	$Ca_{10}($	~ 69	~0.087	[a]
2.0	Tetracalcium phosphate (TTCP)	$Ca_4(PO_4)_2O$	38 - 44	~0.0007	[a]

[a] These compounds cannot be precipitated from aqueous solutions. [b] Cannot be measured precisely. [c] Stable at temperatures above 100°C. [d] Always metastable.





CaP Characterization techniques



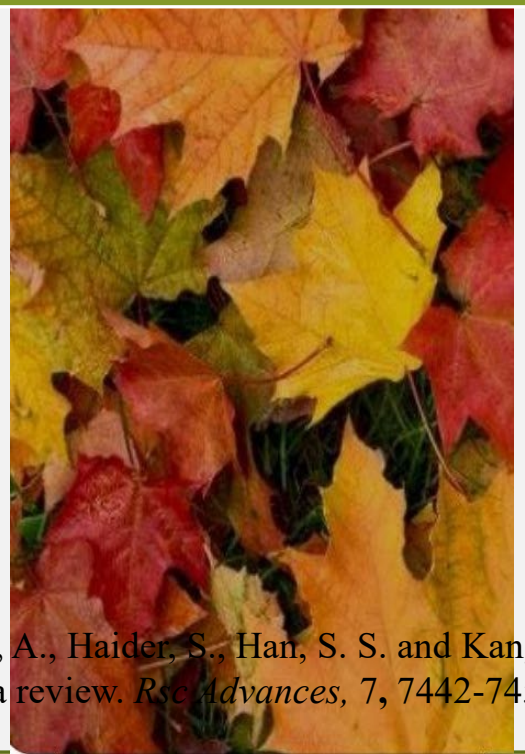
Spectroscopic Techniques

- FTIR
- Raman spectra
- XPS
- XRD
- EDS

Direct visualization

- SEM or FESEM
- TEM
- AFM

Spectroscopic Techniques

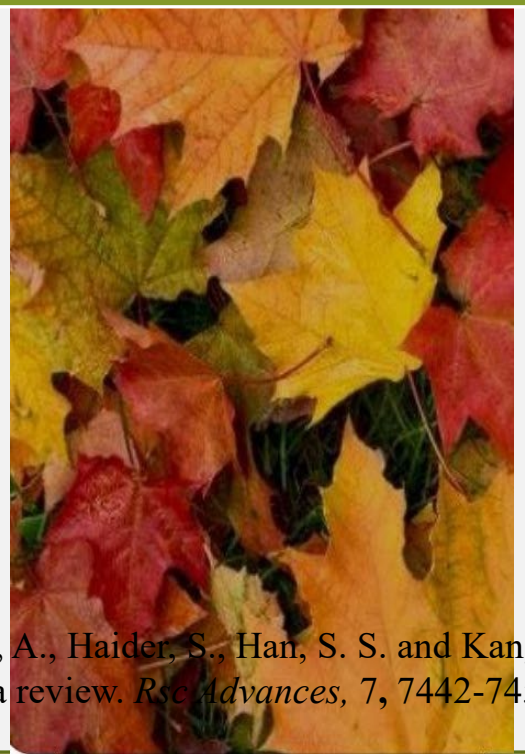


FTIR

- Measures the intensity over a narrow range of wavelengths at a time.
- no external calibration is required.
- Identification of even small concentrations of contaminants.

Haider, A., Haider, S., Han, S. S. and Kang, I.-K. (2017). Recent advances in the synthesis, functionalization and biomedical applications of hydroxyapatite: a review. *Rsc Advances,* 7**,** 7442-7458.

Spectroscopic Techniques



FTIR

Inorganic materials are not easily analyzed by FTIR spectroscopy

Haider, A., Haider, S., Han, S. S. and Kang, I.-K. (2017). Recent advances in the synthesis, functionalization and biomedical applications of hydroxyapatite: a review. *Rsc Advances,* 7**,** 7442-7458.

Spectroscopic Techniques

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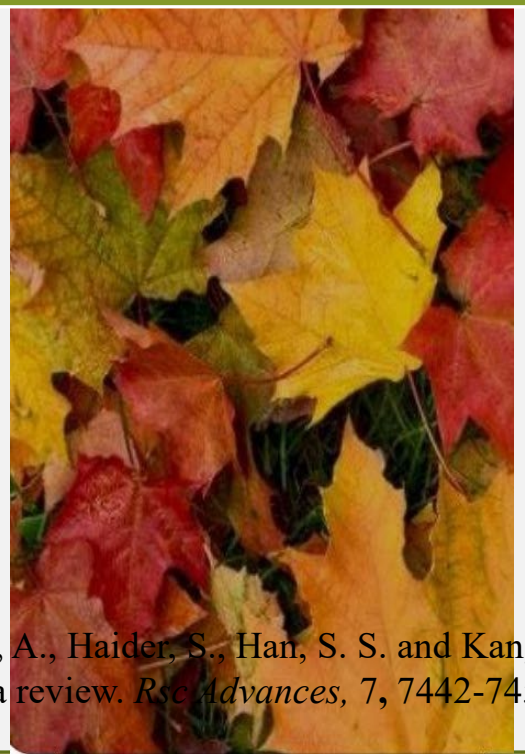
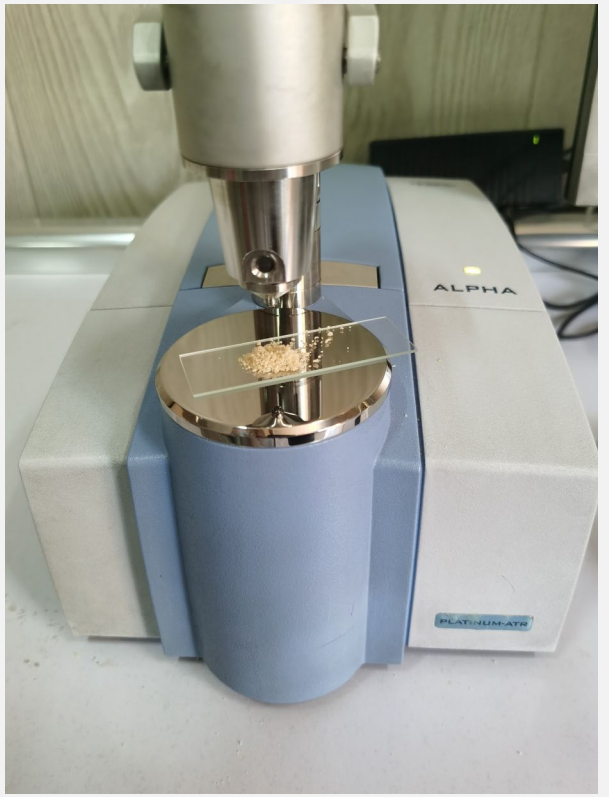


FTIR



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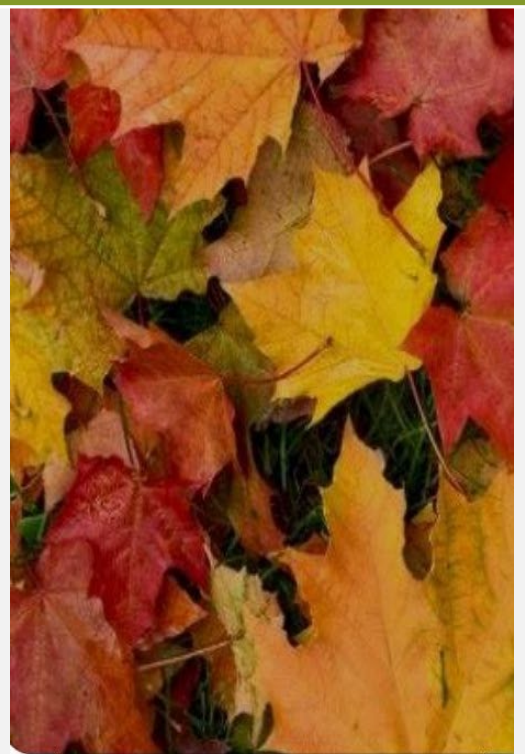
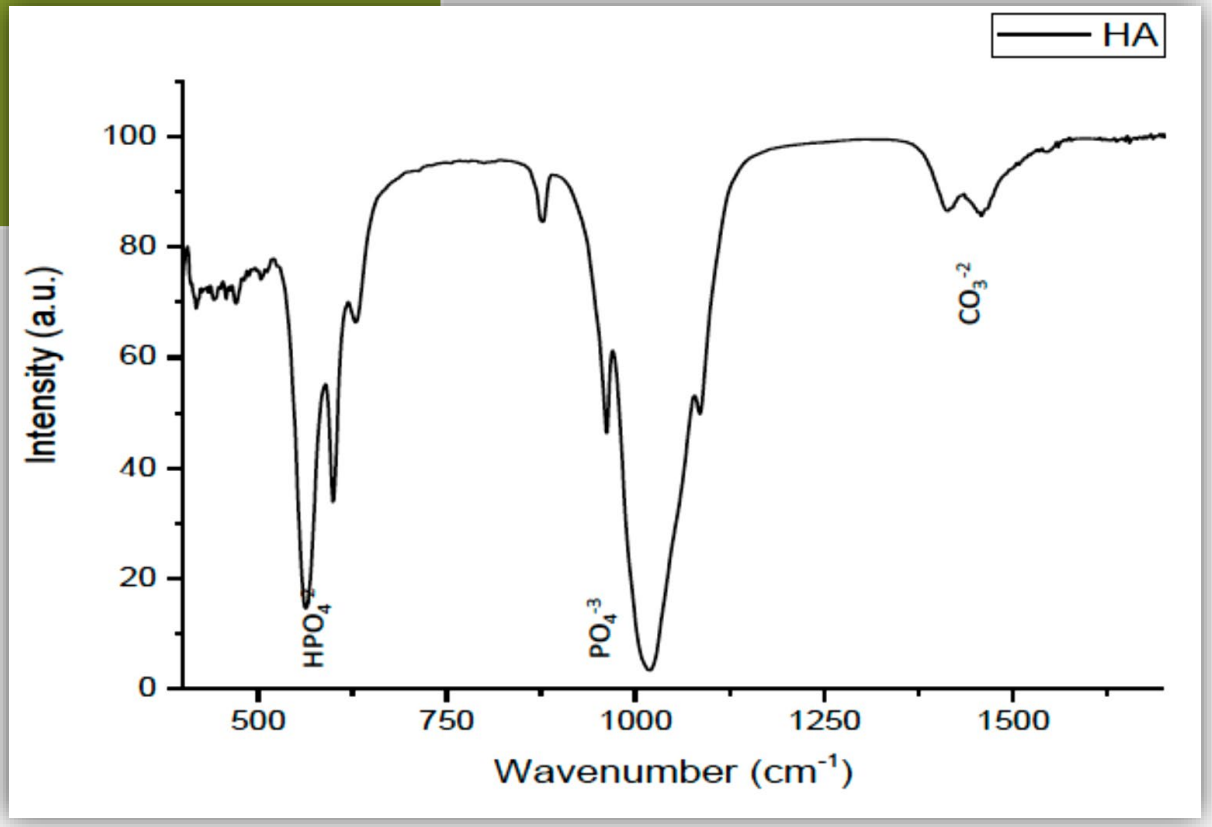
Spectroscopic Techniques

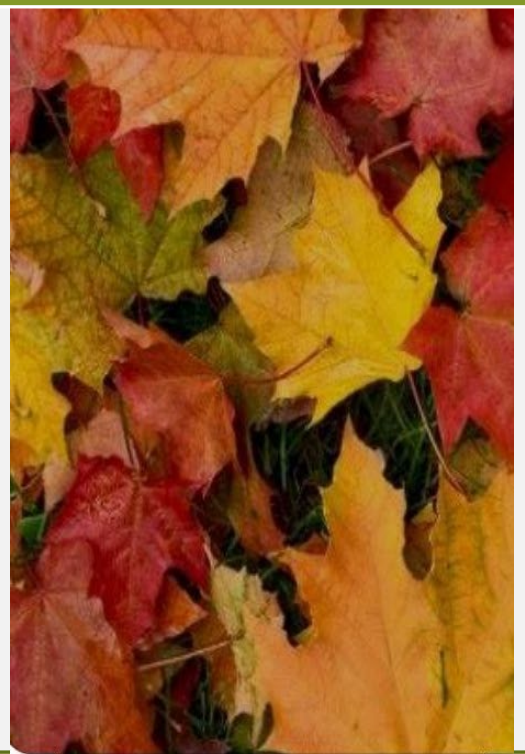


FTIR



peaks at 560 and 1017 cm-1 representing HPO4 and PO4, respectively. peak at 1460 cm-1 indicated CO3.

Spectroscopic Techniques



Raman spectra

- Highly specific
- inorganic materials are easier to analyze

Spectroscopic Techniques

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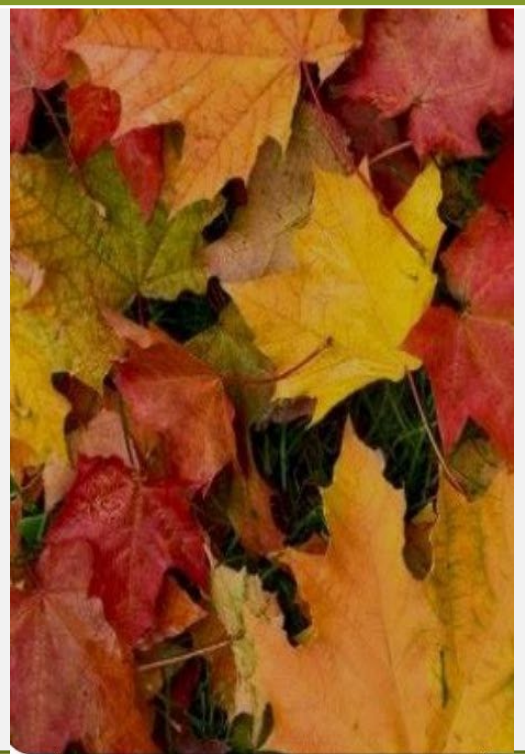

Raman spectra

- The detection requires a sensitive and highly optimized instrument
- Fluorescence of the impurities or of the sample itself can hide the Raman Spectrum
- sample heating.

Spectroscopic Techniques

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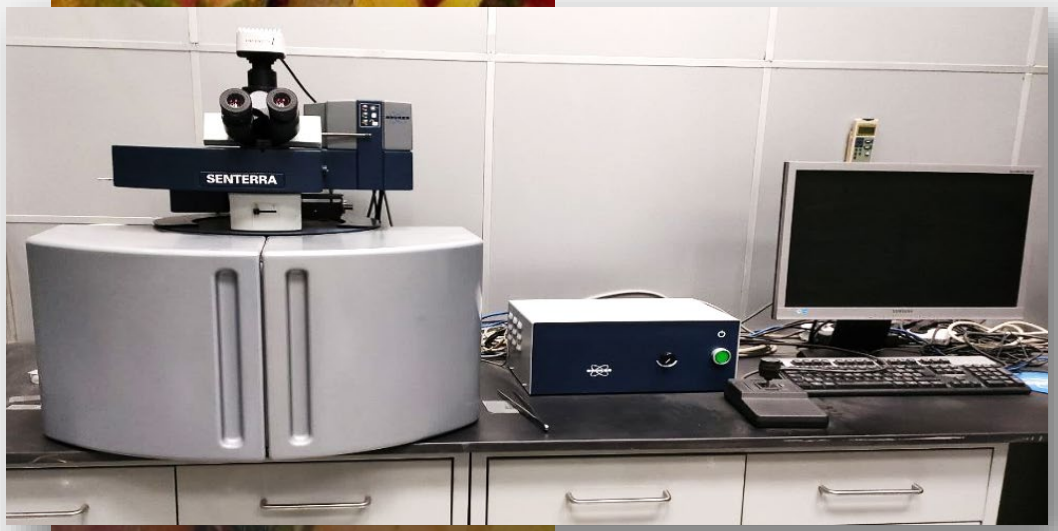
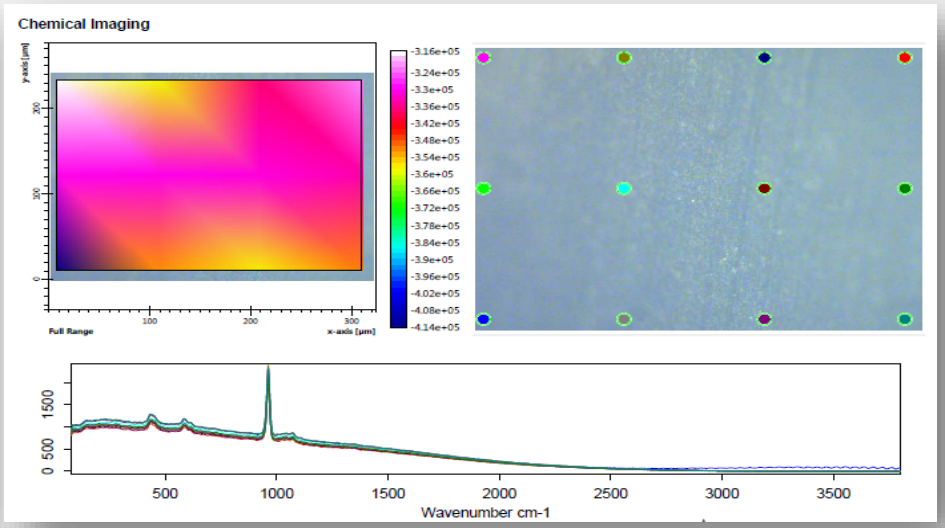
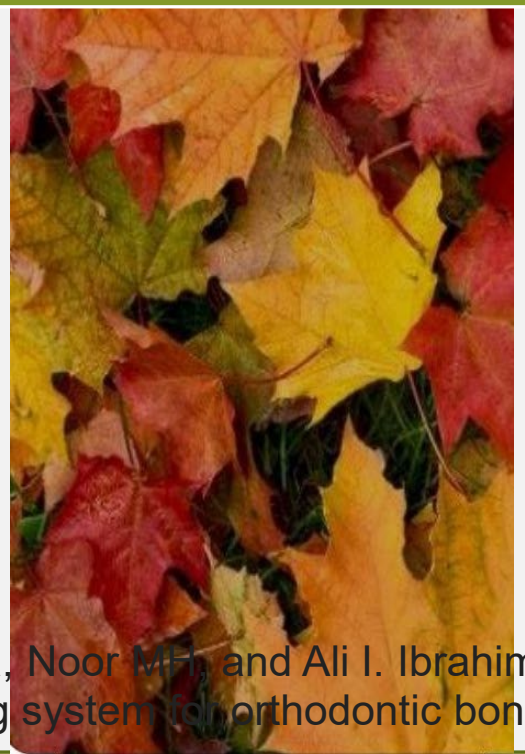
Raman spectra

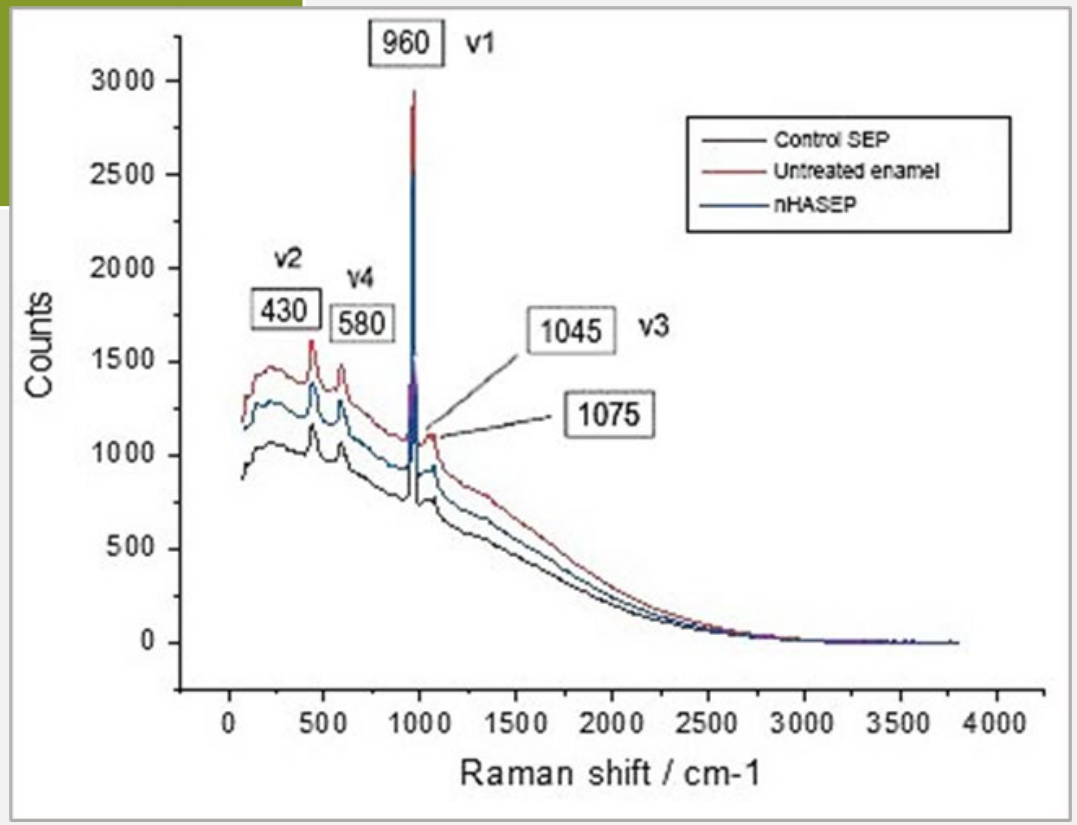




Spectroscopic Techniques

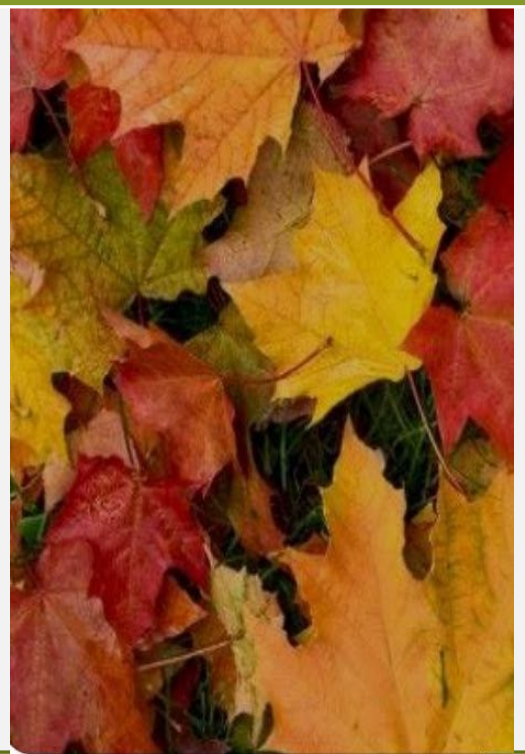


Raman spectra



Garma, Noor MH, and Ali I. Ibrahim. "Development of a remineralizing calcium phosphate nanoparticle-containing self-etching system for orthodontic bonding." *Clinical Oral Investigations* 27.4 (2023): 1483-1497.

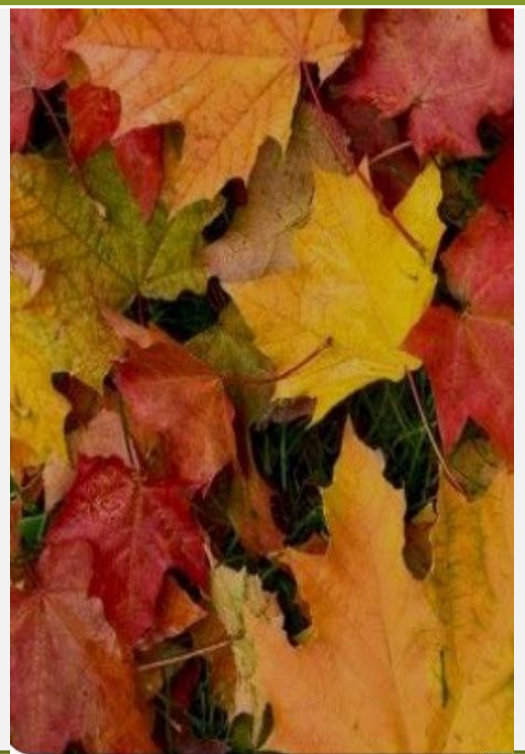
Spectroscopic Techniques



XPS

- Provides unique information about the chemical composition of a material

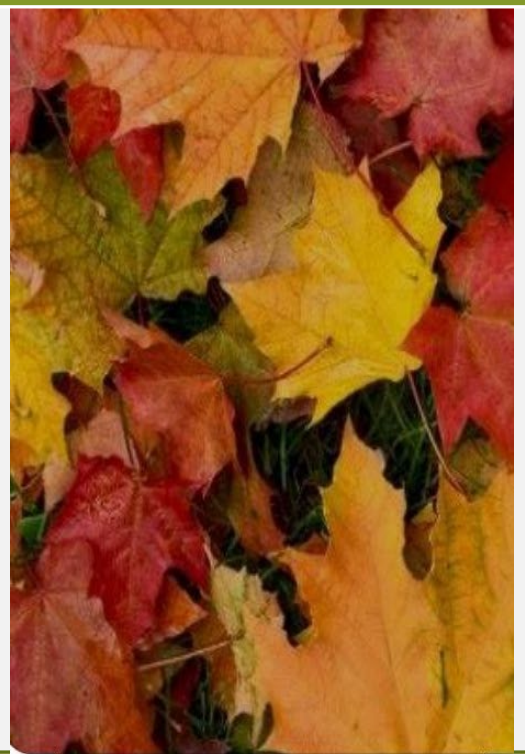
Spectroscopic Techniques



XPS

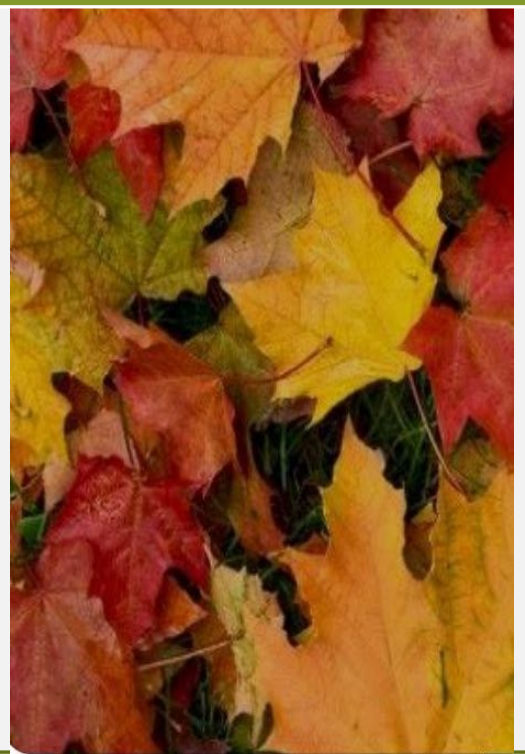
- Slow
- poor spatial resolution
- requires high vacuum

Spectroscopic Techniques



XPS

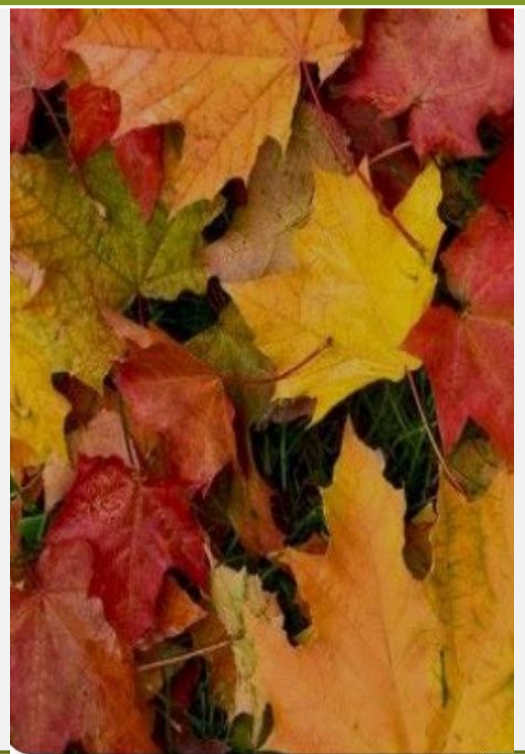
Spectroscopic Techniques



XRD

- Powerful and rapid (<20 min) technique
- provides an unambiguous mineral determination
- data interpretation is relatively straightforward

Spectroscopic Techniques



XRD

- homogeneous and single phase materials are best for identification
- Peak overlay may occur

Spectroscopic Techniques

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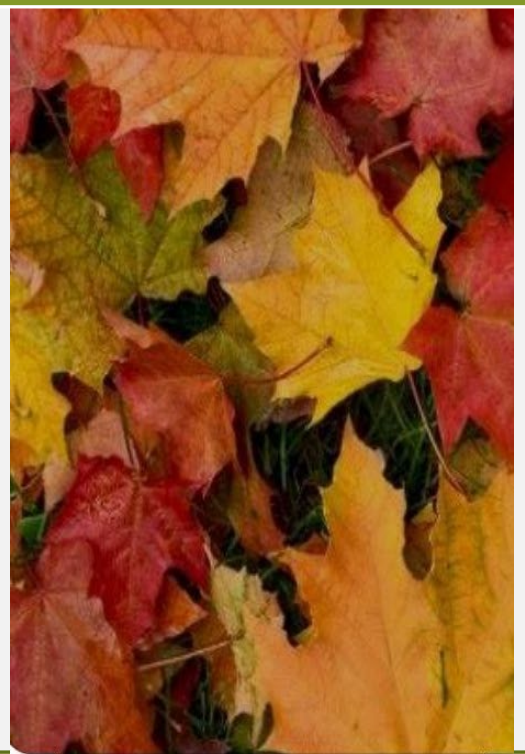
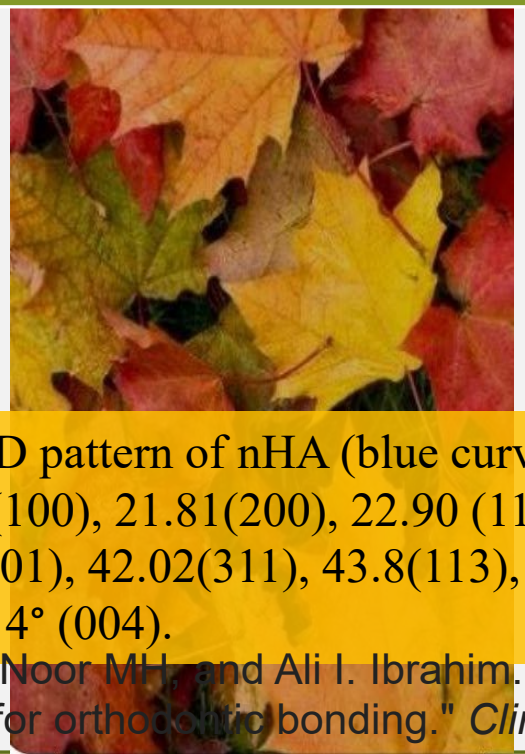
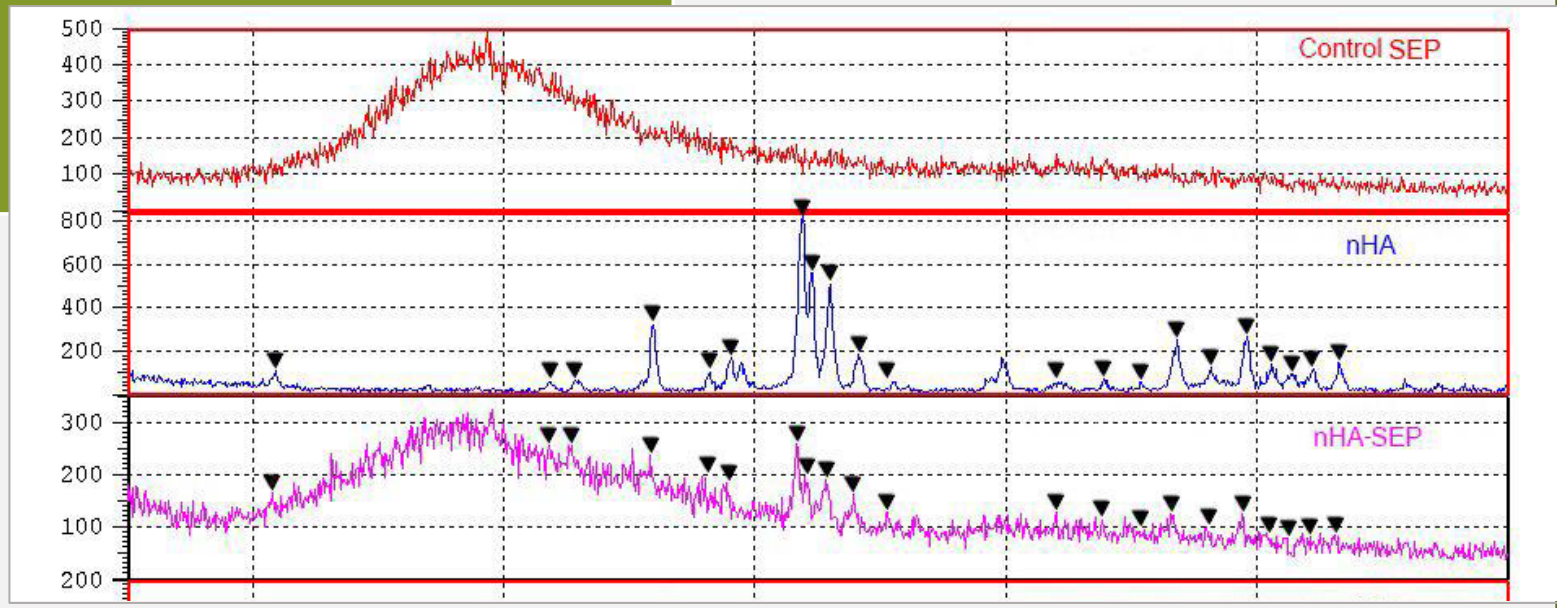


XRD

Spectroscopic Techniques



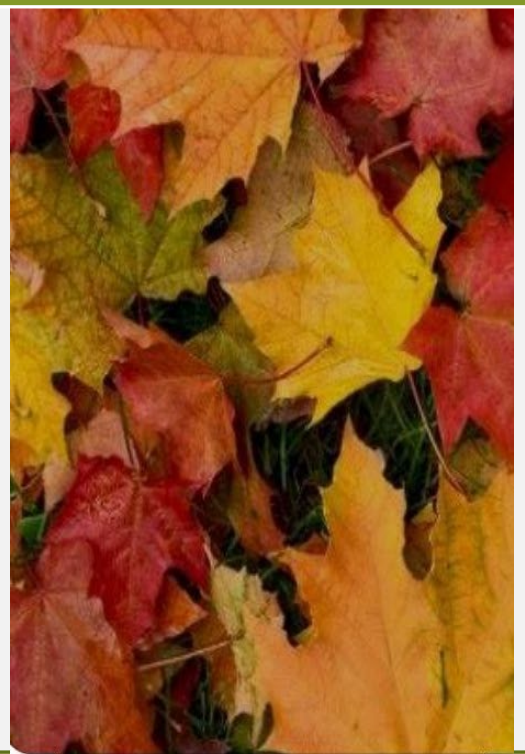
XRD



The XRD pattern of nHA (blue curve) and nHA-SEP (pink curve) exhibited different sharp diffraction peaks located at 2θ =10.82 (100), 21.81(200), 22.90 (111), 25.87 (002), 28.126(102), 28.96(210), 31.77(211), 32.19 (112), 32.9(300), 34.04(202), 35.48 (301), 42.02(311), 43.8(113), 45.3 (203), 46.71(222), 48.10 (312), 49.46 (213), 50.49 (321), 51.28 (410), 52.10° (402), and 53.14° (004).

Garma, Noor MH, and Ali I. Ibrahim. "Development of a remineralizing calcium phosphate nanoparticle-containing self-etching system for orthodontic bonding." *Clinical Oral Investigations* 27.4 (2023): 1483-1497.

Spectroscopic Techniques

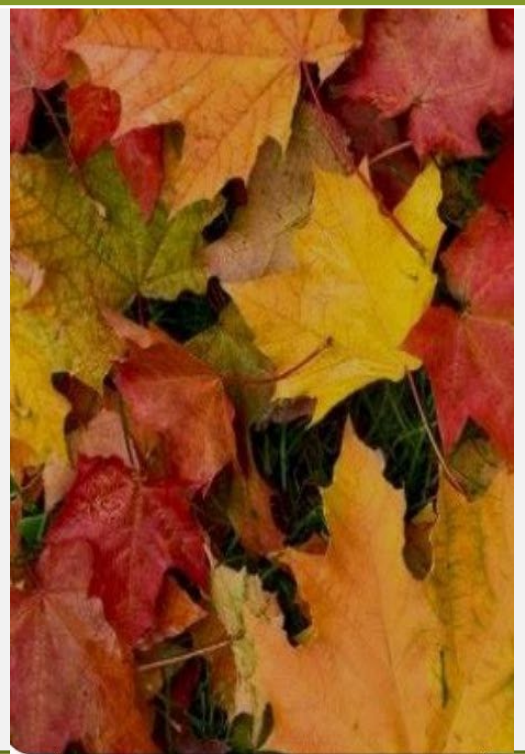


EDS

- Chemical microanalysis technique.
- provides unique peaks characteristic of the atomic structure of the atoms.
- quick and versatile technique.

Spectroscopic Techniques

3-

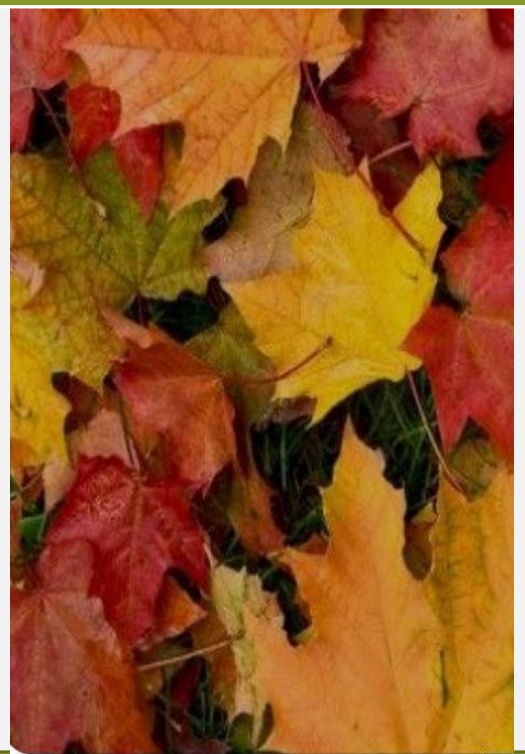


EDS

- semi-quantitative.
- Comparatively lower precision.

Spectroscopic Techniques

3-



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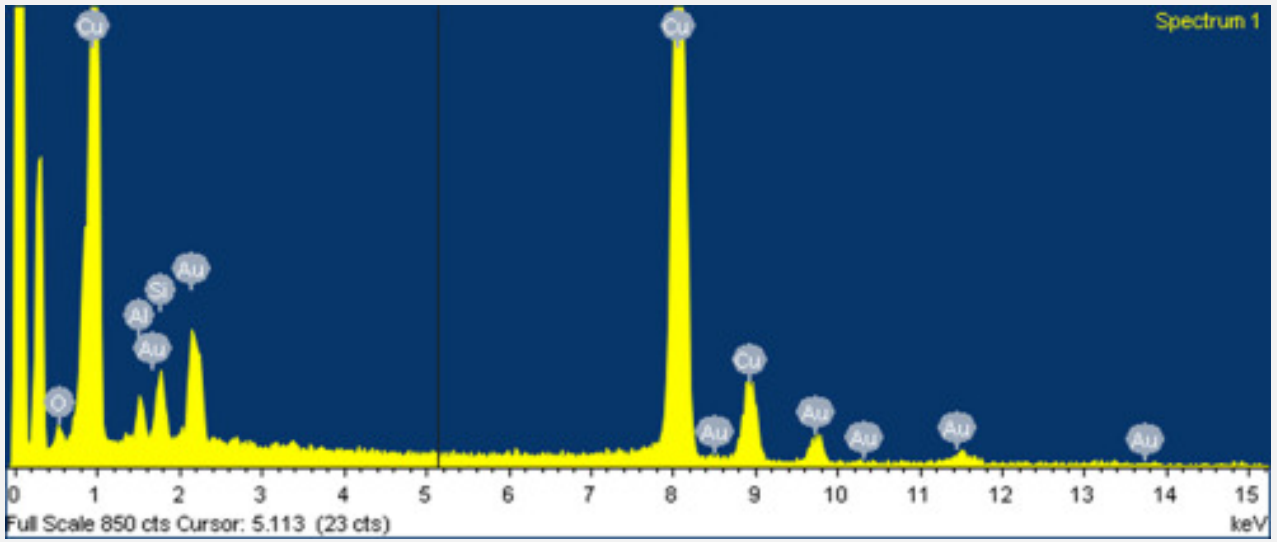

Spectroscopic Techniques

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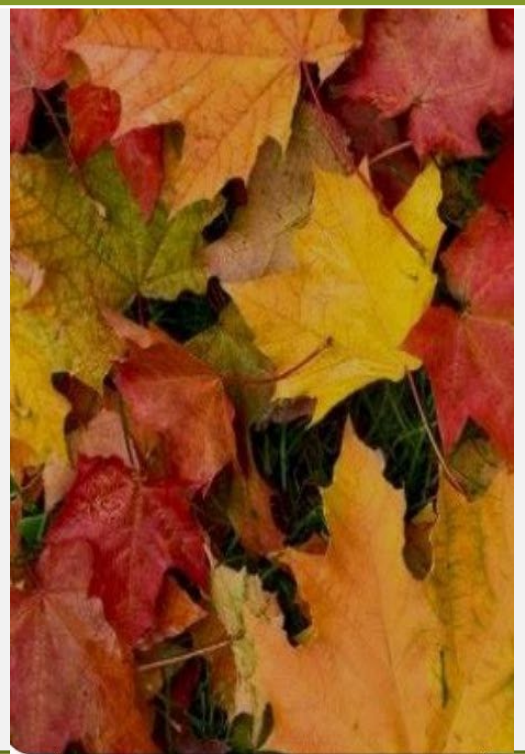
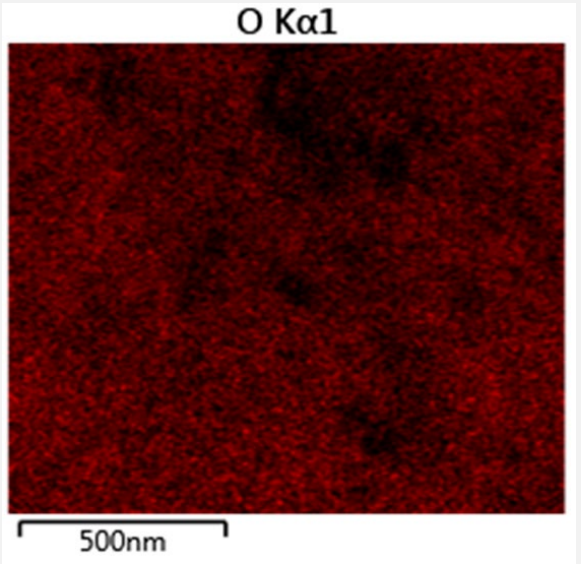
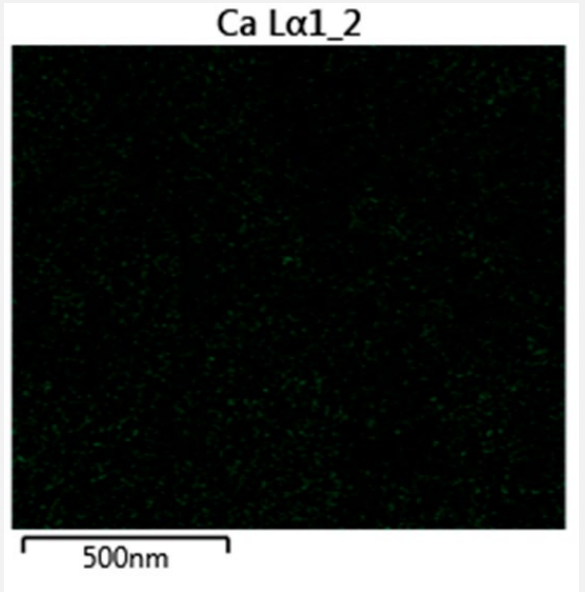
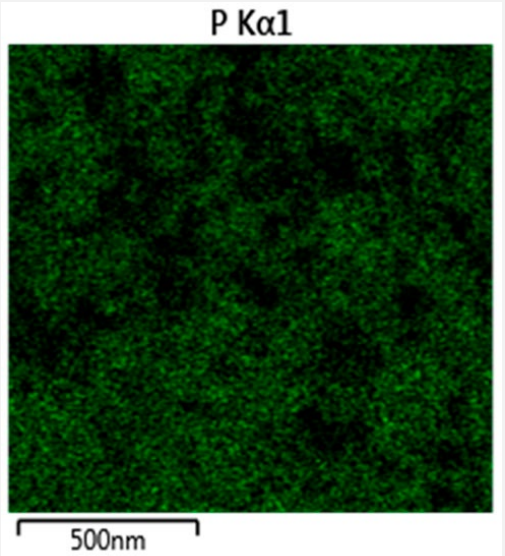


EDS







Direct Visualization Techniques

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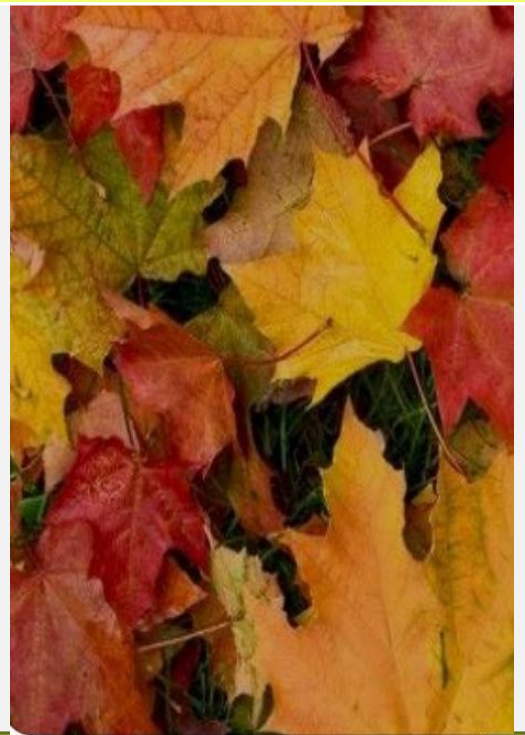
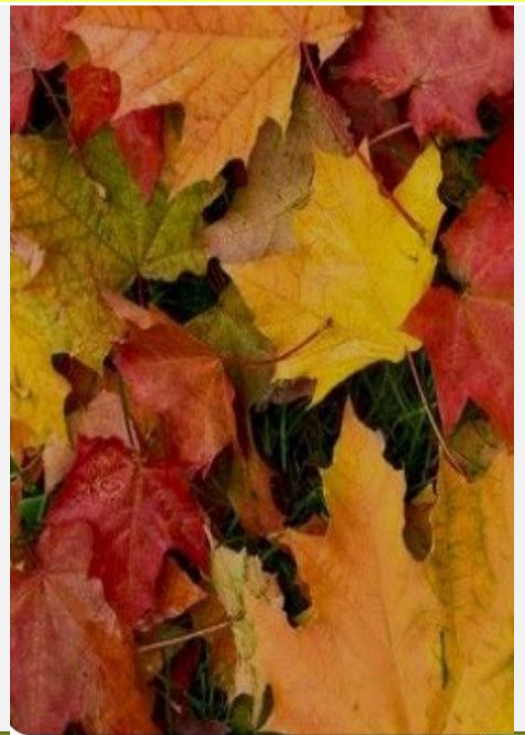


FESEM, TEM, and AFM provide information about the shape, size, morphology, and distribution of the CaP nanoparticles (Haider et al., 2017 ; Balhuc et al., 2021)

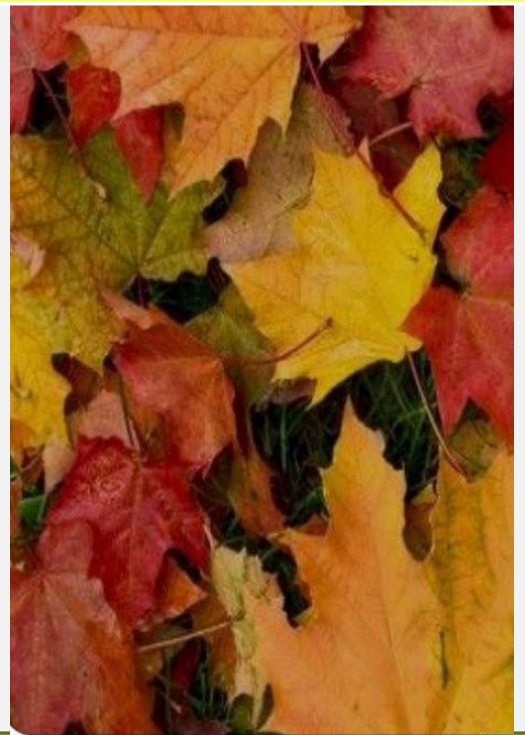
Direct Visualization Techniques



AFM

- High size resolution
- 3D profile.

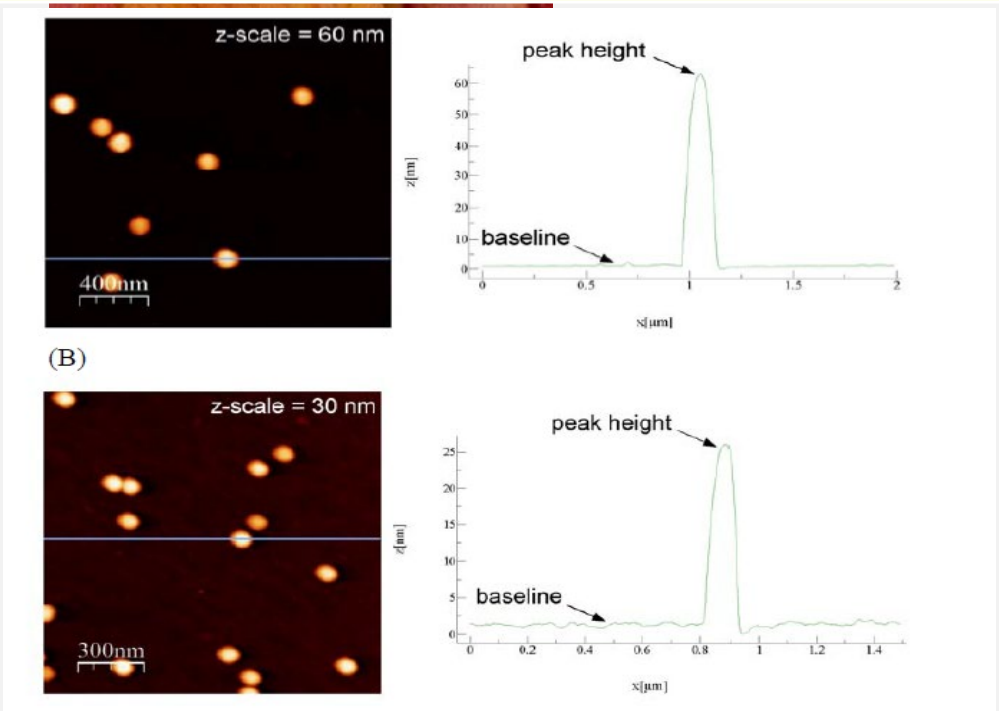
Direct Visualization Techniques

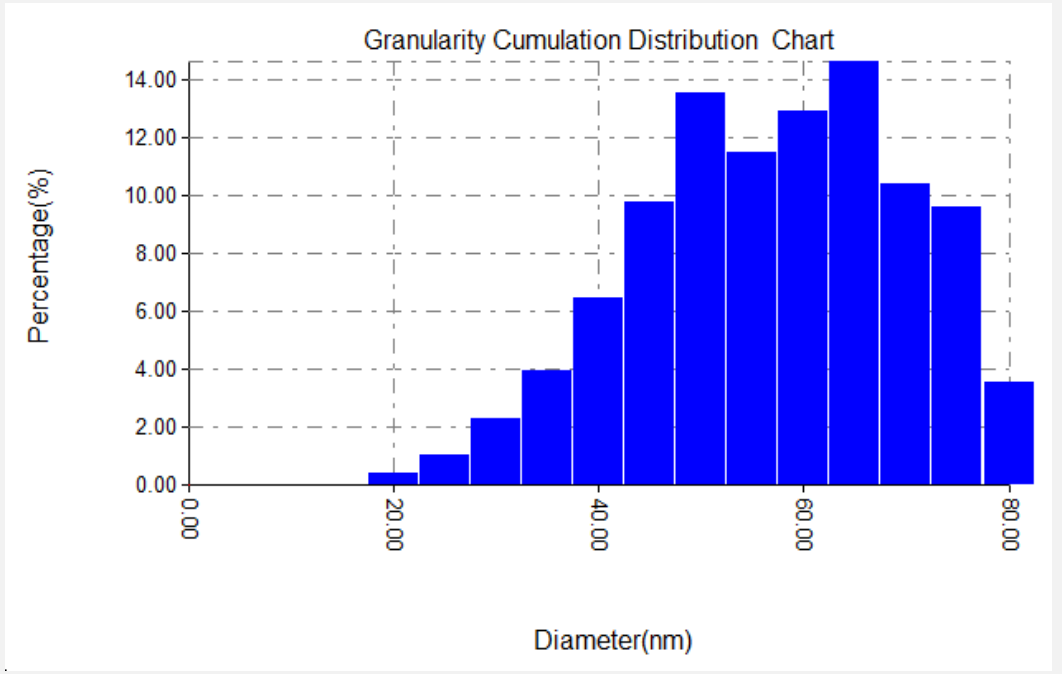


AFM

- Slow speed
- limited scanning area

Direct Visualization Techniques





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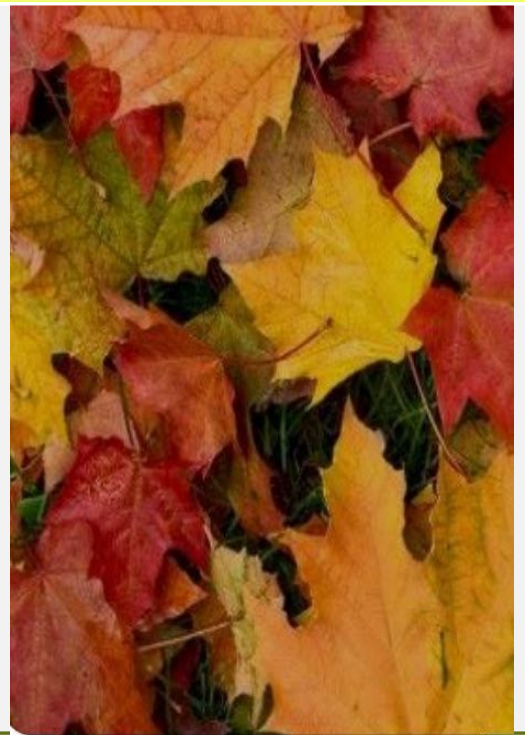
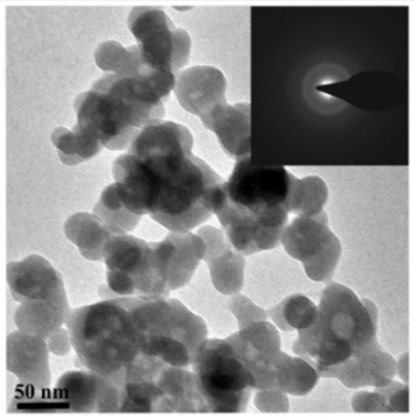
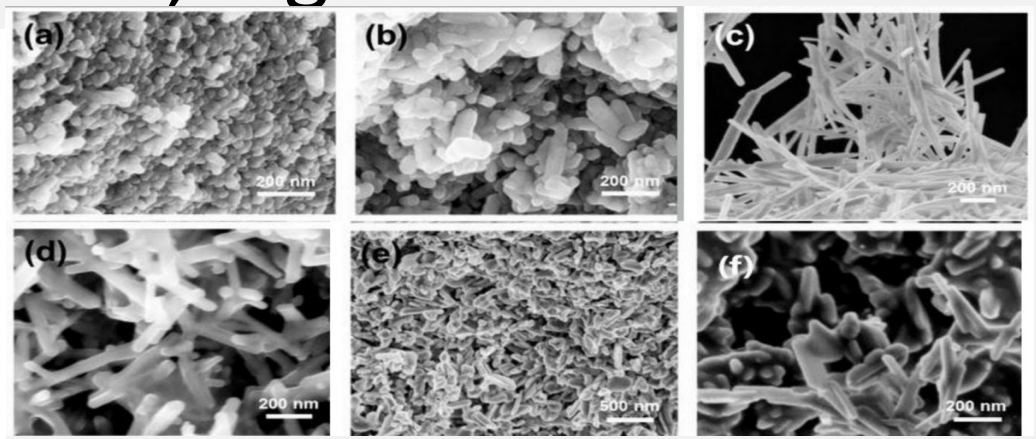


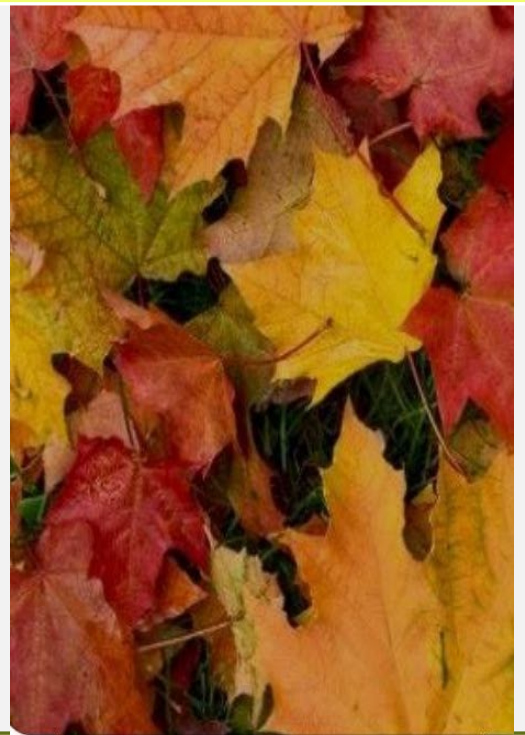
TEM , SEM or FE-SEM

Direct visualization, high resolution

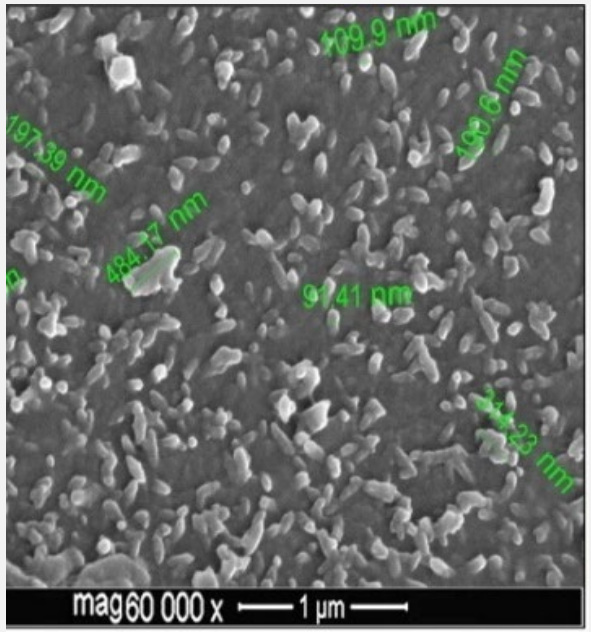


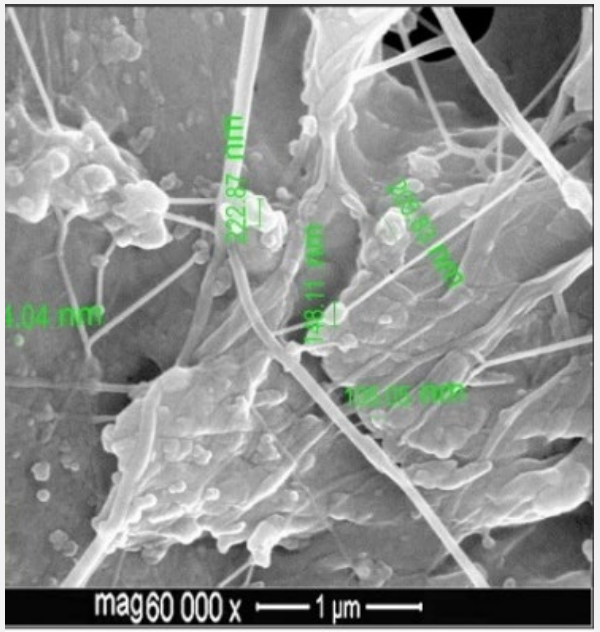


Direct Visualization Techniques



FE-SEM





CONCLUSION

- In spite of almost the 250-year-long history of the CaP_4 research and many important discoveries, still many gaps remain in our knowledge to be investigated in future.
- The knowledge of the specifications and limitations of different characterization techniques entail opportunities to accomplish the task of filling this gap of knowledge.


Thank
you!