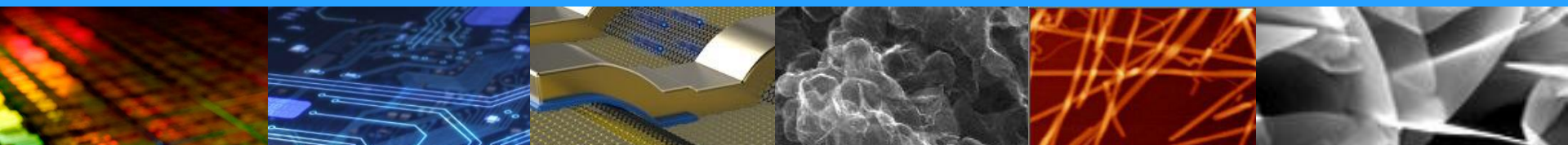
National Physical Laboratory

NPL Good Practice Guide and future standards for Graphene

Charles Clifford

Surface Technology Group, National Physical Laboratory, UK

charles.clifford@npl.co.uk



NPL: Who are we

The UK's national standards laboratory world-leading **National Measurement Institute**

~750 staff; State-of-the-art laboratory facilities

Critical importance of **Partnership** with industry and academia

New model - NPL operates as a government company, wholly owned by BEIS (business dept).

We provide confidence in measurement with independence integrity and impartiality, and accelerate the application of Science & Technology

Surface Technology Group

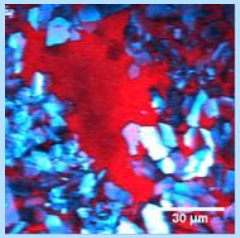
NPL National Physical Laboratory

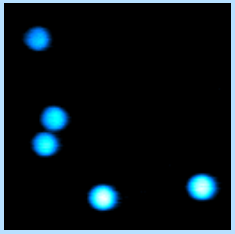
Standards

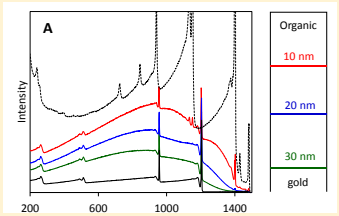
Unique reference materials, interlaboratory studies and documentary standards

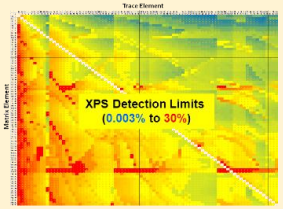
Surface Chemical Analysis

Improved methods for surface analysis: XPS, UPS, AES, SIMS, ISS, AFM, TERS







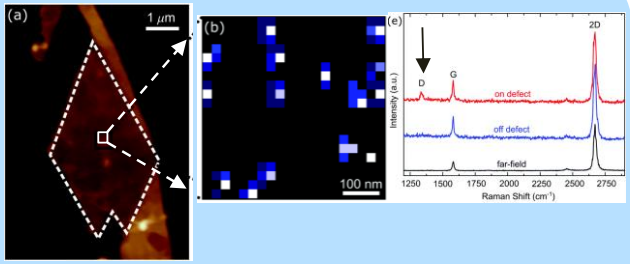


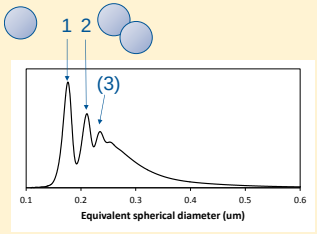
Real Time, *in-situ* Chemical Imaging

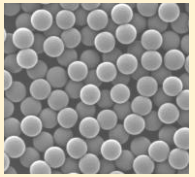
Raman spectroscopy and imaging, stimulated Raman and non-linear optical imaging

Nanoparticle Analysis

Accurate and novel methods for particle size, concentration, chemistry and structure







Graphene and 2D Materials

Supporting industrial uptake of novel materials: accurate and practical measurements

Graphene at NPL

NPL National Physical Laboratory

- NPL has 20+ scientists and engineers working on 2D material related projects (and 10+ students)
- Improved access for Industry, Academia and Government to 2D material capability across NPL:
  - Characterisation
  - Metrology for Graphene
  - Graphene for Metrology
  - Standardisation
  - Quality Control

NGMC National Graphene Metrology Centre

- Different properties of materials require different approaches
- Formalised strategic partnering with key organisations

What is a standard?

A standard is a …

'document, established by consensus and approved by a recognized body, that provides, for common and repeated use, rules, guidelines or characteristics for activities or their results, aimed at the achievement of the optimum degree of order in a given context'

(ISO/IEC Guide 21-1:2005, 3.1)

International Organization for Standardization

NPL National Physical Laboratory

ISO TC 201 Surface Chemical Analysis
ISO TC 229 Nanotechnologies

VAMAS

Pre-standardisation interlab testing

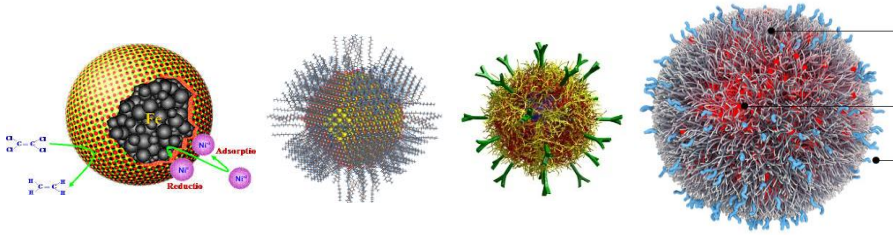
VAMAS TWA2 - Surface chemical analysis
VAMAS TWA34 - Nanoparticle populations
VAMAS TWA41 - Graphene
VAMAS TWA42 - Raman

Industrial Developments in Nano

High Volume, low Cost

- Production volume can outstrip application need
- Race to the lowest price
- Leads to poor quality
- Garbage in, Garbage out
- Standards necessary for quality and assurance !

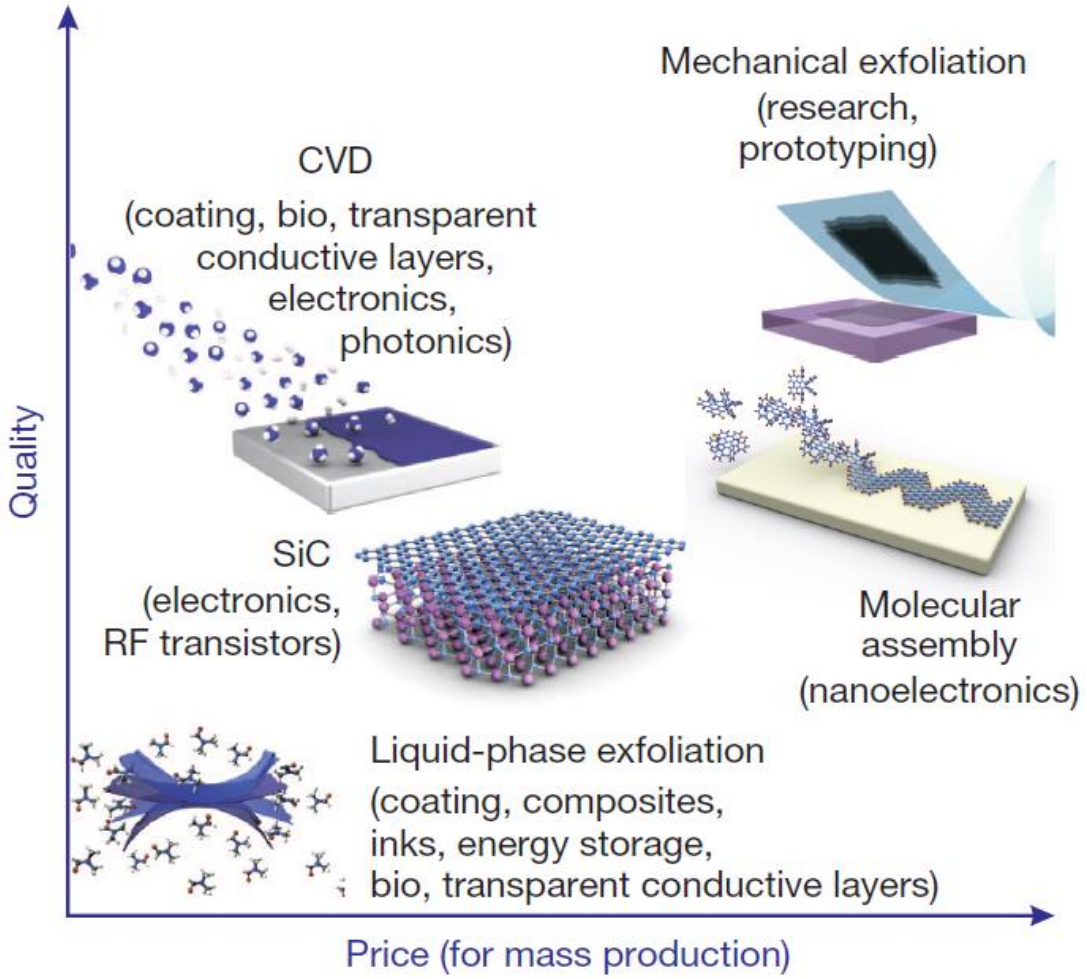
Highly specialised



- Particle properties tailored to application
- Highly specific size, shape, chemistry, surface chemistry
- Need Standards!

Graphene and related 2D Material Production

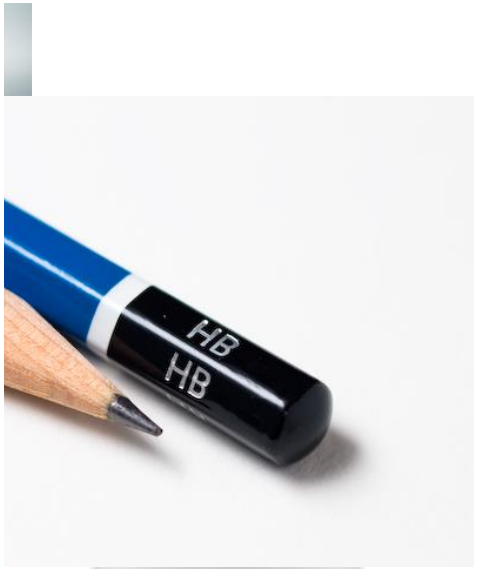
- Many different ways of producing graphene
- Difference:
  - Scalability
  - Dimensions
  - Level of disorder/defects ('quality')
  - Cost
  - Application compatibility
- Can be separated into two groups
  - Graphene on a substrate
  - Graphene powder/dispersion



Novoselov *et al.* Nature. **490,** 192 (2012)

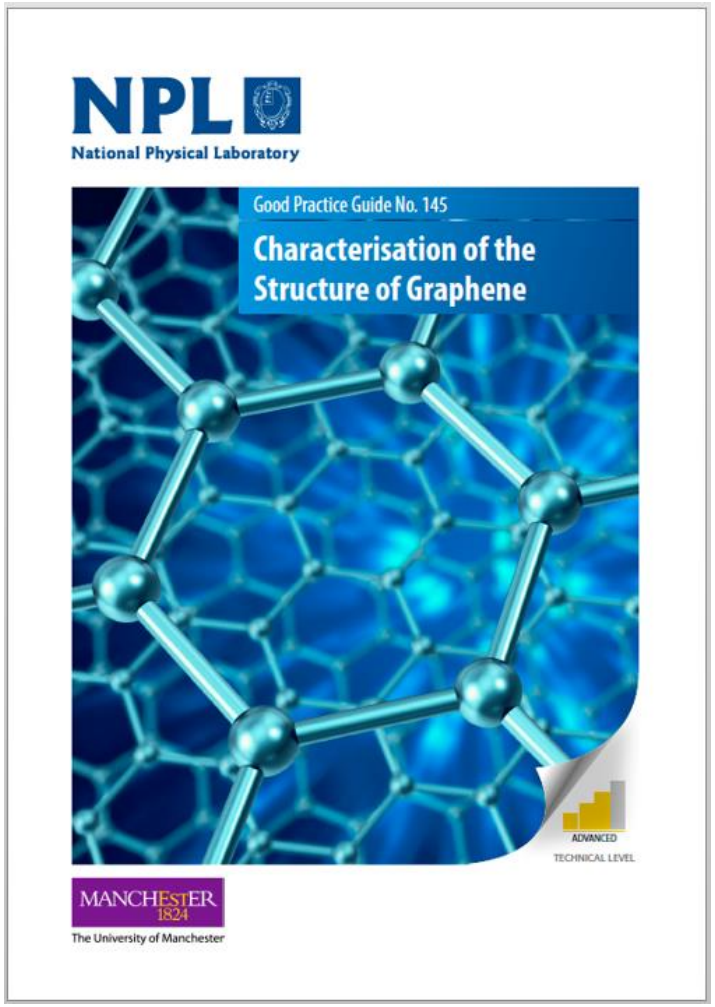
What is this stuff?!

NPL National Physical Laboratory



www.graphenea.com
www.appliedgraphenematerials.com
DerHexer, Wikimedia Commons, CC-by-sa 4.0
www.davidkelly.me

NPL Good Practice Guide

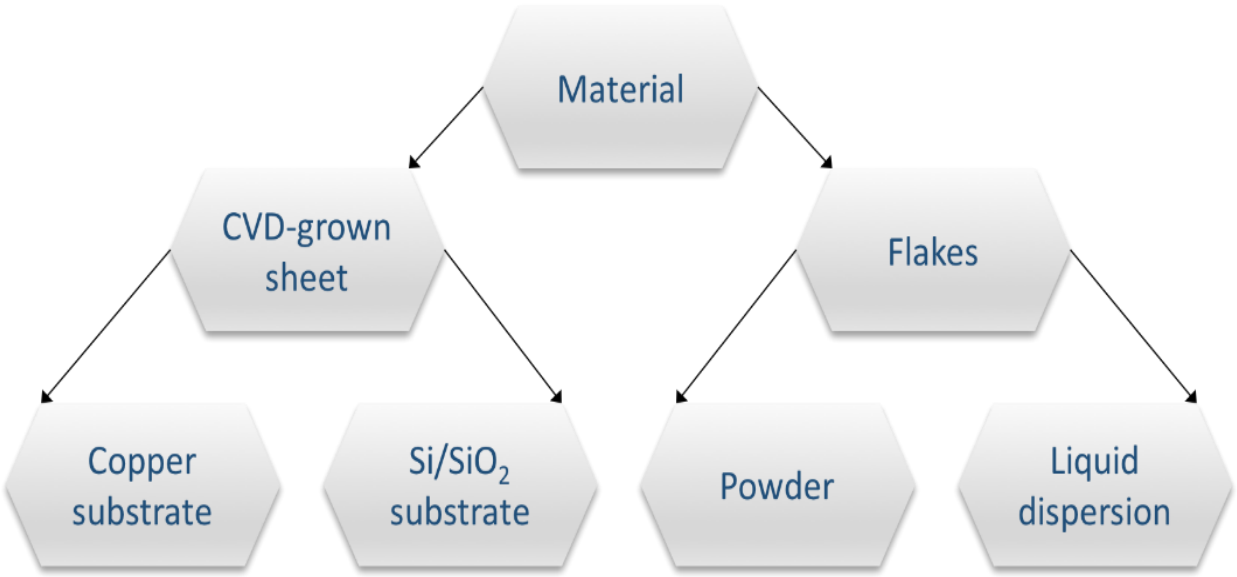


- Joint NPL and NGI (University of Manchester)
- Technique, issues, protocol, data analysis
- Optical, Raman, SEM, TEM, AFM,

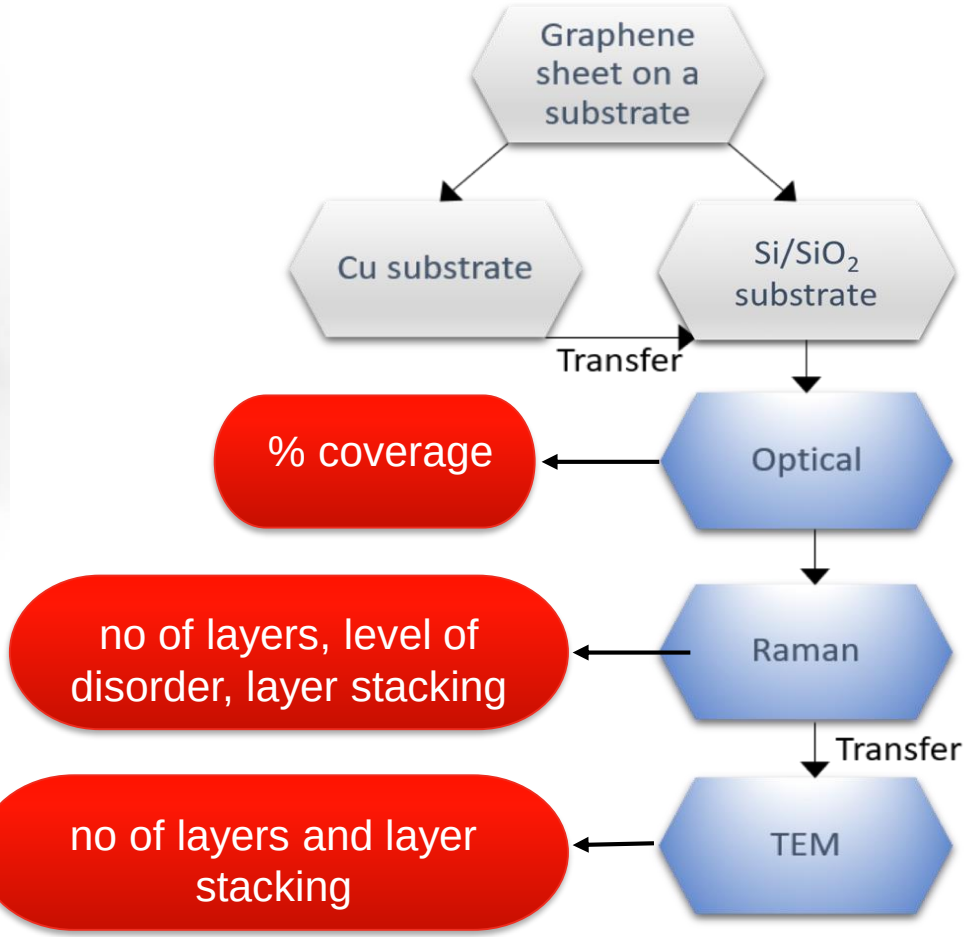
www.npl.co.uk/graphene-guide

- GPG can be used as interim source of measurement protocols as international standard developed
- Will be used as basis for standards

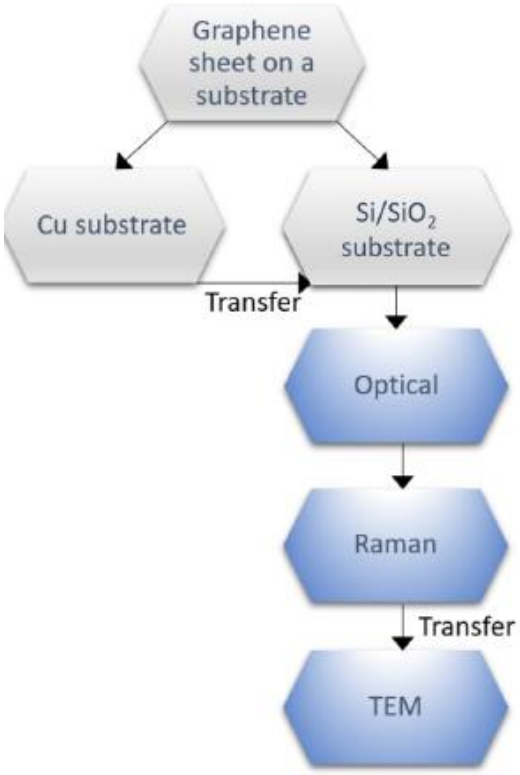
Type of material



CVD-grown Graphene

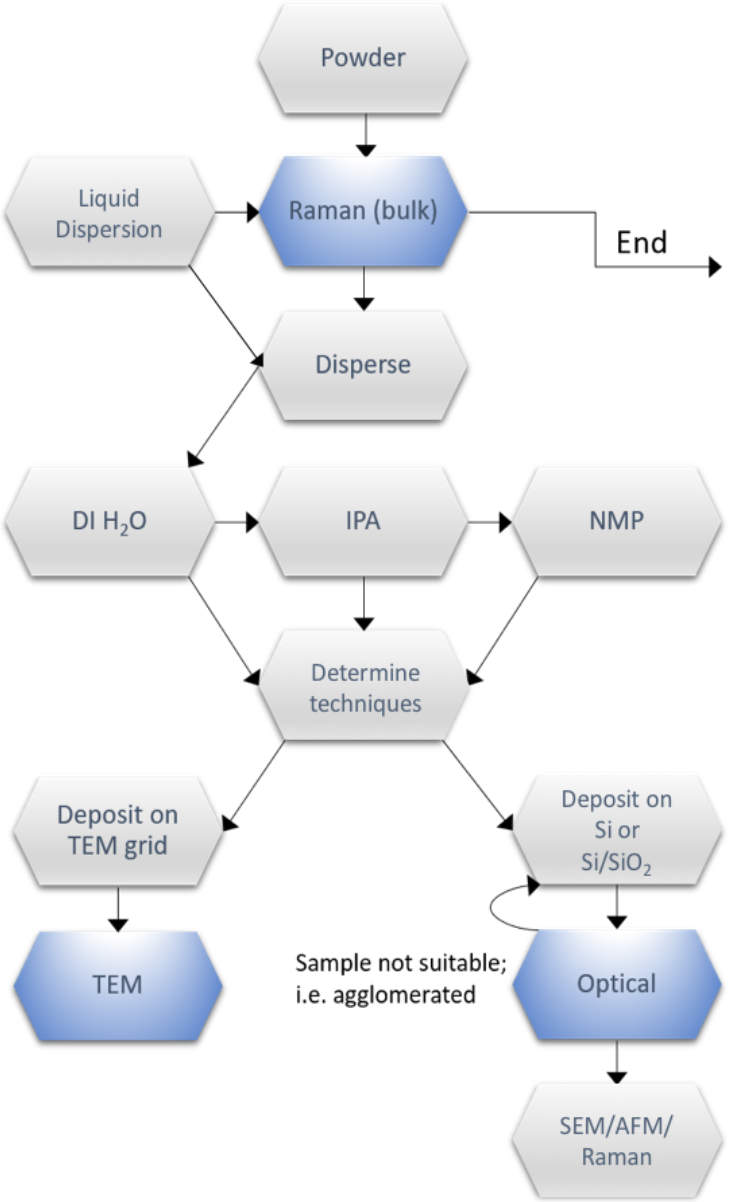


Future possible PWI 21356-2 Structural Characterisation of CVD grown Graphene

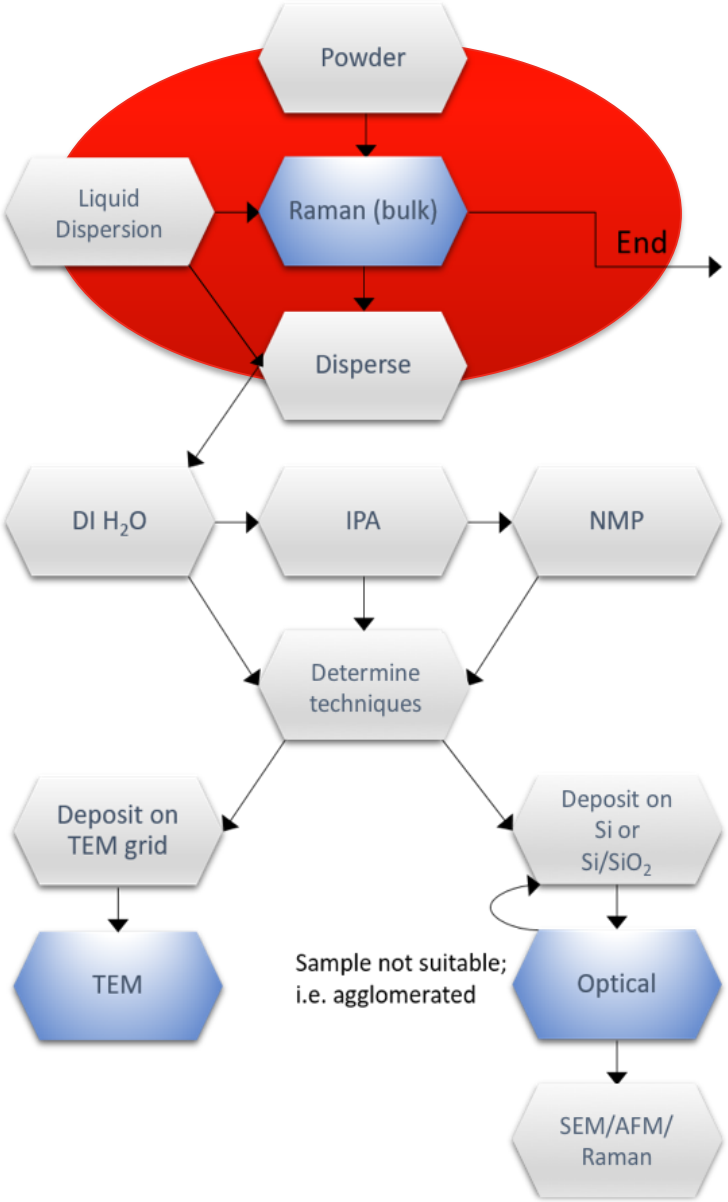


- Proposal led by UK (C Clifford, A Pollard)
- order of methods for characterising the structural properties of CVD grown graphene
- Methods: Optical microscopy, Raman and TEM
- Properties covered: % coverage, number of layers (thickness), level of disorder, layer stacking
- Measurement protocols, sample preparation routines and data analysis given.
- Currently out for ballot to see whether it should become a provisional work item
- Your support and input are welcome!

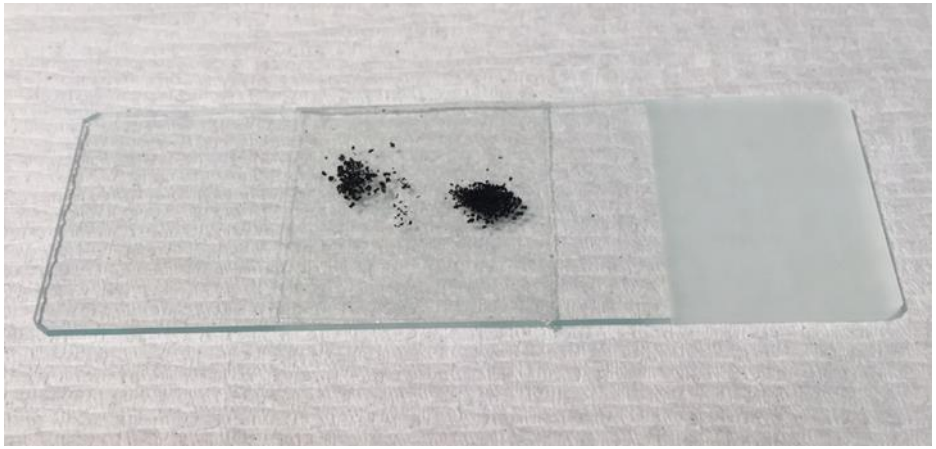
Powders/Dispersions

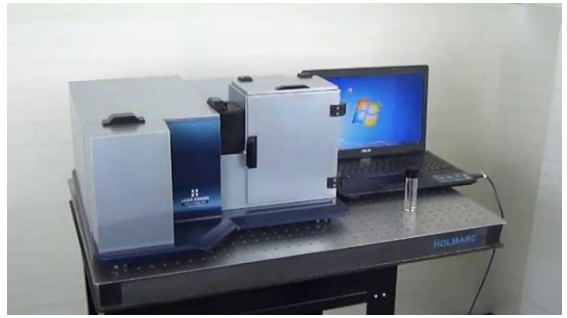


Powders/Dispersions

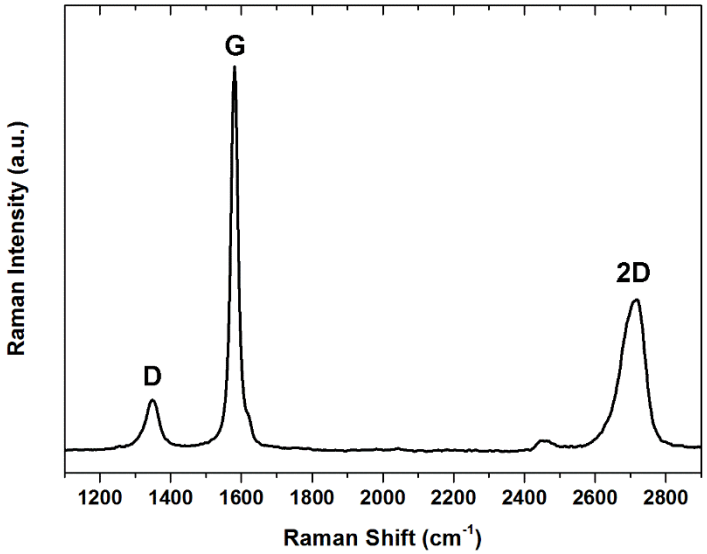


Quick Check - Raman



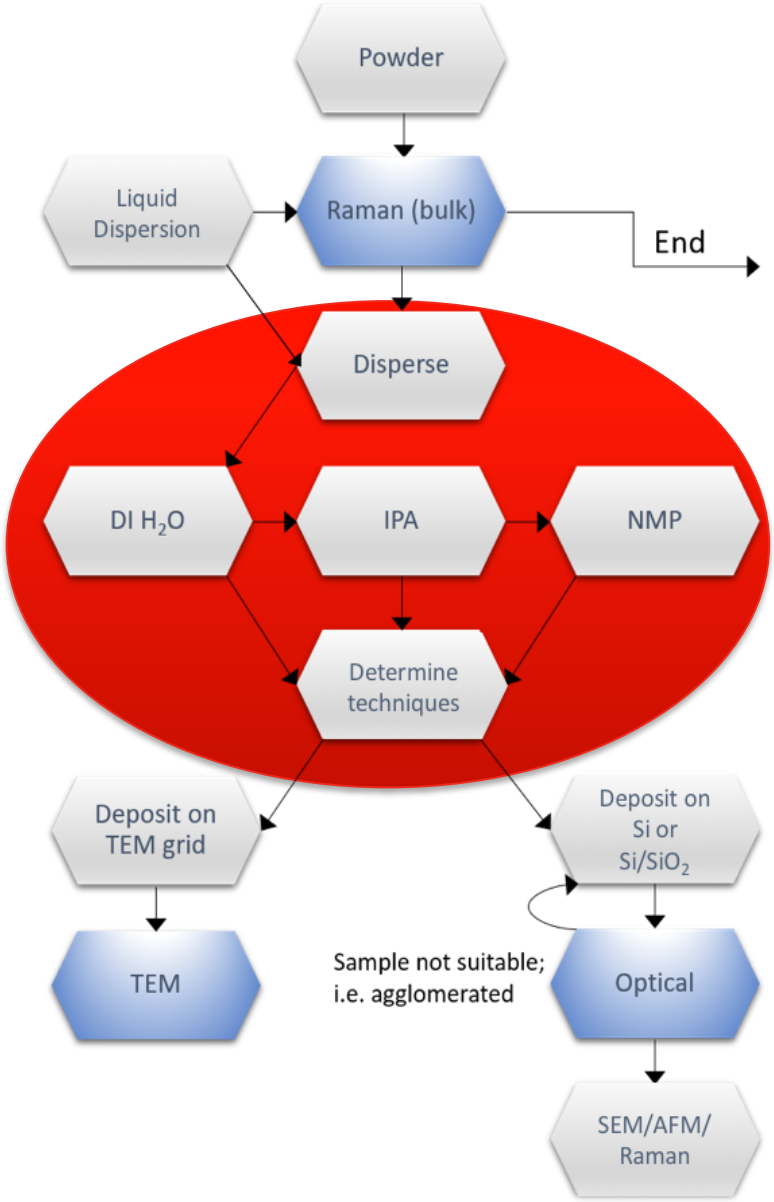


If the G and 2D peaks are not present, further characterisation is not required,



Powders/Dispersions

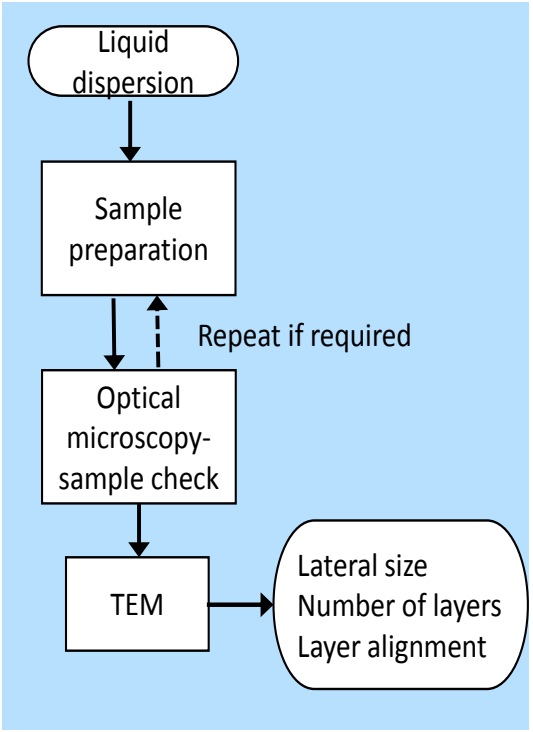
National Physical Laboratory

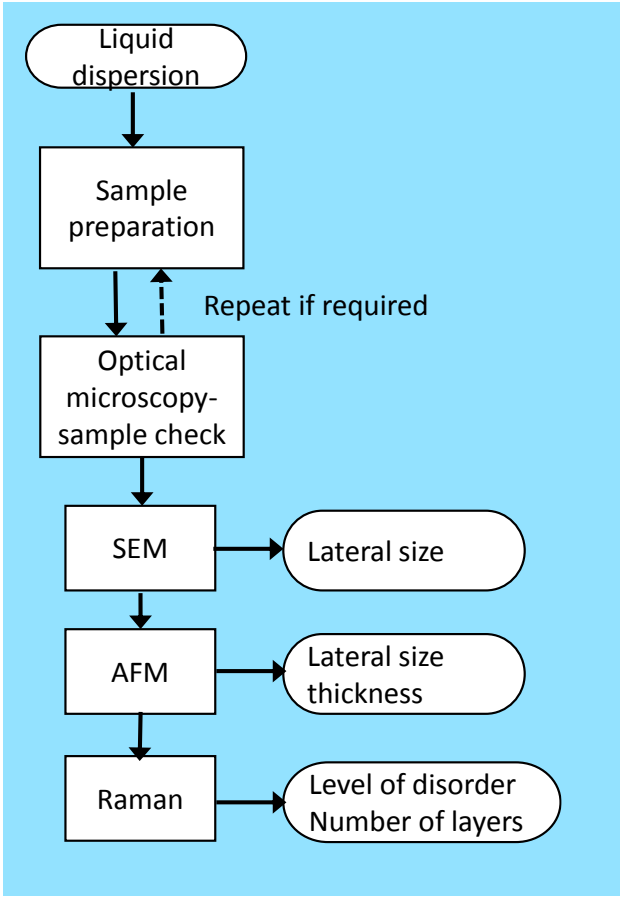


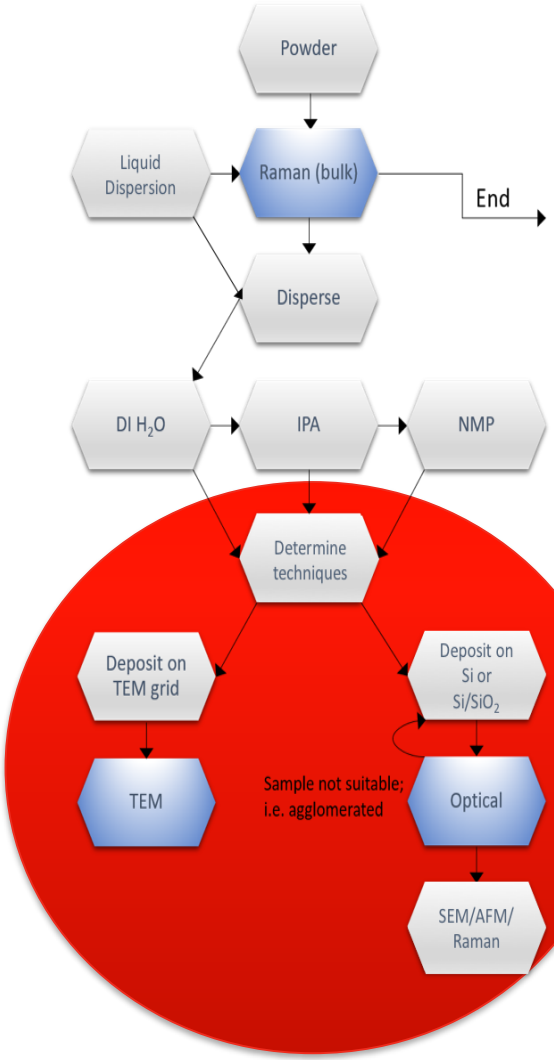
Powders/Dispersions

NPL National Physical Laboratory

TEM or SEM, AFM, Raman



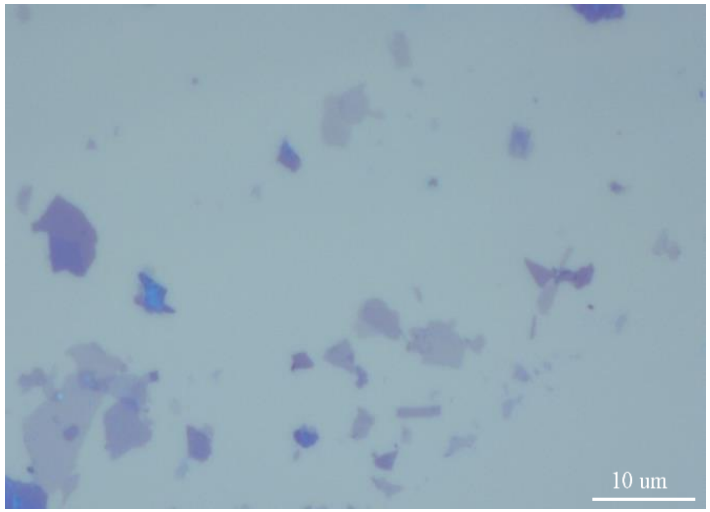


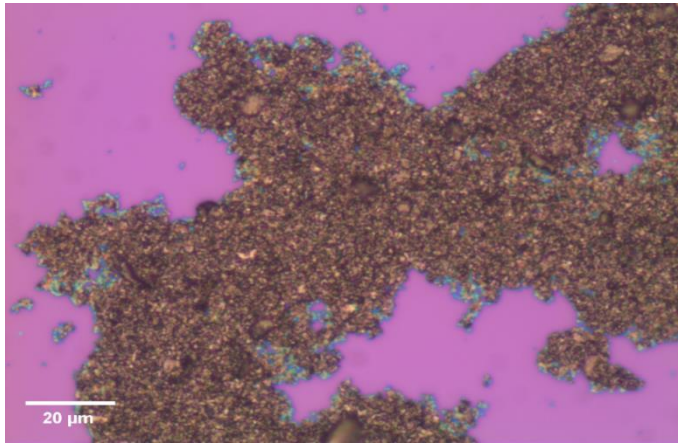


Optical Check

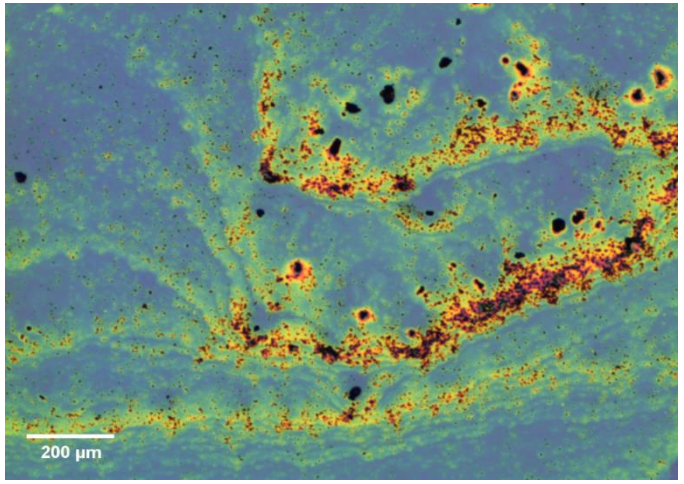
NPL National Physical Laboratory

Before microscopy (here SEM) to check sample prep





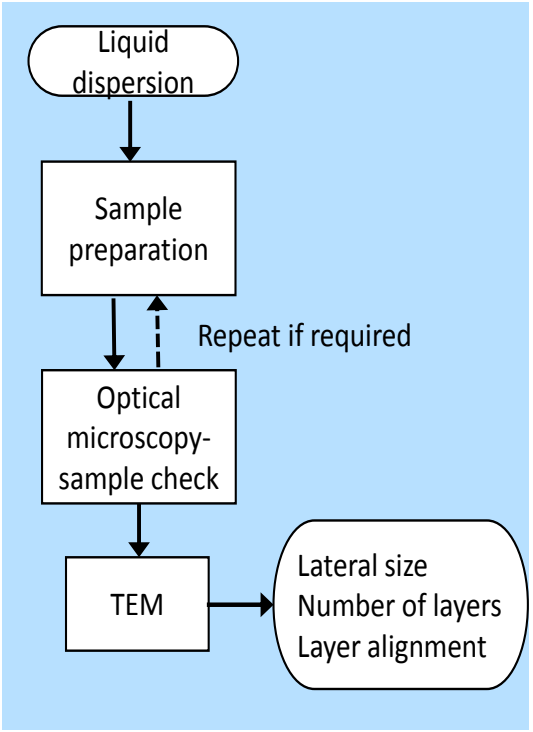
The Good, the Bad and the Ugly

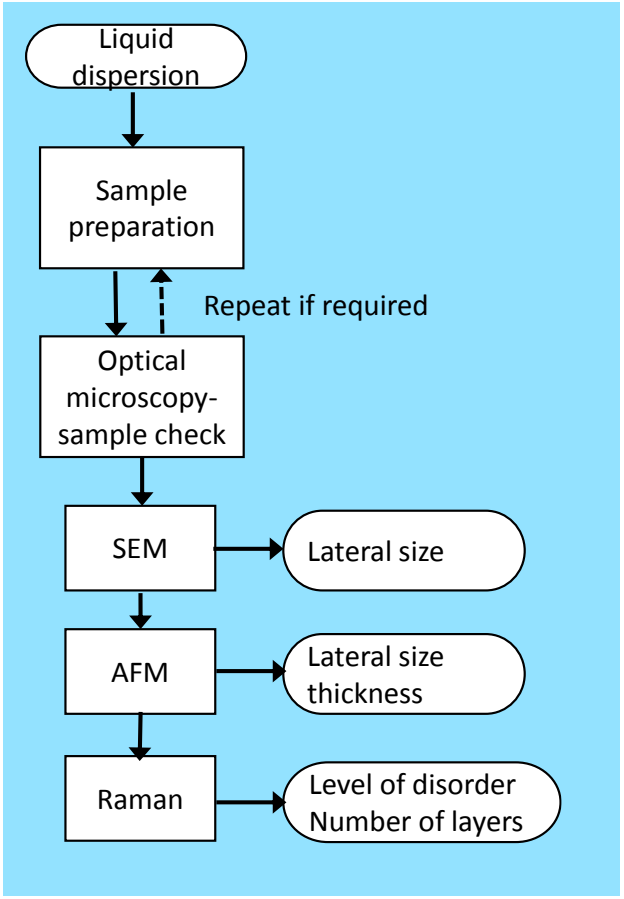


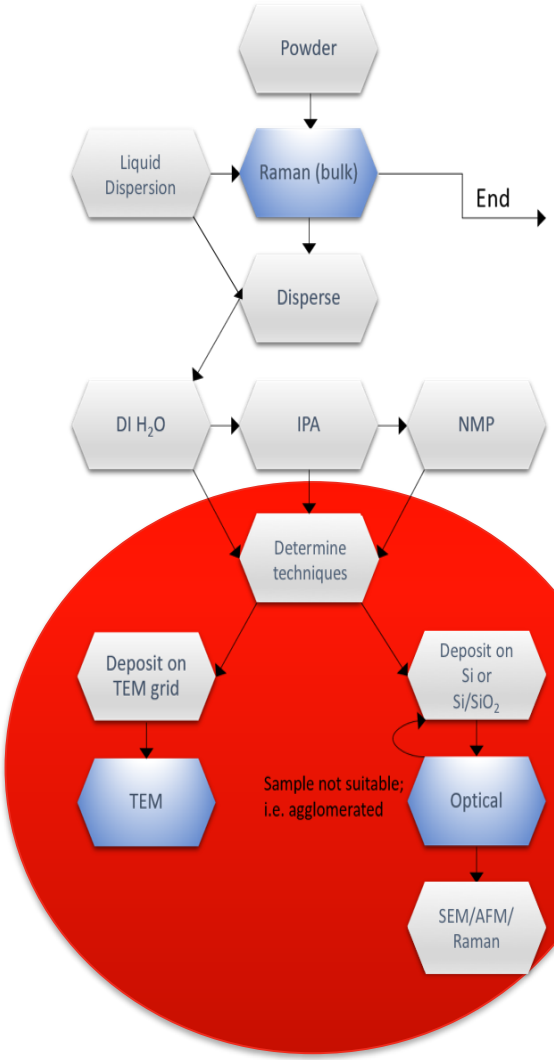
Powders/Dispersions

NPL National Physical Laboratory

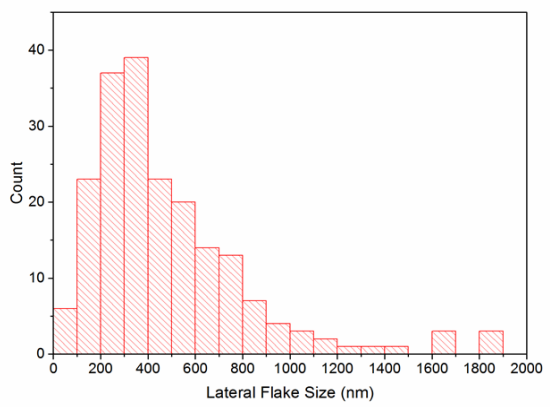
TEM or SEM, AFM, Raman



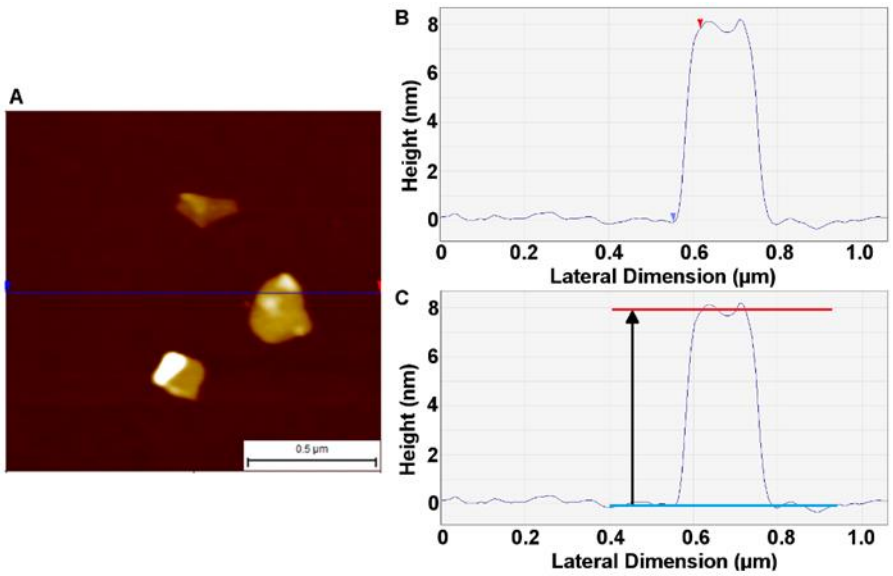




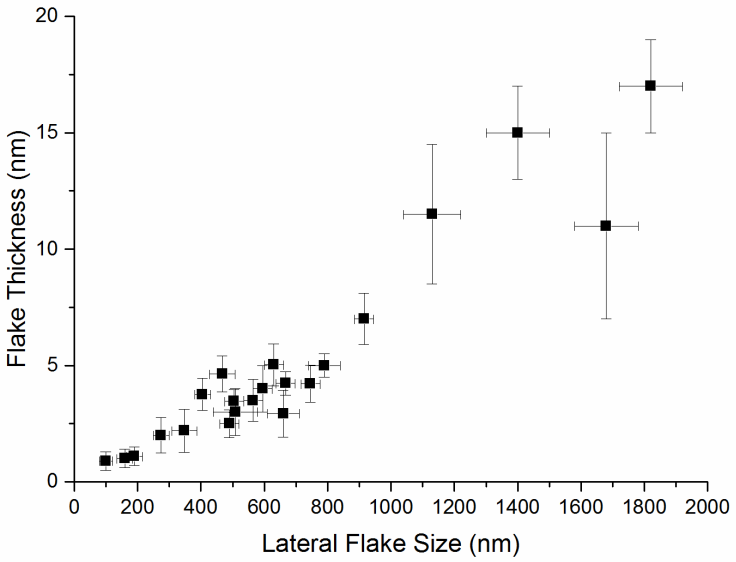
SEM and AFM



Lateral Flake Size
SEM, at least 200 flakes



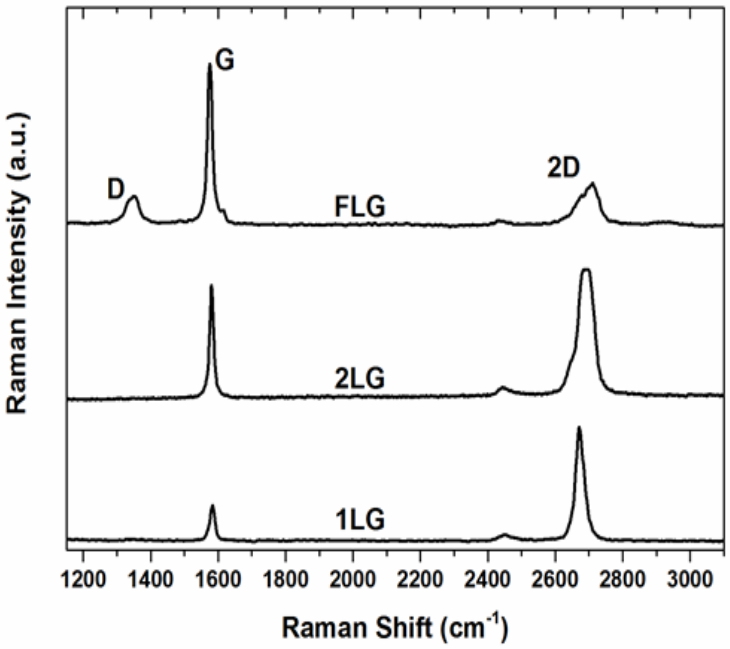
Flake thickness using AFM



Flake thickness vs lateral flake size from AFM

Number of layers

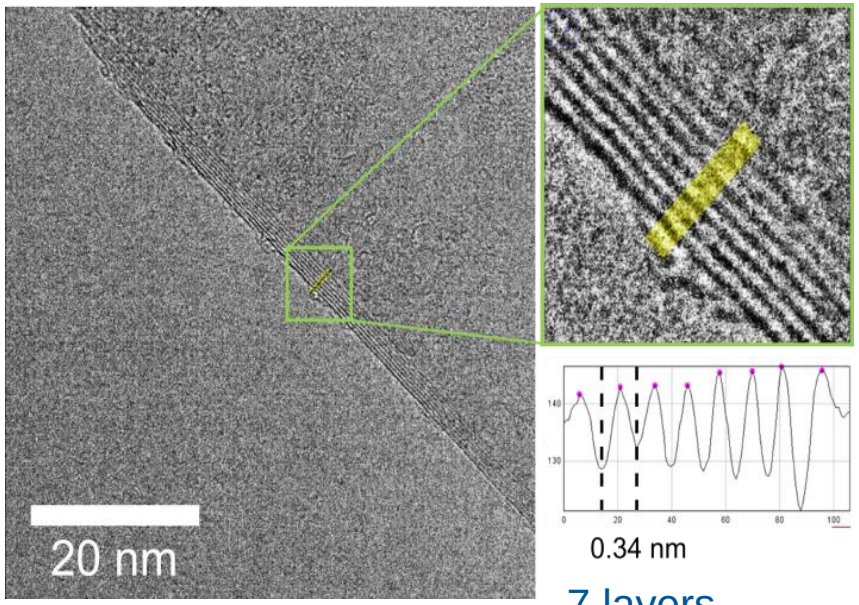
Raman



Peak intensity ratio determines no of layers

Simple, quick

TEM

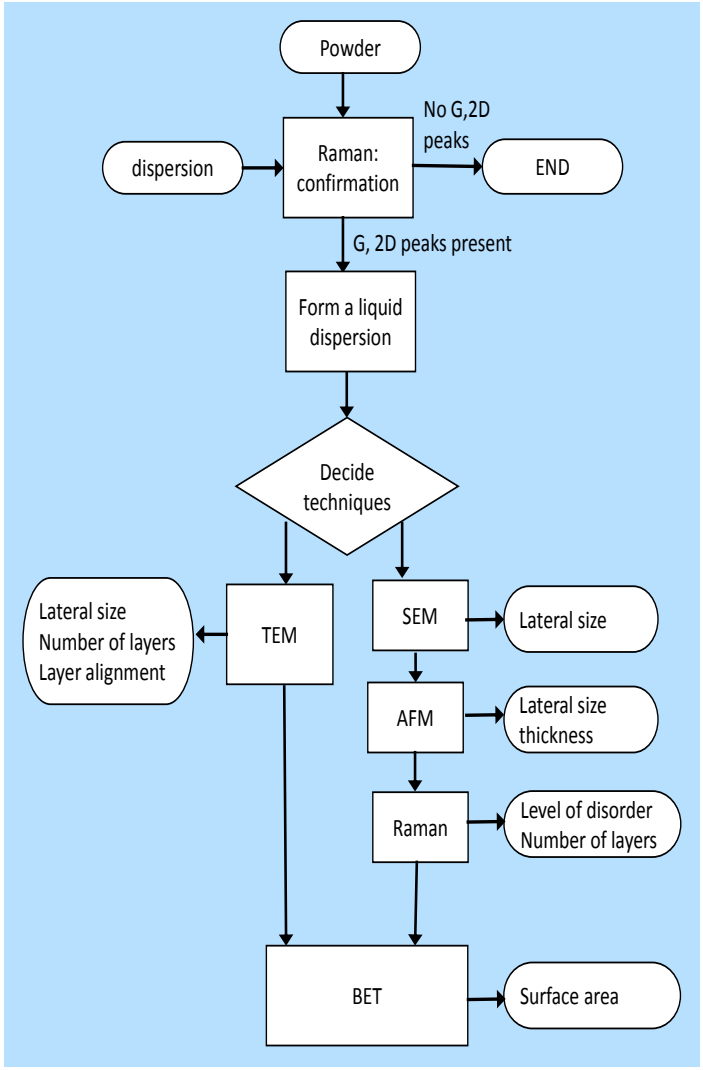


7 layers

Count the layers on the edge!

Time consuming, expensive

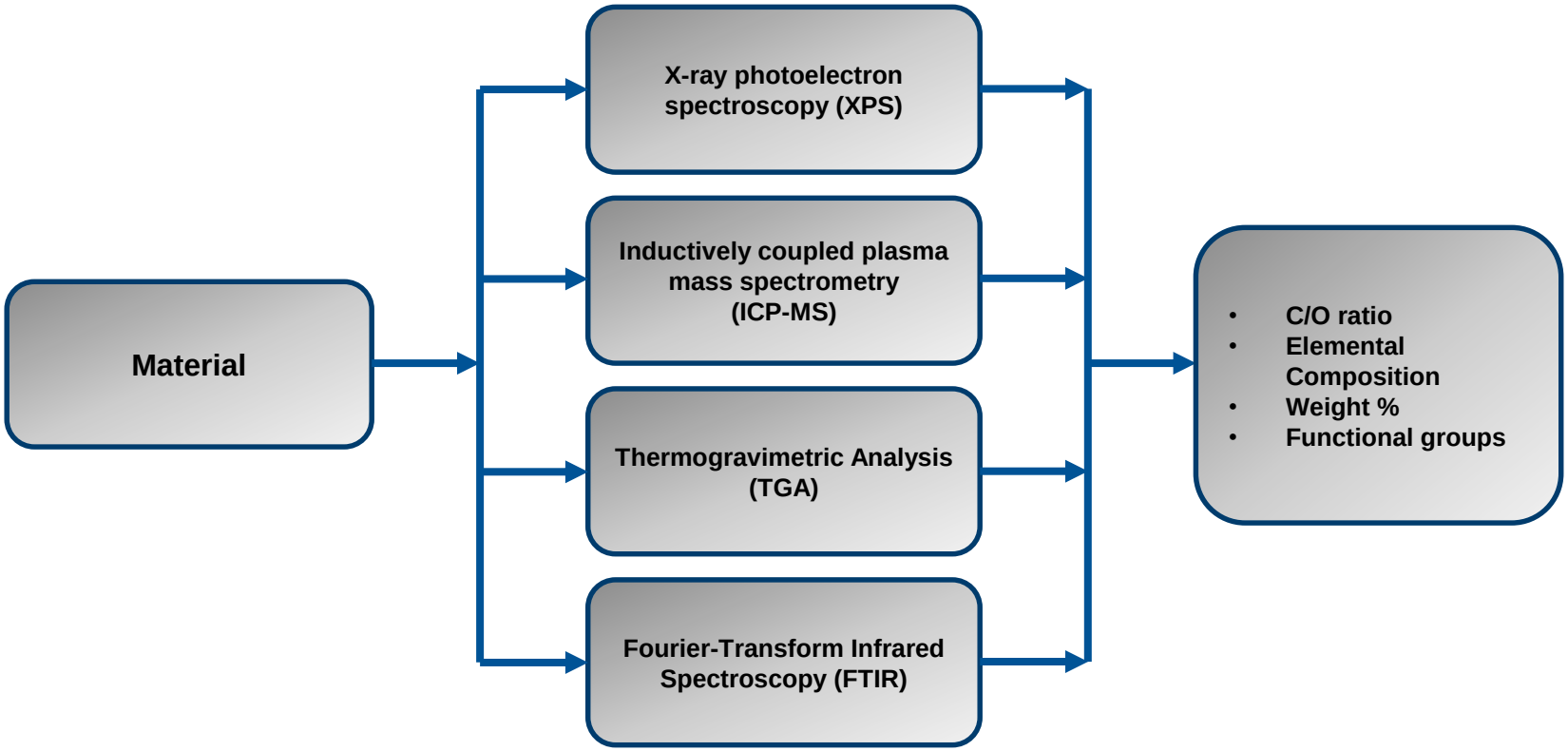
ISO PWI 21356-1 Structural Characterisation of Graphene from powders and dispersions



- Led by UK (C Clifford, A Pollard)
- order of methods for characterising the structural properties of graphene from powders and dispersions
- properties covered are the number of layers (thickness), lateral flake size, the level of disorder, layer stacking and specific surface area. Suggested measurement protocols, sample preparation routines and data analysis given.
- Currently out for New work item ballot
- Technical experts and comments requested

Nanotechnologies -- Chemical characterisation for graphene in powders and suspensions

Provisional work item led by UK (C Clifford and China (LL Ren)
Include sample preparation, protocols and data analysis



National Physical Laboratory

VAMAS
Interlaboratory Studies
Pre-standardisation

Caterina Minelli, Alex Shard, Charles Clifford

Graphene Interlaboratory Studies

- New VAMAS TWA 41: ‘Graphene and Related 2D Materials’
- Aim: Validate different methodologies of measurement for graphene and related 2D materials. Determining the uncertainties associated in measurement, sample preparation, and data analysis. Interlaboratory studies will be conducted and the results will form the basis for future standardisation.
- Contact:

Dr. Lingling Ren renll@nim.ac.cn
Dr. Andrew Pollard andrew.pollard@npl.co.uk

VAMAS: Raman of CVD graphene

Based on NPL GPG protocol
Led by A Pollard, NPL
Measuring: no of layers, layer stacking/alignment, level of disorder.
Launching: summer/autumn 2018

VAMAS: Chemical Composition of Graphene & GO Flakes by XPS:

Elemental analysis, oxygen content and C:O ratio

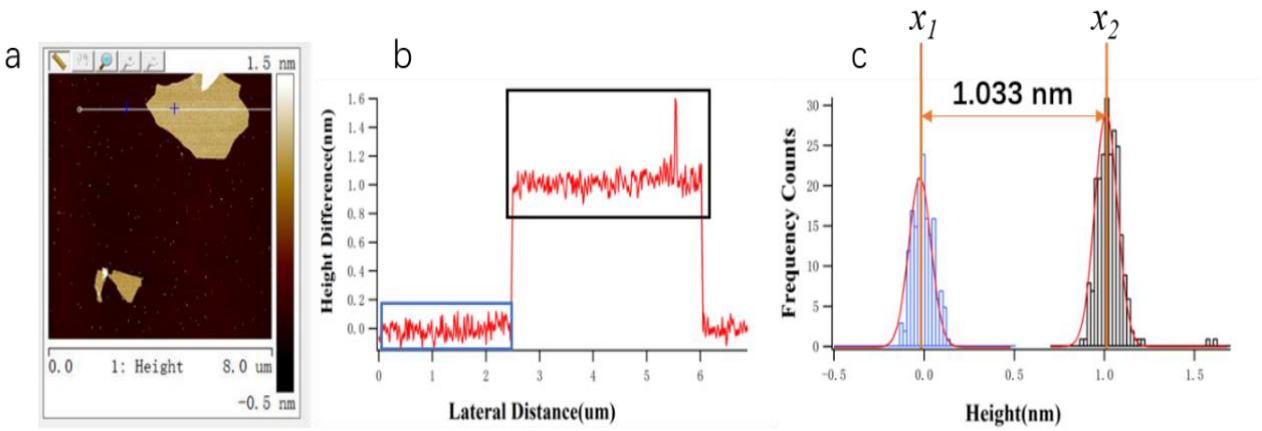
- Led by LingLing Ren, NIM, China
- 3 types of graphene/graphene oxide samples to be tested
- contents of carbon (C), oxygen (O), sulfur (S), chlorine (Cl) and nitrogen (N) elements
- C:O ratio

VAMAS: thickness measurements of Graphene Oxide flakes using AFM

Using Graphene oxide

Measurand – Flake thickness and hence no of layers

- Led by NIM, China
- Protocol and procedure still being refined…..



Terminology

TS 80004-13 - Nanotechnologies -- Vocabulary -- Part 13: Graphene and related two dimensional materials

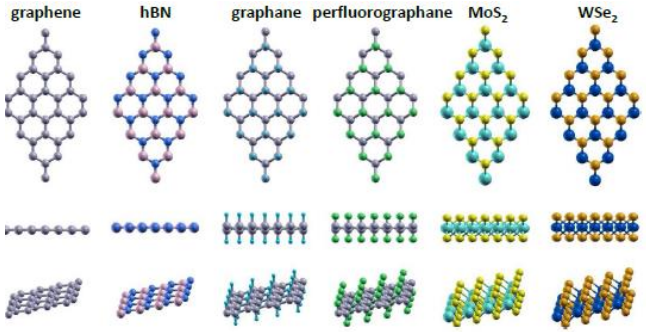
National Physical Laboratory

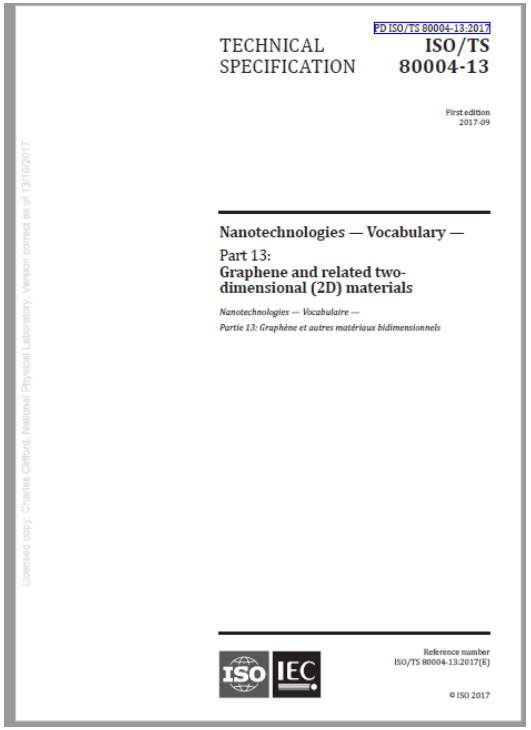
Published September 2017

99 Terms and definitions:

- related to materials
- methods for producing 2D materials
- characterizing 2D materials
- 2D materials characteristics

Freely available on ISO OBP




PD ISO/TS 80004-13:2017

TECHNICAL SPECIFICATION

ISO/TS 80004-13

First edition 2017-09

Nanotechnologies — Vocabulary —
Part 13:
Graphene and related two-dimensional (2D) materials

Nanotechnologies — Vocabulaire —
Partie 13: Graphène et autres matériaux bidimensionnels

Reference number ISO/TS 80004-13:2017(E)

© ISO 2017

2D materials Terminology Standard

NPL National Physical Laboratory

3.1.1.1
two-dimensional material
2D material
material, consisting of one or several layers with the atoms in each layer strongly bonded to neighbouring atoms in the same layer, which has one dimension, its thickness, in the nanoscale or smaller and the other two dimensions generally at larger scales

Note 1 to entry: The number of layers when a two-dimensional material becomes a bulk material varies depending on both the material being measured and its properties. In the case of graphene layers, it is a two-dimensional material up to 10 layers thick for electrical measurements, beyond which the electrical properties of the material are not distinct from those for the bulk [also known as graphite].
Note 2 to entry: Interlayer bonding is distinct from and weaker than intralayer bonding.
Note 3 to entry: Each layer may contain more than one element.
Note 4 to entry: A two-dimensional material can be a nanoplate.

3.1.2.1
graphene
graphene layer
single layer graphene
monolayer graphene
single layer of carbon atoms with each atom bound to three neighbours in a honeycomb structure

Note 1 to entry: It is an important building block of many carbon nano-objects.
Note 2 to entry: As graphene is a single layer, it is also sometimes called monolayer graphene or single layer graphene and abbreviated as 1LG to distinguish it from bilayer graphene (2LG) and few-layered graphene (FLG).
Note 3 to entry: Graphene has edges and can have defects and grain boundaries where the bonding is disrupted.

3.1.2.10
few-layer graphene
FLG
two-dimensional material consisting of three to ten well-defined stacked graphene layers

3.1.2.13
graphene oxide
GO
chemically modified graphene prepared by oxidation and exfoliation of graphite, causing extensive oxidative modification of the basal plane

Note 1 to entry: Graphene oxide is a single-layer material with a high oxygen content, typically characterized by C/O atomic ratios of approximately 2,0 depending on the method of synthesis.

4 Abbreviated terms

1L	monolayer/single-layer
1LG	monolayer/single-layer graphene
2D	two-dimensional
2L	bilayer
2LG	bilayer graphene
3L	trilayer
3LG	trilayer graphene
CVD	chemical vapour deposition
FL	few-layer
FLG	few-layer graphene
GNP	graphene nanoplatelet
GO	graphene oxide
hBN	hexagonal boron nitride
rGO	reduced graphene oxide

Summary

- NPL Good Practice Guide on measurement of graphene structure now published
- Many standards currently in development with activity growing
- Graphene Measurements Standards being developed
- Graphene Terminology Standard now published
- Interlaboratory comparisons through VAMAS

Thanks

Alex Shard, Andrew Pollard, Keith Paton, Elizabeth Legge, Barry Brennan from NPL

University of Manchester: Antonios Oikonomou, Sarah Haigh, Cinzia Casiraghi

ISO TC229 experts

FUNDED BY BEIS

DTR 19733 Matrix of properties and measurement techniques for graphene and related 2D materials

NPL National Physical Laboratory

Led by Korea (Clare Byeon) and USA (A Hight- Walker)

Properties	Techniques	AFM	KPFM	BET	EPMA	ESR (EPR)	ICP-MS	LEEM	Optical Microscopy	Raman	UV-VIS-NIR Spectroscopy	SEM	SIMS	STM	TEM	UPS	XPS	TGA	Combustion	Titration	4-point Porbe	Hall Bar
Structural	Number of Layers	○						○	○	○	○				○							
	Thickness	○						○							○							
	Stacking Angle									○				○	○							
	Flake Size	○							○	○		○			○							
	Domain (grain) Size	○							○	○	○			○	○							
	Surface Area			○							○											
	Crystal Defect	○			○	○				○		○		○	○							
Chemical	Non-Graphene Contents & Residue									○			○				○	○	○			
	Oxygen Contents				○								○				○	○		○		
	Metal Contents				○		○						○				○					
Mechanical	Modulus	○								○												
Thermal	Thermal Conductivity									○												
Optical	Transmittance								○		○											
Electrical/ Electronic	Sheet Resistance																				○	○
	Mobility																				○	○
	Charge Carrier Concentration		○																		○	○
	Work Function		○													○						

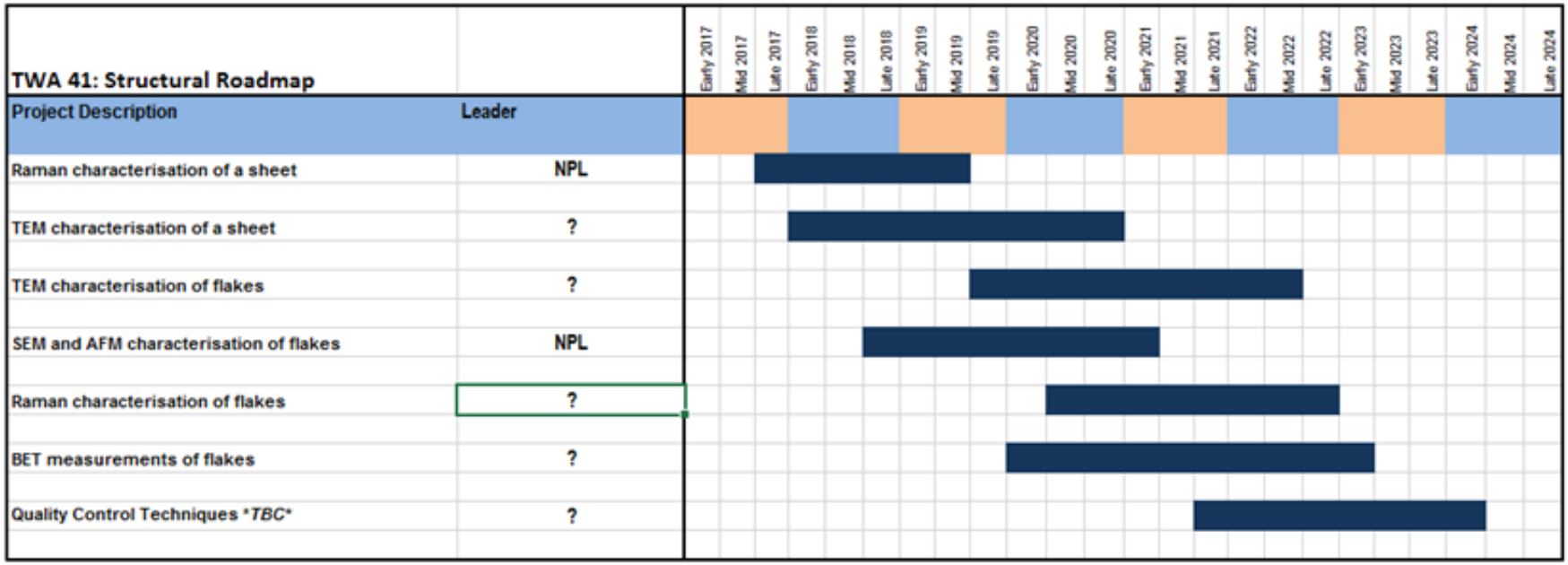
Draft technical report

Properties and techniques described

Currently out for DTR ballot (closes end April)

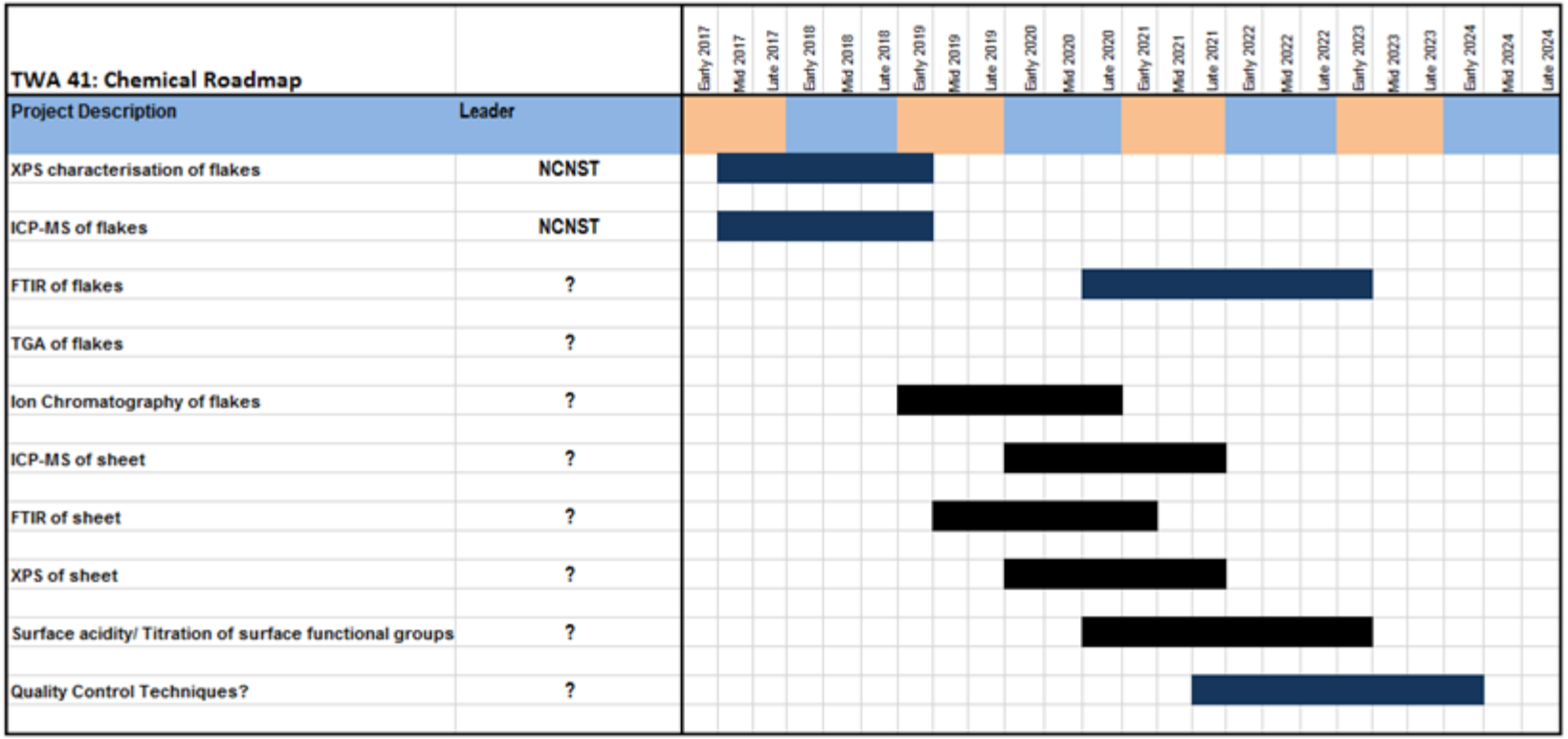
VAMAS Roadmap

- Series of structural characterisation projects over the next 7 years.



VAMAS Roadmap

- Chemical characterisation projects that will lead to chemical characterisation ISO standards



Nanotechnology Standardisation

NPL National Physical Laboratory

International Standardization Committees

Committee	When Founded	Membership	Developed Standards	Standards[2] under development
ISO/TC 229 Nanotechnologies	2005	37 Participating countries 14 Observing countries	52	42
CEN/TC 352 Nanotechnologies	2005	34 Countries	14	13
IEC TC 113 Nanotechnology for electrotechnical products and systems	2006	15 Participating countries 19 Observer countries	27	37
ASTM International TC E56 Nanotechnology	2005	Over 180 members	18	8

[1] ISO - International Organization for Standardization, CEN - The European Committee for Standardization, IEC - International Electrotechnical Commission

[2] Term "standard" used here includes technical reports, technical specifications and standard test methods.