PUB SINGAPORE'S NATIONAL WATER AGENCY

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Quick and Easy Characterization of Microplastics in Surface Water and Treated Effluent

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Introduction

Introduction

Microplastics and Motivation of Study

- **About Microplastics (MPs)**
  - a Contaminant of Emerging Concern (CEC)
  - generally defined as solid, insoluble, synthetic organic polymeric materials with sizes smaller than 5 mm

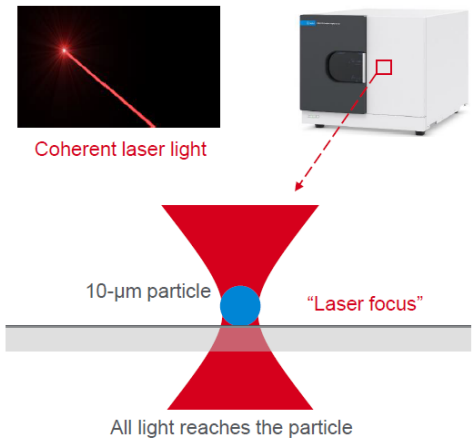
- **Motivation of Study**
  - Conventional analysis for MPs, generally involves laborious sample clean-up procedures; use of hazardous chemicals; and long man-hours – particularly so, for complex water matrices.

  - Through leveraging on the affordances of Laser Direct Infrared (LDIR) Chemical Imaging System - a new technology – we explore the quicker and easier analysis of MPs in complex water matrices like Surface Water and Treated Effluent.

Introduction

About LDIR

Key Technology	Key Benefits
Quantum Cascade Laser (QCL) technology • brighter output, higher directionality • focuses all laser power onto a single particle	• improved sensitivity • shorter spectrum collection time (1 sec/spectrum)
Automated, rapid scanning optics • movement of sample relative to IR beam is fully automated	• 'load-and-go' • reduced man-hours
Discrete frequency infrared imaging capability • images a large area quickly using a monochromatic beam • discriminates background and matrix interferences (without IR signals) from suspect particles (with IR signals)	• collects spectra only from microplastics-like particles • higher through-put than conventional analysis

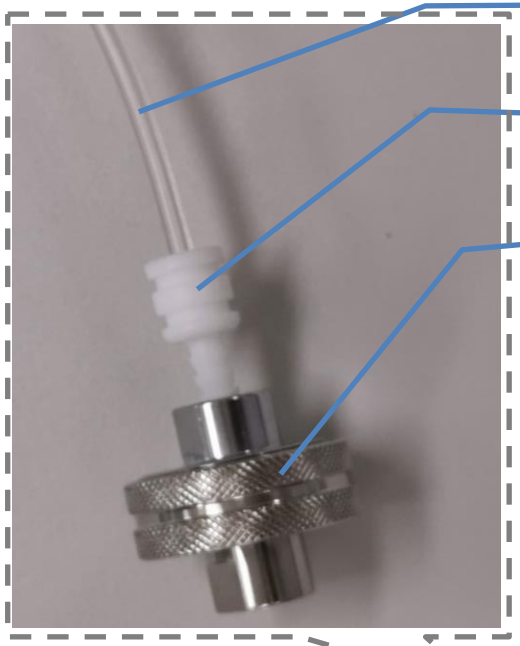


- Bright, coherent light source
- Focus all laser power onto a particle
- New instrument architecture
- Proprietary Agilent quantum cascade laser (QCL) technology
- Rapidly tunable across the mid-infrared for spectroscopy
- One second per spectrum

Methods

Methods

Sample preparation workflow



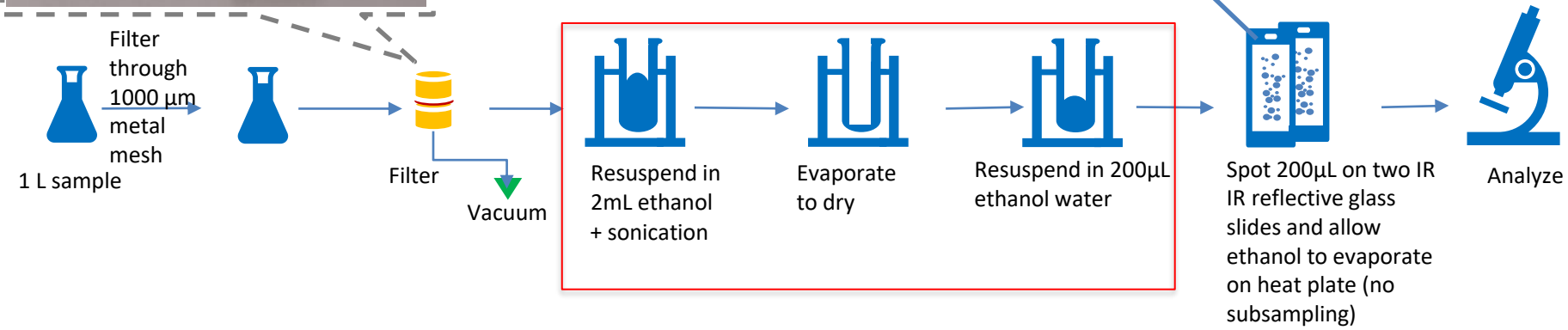
Solvent Tubing

Filter frit adapters

Semi prep filter (hardware) +
filter disk, 10µm pore size

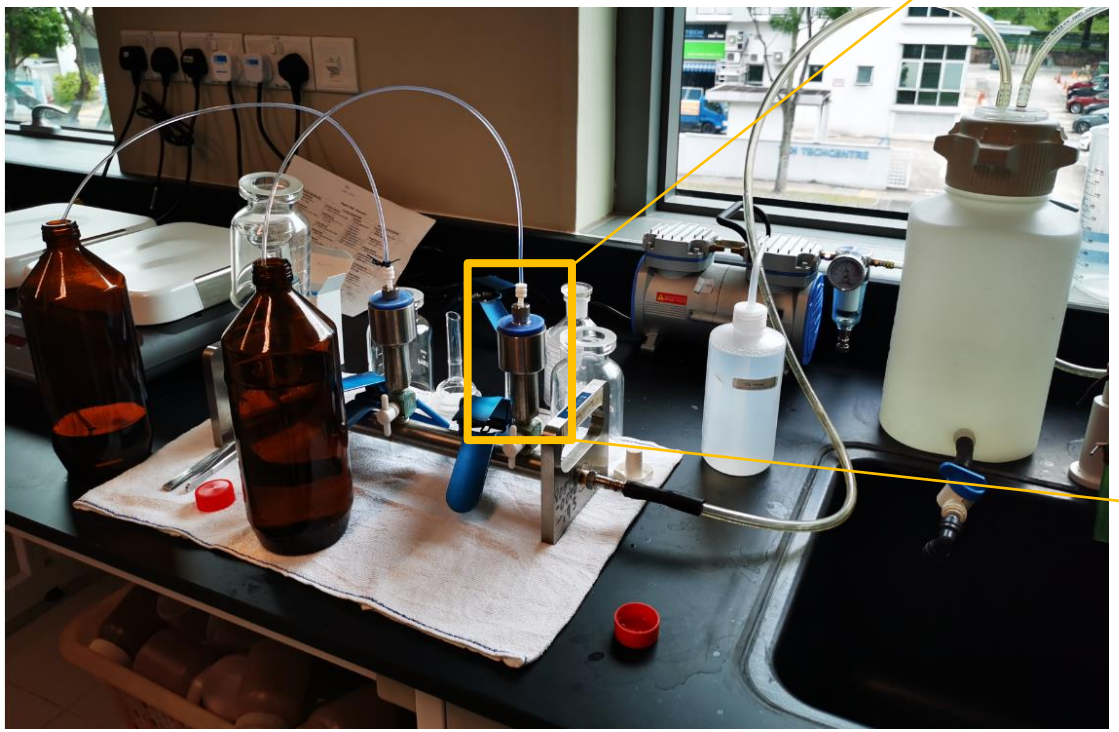
Infrared reflective glass slides
(7.5 × 2.5cm; MirrIR, Kevley Technologies)

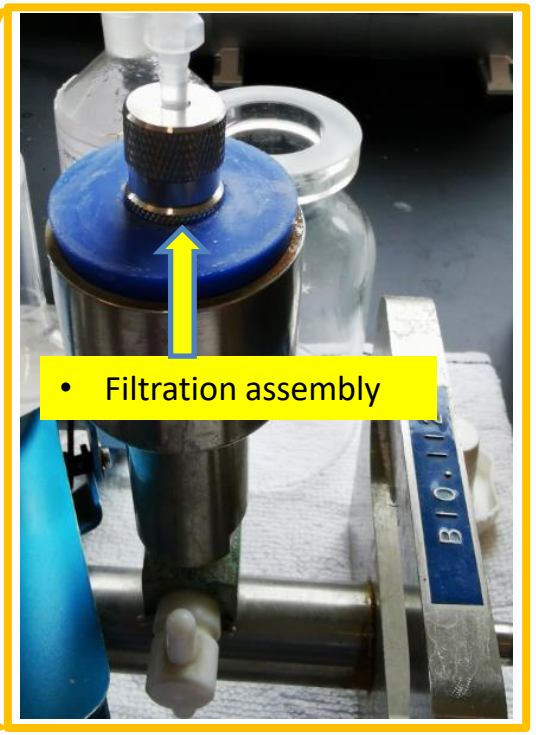
- No chemical/enzymatic digestion
- No density separation



Methods

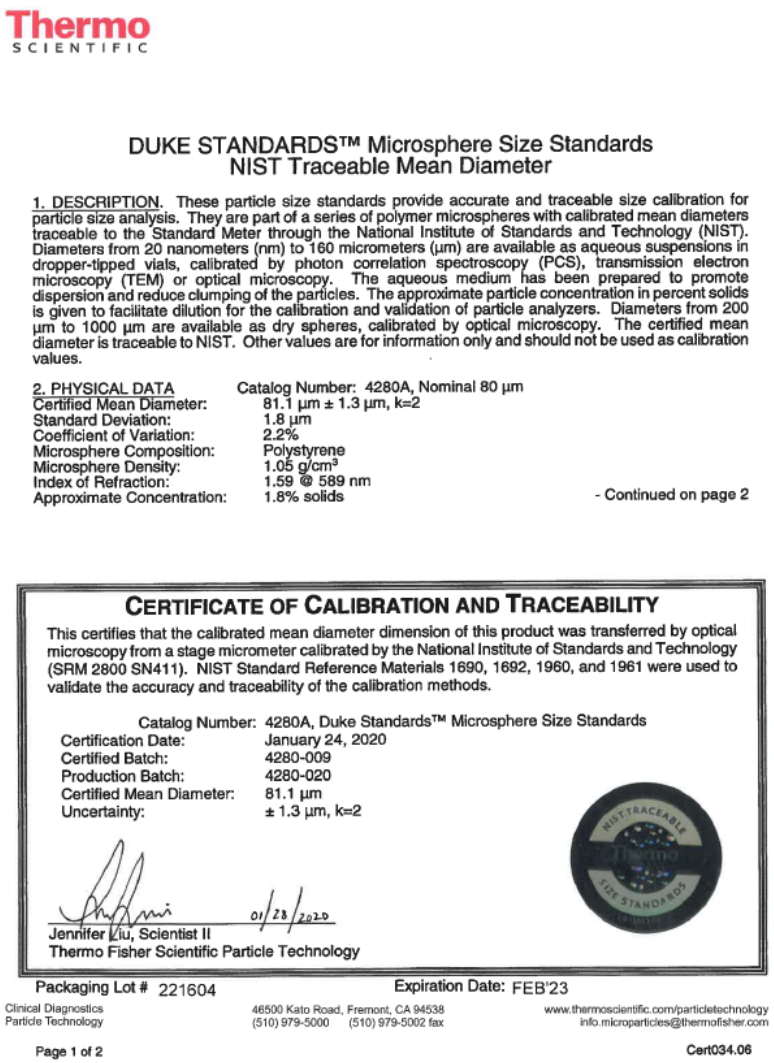
Sample preparation workflow





Methods

Positive Controls



Thermo SCIENTIFIC

DUKE STANDARDS™ Microsphere Size Standards
NIST Traceable Mean Diameter

1. DESCRIPTION. These particle size standards provide accurate and traceable size calibration for particle size analysis. They are part of a series of polymer microspheres with calibrated mean diameters traceable to the Standard Meter through the National Institute of Standards and Technology (NIST). Diameters from 20 nanometers (nm) to 160 micrometers (µm) are available as aqueous suspensions in dropper-tipped vials, calibrated by photon correlation spectroscopy (PCS), transmission electron microscopy (TEM) or optical microscopy. The aqueous medium has been prepared to promote dispersion and reduce clumping of the particles. The approximate particle concentration in percent solids is given to facilitate dilution for the calibration and validation of particle analyzers. Diameters from 200 µm to 1000 µm are available as dry spheres, calibrated by optical microscopy. The certified mean diameter is traceable to NIST. Other values are for information only and should not be used as calibration values.

2. PHYSICAL DATA — Catalog Number: 4280A, Nominal 80 µm

Certified Mean Diameter:	81.1 µm ± 1.3 µm, k=2
Standard Deviation:	1.8 µm
Coefficient of Variation:	2.2%
Microsphere Composition:	Polystyrene
Microsphere Density:	1.05 g/cm³
Index of Refraction:	1.59 @ 589 nm
Approximate Concentration:	1.8% solids

- Continued on page 2

CERTIFICATE OF CALIBRATION AND TRACEABILITY

This certifies that the calibrated mean diameter dimension of this product was transferred by optical microscopy from a stage micrometer calibrated by the National Institute of Standards and Technology (SRM 2800 SN411). NIST Standard Reference Materials 1690, 1692, 1960, and 1961 were used to validate the accuracy and traceability of the calibration methods.

Catalog Number:	4280A, Duke Standards™ Microsphere Size Standards
Certification Date:	January 24, 2020
Certified Batch:	4280-009
Production Batch:	4280-020
Certified Mean Diameter:	81.1 µm
Uncertainty:	± 1.3 µm, k=2

01/28/2020

Jennifer Liu, Scientist II
Thermo Fisher Scientific Particle Technology

Packaging Lot # 221604 Expiration Date: FEB'23

Clinical Diagnostics
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- 80µm Polystyrene (PS) microspheres, suspended in aqueous medium to promote dispersion and reduced clumping, were purchased from Thermo Scientific.
- The approximate particle concentration is calculated to facilitate dilution.

 # Microspheres/mL

$$N = \frac{6 \times 10^{10} \bullet S \bullet \rho_L}{\pi \bullet \rho_S \bullet d^3}$$

N	=	# microspheres/mL for suspensions in water
S	=	weight % solids (for 10% solids suspension, S=10)
ρL	=	density of microsphere suspension (g/mL)
ρ_L	=	$100 \bullet \rho_S / [S(1-\rho_S) + (100 \bullet \rho_S)]$
ρ_S	=	density of solid sphere (g/cm³)
d	=	mean diameter (µm)

- Approximate particle concentration based on COA:

(**6.4 x 10^4 PS microspheres/mL**)

Methods

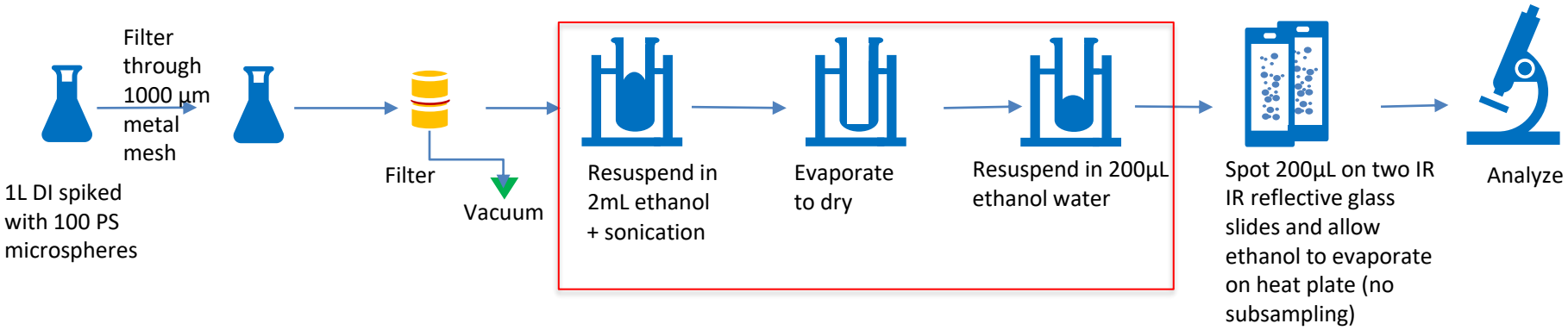
Positive Controls

- To verify the sample processing efficiency and to quantify any particle loss, recovery analysis using positive controls were performed.

- Six technical replicates of the positive controls were prepared by spiking about 100 PS microspheres (80 µm in diameter) in 1 L of DI water.

    - observed average recovery was **<u>73%</u>** with repeatability of **<u><10% RSD</u>**.

- The good recovery rate and % RSD values provided assurance on the efficiency of the sample preparation workflow.



Results and Discussion

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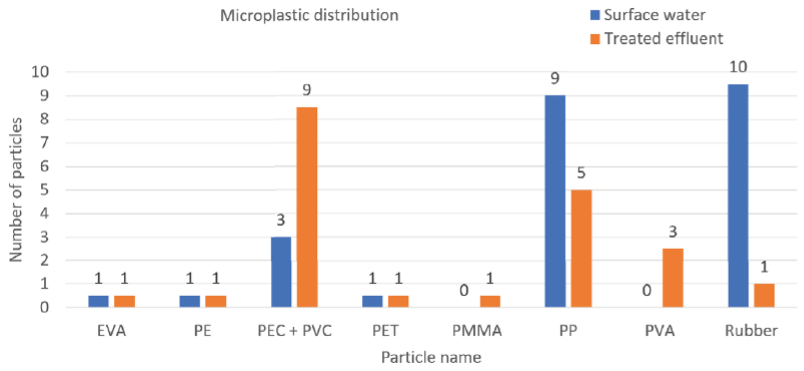
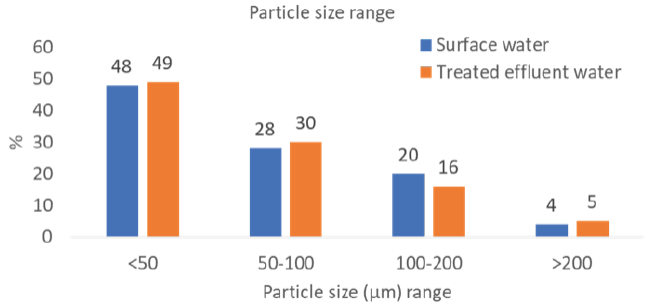
- **Surface Water Results**
  - Average of 25 microplastic particles/L were detected in investigated surface water
- **Treated Effluent Results**
  - Average of 22 microplastic particles/L were detected in investigated treated effluent
- **Matrix Spike Recovery**
  - Recoveries of 80 µm PS microspheres spiked in surface and treated effluent water samples were >73%
- **Negative Control**
  - 0-5 microplastic particles/L, were detected in negative controls, from Milli Q water purification system



Abbreviation	Particle	Particle size range (µm)	
		Surface water	Treated effluent
EVA	Ethylene Vinyl Acetate	29	49
PE	Polyethylene (PE)	43	13
PEC + PVC	Polyethylene Chlorinated + Polyvinylchloride	26 - 36	31 - 286
PET	Polyethylene Terephthalate (PET)	80	36
PMMA	Polymethylmethacrylate (PMMA)	-	28
PP	Polypropylene (PP)	30 - 549	63 - 110
PVA	Polyvinyl alcohol	-	42 - 65
Rubber	Rubber	32 - 128	38

Microplastics types and counts in surface and treated effluent water samples.

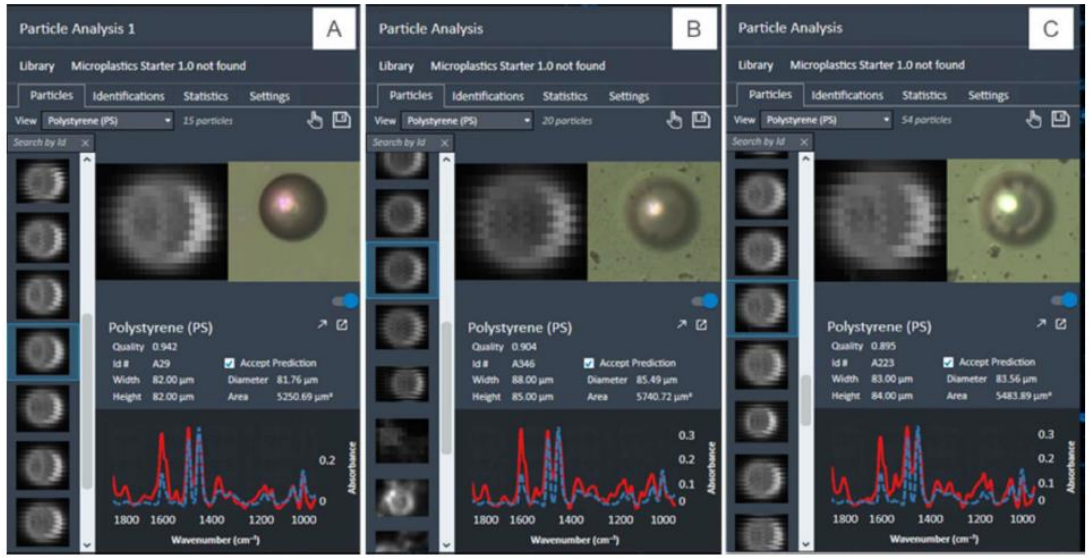


Particle size (µm) distribution in surface and treated effluent water samples

Conclusion

Conclusion

- The LDIR enabled the confident identification of PS beads even in complex water matrices like surface and treated effluent.



Increased complexity in water matrices, as illustrated in the visuals of identified PS microspheres.

***A**: DI water, **B**: surface water, **C**: treated effluent*

- The ability of the LDIR to discriminate between microplastics and non-microplastics enables the simplification of the sample preparation steps to straightforward vacuum filtration and resuspension.

- Overall, a promising sample preparation and analysis method for microplastics in complex water matrices is being presented.

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THANK YOU