Solvent Replacement Activities

International Workshop On Environment And Energy

Materials Management and Substitution in Support of Space Operations

Claire TONON // 15/11/11

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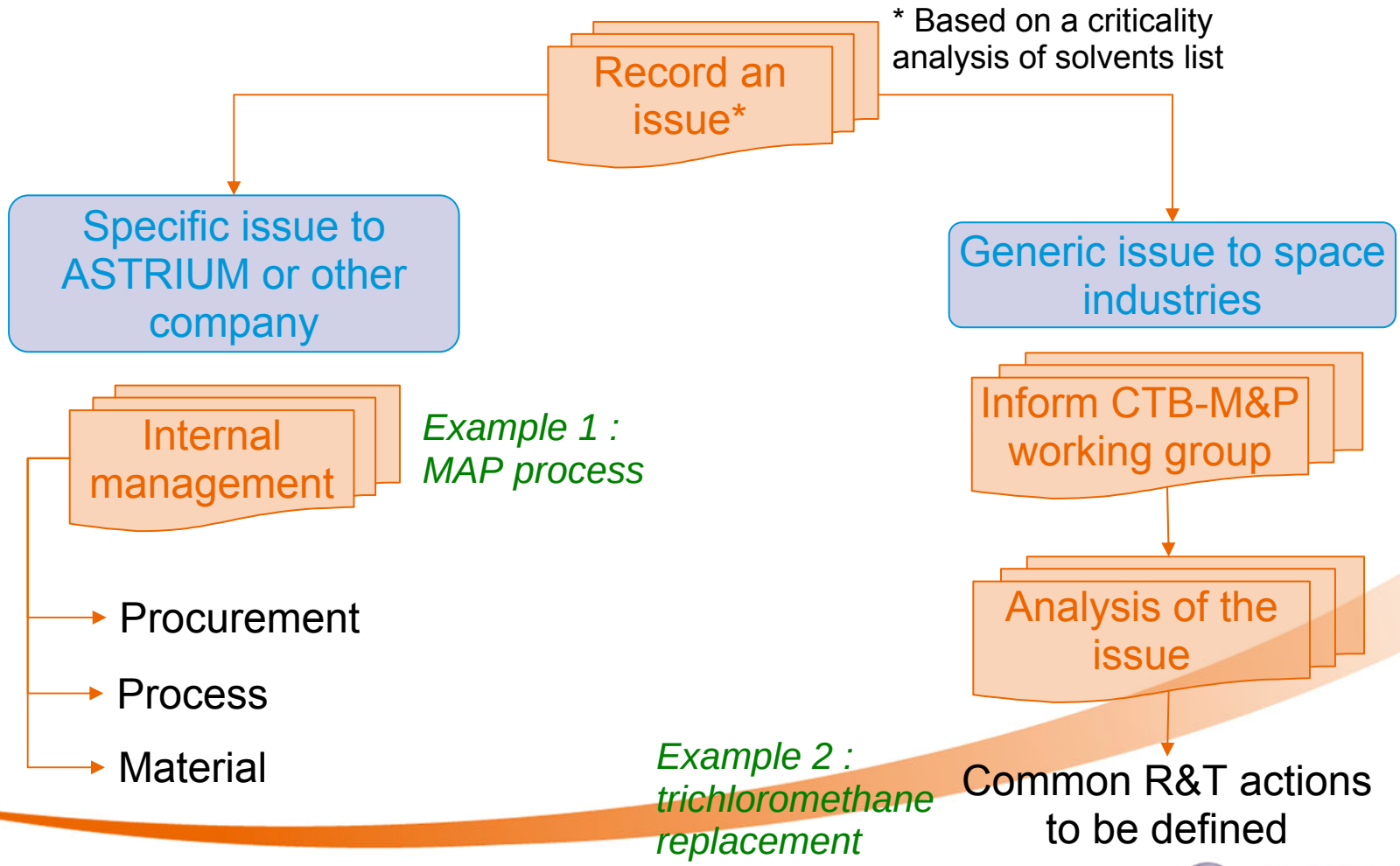
Outline

- Process management for solvent replacement
- Example 1 – Substitution of solvents in MAP products
- Example 2 – Trichloromethane replacement for molecular contamination test

Process management for solvent replacement

How to manage solvent replacement within REACh process



Criticality analysis – Evaluation based on 3 criteria

- **Quantity used**

x ≤ 1 L	1 < x ≤ 50 L	50 < x ≤ 100 L	100 L < x
1	2	3	4

- **CMR status**

No CMR	CMR 3	CMR 1&2
1	2	3

- **Hazard classes**

Classe 1	Classe 2	Classe 3	Classe 4
Substance or preparation no concerned by health hazard labelling.	***Xn***	***T***	***T+***
	R 65	R 23	R 26
	Xi	R 48	R 27
	R 36	***Xn***	R 28
	R 38	R 20	R 39
	R 43	R 21	***T***
		R 22	R 23
		R 40	R 24
		R 42	R 25
		R 48	R 39
		R 62	R 45
		R 63	R 46
		R 68	R 48
		Xi	R 49
		R 37	R 60
		R 41	R 61
		C	***Xn***
		R 34	R 20
			R 21
			R 22
			R 68
			C
			R 35
1	2	3	4

X

CMR status \ Quantity used	1	2	3	4
1	1	2	3	4
2	2	4	6	8
3	3	6	9	12

CRITICALITY

=

Quantity used * CMR status * Health hazard classes

X

Hazard classes \ Quantity used * CMR status	1	2	3	4	6	8	9	12
1	1	2	3	4	6	8	9	12
2	2	4	6	8	12	16	18	24
3	3	6	9	12	18	24	27	36
4	4	8	12	16	24	32	36	48

1 - Low
2- Medium
3- High
4- Very high

Example : First list of critical solvents identified within ASL

Name	CAS number	Use	Action
Trichloromethane	67-66-3	Cleaning, Use for contamination analyses	Substitute under investigation for contamination analyses
Dichloromethane	75-09-2	Included in solvent for chemical stripping	Substitute identified and qualified
Solvent naphtha (petroleum), light aromatic	64742-95-6	Included in solvent for chemical stripping, in primer or for cleaning	Case by case analysis
Solvent Naphtha (Petroleum) , light aliphatic	64742-89-8	Priming metal surfaces ; fixation of RF absorbant	Case by case analysis

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Example 1 – Substitution of solvents in MAP products

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Presentation of MAP

Our customers…

MAP Compagny is specialized in

- **Design and development** (synthesis/formulation)
- **Manufacturing**
- **Application**

of coatings (Paints, Adhesives, Elastomeres et Greases) for Space and High-tech industries.

i.e.paints for thermo-optical regulation, qualified by CNES and applied on many parts of satellites.

Start of activities	Localisation	Certifications	Member of
1986	France (Pamiers)	ISO 9001 EN (AS) 9100	• **Aerospace Valley** (Space Ind.) • **M&P WG** (ESA)

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Day work

- REACH: human force and plan

With specific human personnel, MAP use a dedicated REACH process with an up-updated plan.

- Internal REACH process for 4 key steps

1- The list of all substances including CAS n°, link to the preparations, REACH status with a level of criticality,…

2- Taking into account of results of the M&P WG

3- Internal REACH status enquiries: the objective is to have all information or constraints as early as possible

4- Final list of substitution list including minor/major modifications of MAP products connected with:

-REACH regulation

- internal/customer criticality

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The modifications

Level of modifications: the objectives is to anticipate REACH regulation impact

Minor modifications 1.Impacted substances 2.Tests de Qualification tests 3.Commercial impact	Major modifications 1-Impacted substances 2-Tests de Qualification tests 3-Commercial impact
1-Non critical raw material (i.e. solvent).	**Major modification with re-formulation or new manufacturing process.** Replacement of raw material or new technology.
2-Complementary qualification : simple characterization and control of applicability	**Major qualification:** Complete qualification with analysis of all characteristics and applicability.
Same commercial name: the modification is under quality system and traceability MAP examples of paints: SG121FD, PCBE, SCK5…	**The trade name will change** Example for above MAP products: MAP ® AQ PU1, MAP ® AQ PUK, MAPSIL ® AS, MAP ® AQ STATIC …

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Alternative already closed

Even if MAP®AQ PU1 is already qualified for Space applications, MAP Company still manufacture PU1 paint.

PU1 Polyurethane Solvent  R11 R67 R63 R26 R40 R42/43 R36/38 R48/20	**Major modifications** **1-Impacted substances** **2-Qualification tests** **3-Commercial impact**	**MAP®AQPU1 Polyurethane Water based formulation**  R10 R23 R34 R20/21/22
1a-Solvent identified as critical: toluene (CMR3= high level criticity) 2a- other CAS numbers (with high level of criticity)	**Major modification with re-formulation or new manufacturing process.** Replacement of raw material or new technology.	1-New formulation with new raw materials and new technology= no impacted substance (under REACH, French regulation,….)
2-Qualification as a Space paint	**Major qualification:** Complete qualification with analysis of all characteristics and applicability.	2-New qualification by CNES
3-New trade name	**New trade name** MAP ® AQ PU1	3-Information to customers

Example 2 – Trichloromethane replacement for molecular contamination test

Context

- Trichloromethane is used for surface contamination test according to ECSS-Q-ST-70-05C
- Trichloromethane is classified carcinogenic (CMR 3) and toxic for reproduction

Mid-term risk for inclusion in candidate list of SVHC

Problems:

➔Industrial point of view: supplying difficulties

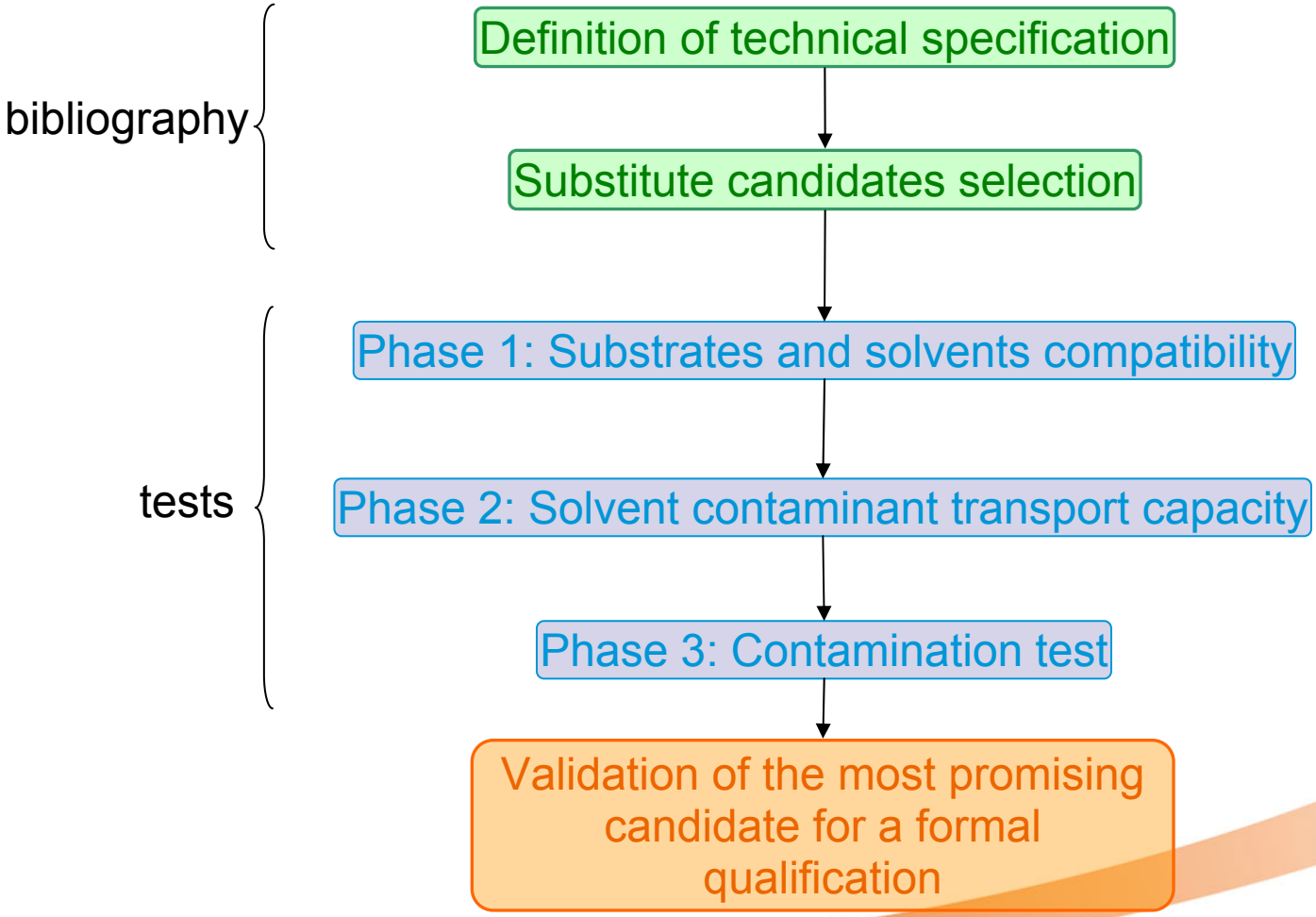
➔Authorisation file expensive and with a limit term

➔Risk of product obsolescence because of a lack of supplier

Action to anticipate the risk : search for a substitute

Partnership between ASTRIUM and CNES

Roadmap



Technical specification

- Candidates solvents:
  - Must not have same spectral absorbance as contaminants.
  - Have to make soluble the 4 contaminants families:

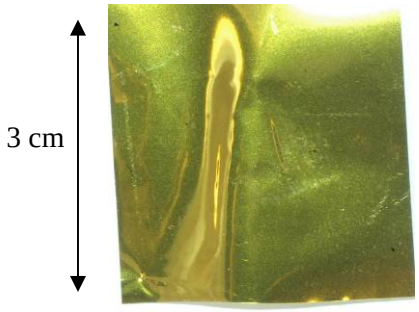
Contaminant	Absorbance peak	Formula
Hydrocarbures	2920 cm^{-1}	C_nH_{2n+2}
Esters	1735 cm^{-1}	RCOOR’
Methylsilicones	1260 cm^{-1} et 805 cm^{-1}	CH_3-$(SiO)_n$-CH_3
Methylphenylsilicones	1260 cm^{-1}, 1120 cm^{-1} et 805 cm^{-1}	C_6H_5-$(SiO)_n$-CH_3

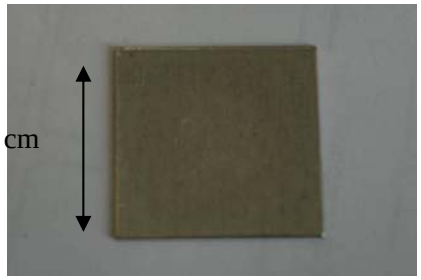
  - Have to evaporate quickly at room temperature.
  - Must not damage any substrate.
  - Must not have a NVR ≥ 5mg/L.
  - Must not be carcinogen, mutagen or be toxic for reproduction.

Solvents selection

- 7 solvents have been identified to be compliant with technical requirements :
  - *Acetonitrile*
  - *Isopropanol*
  - *Pentane*
  - *Dimethylsulfoxide*
  - *Diisopropyl ether*
  - *111 trifluorotoluene*
  - *Promosolv70® (an azeotropic mix of 1,2-trans-dichloroethylene and methoxynonafluorobutane*

Phase 1: Substrates and solvents compatibility Test protocol

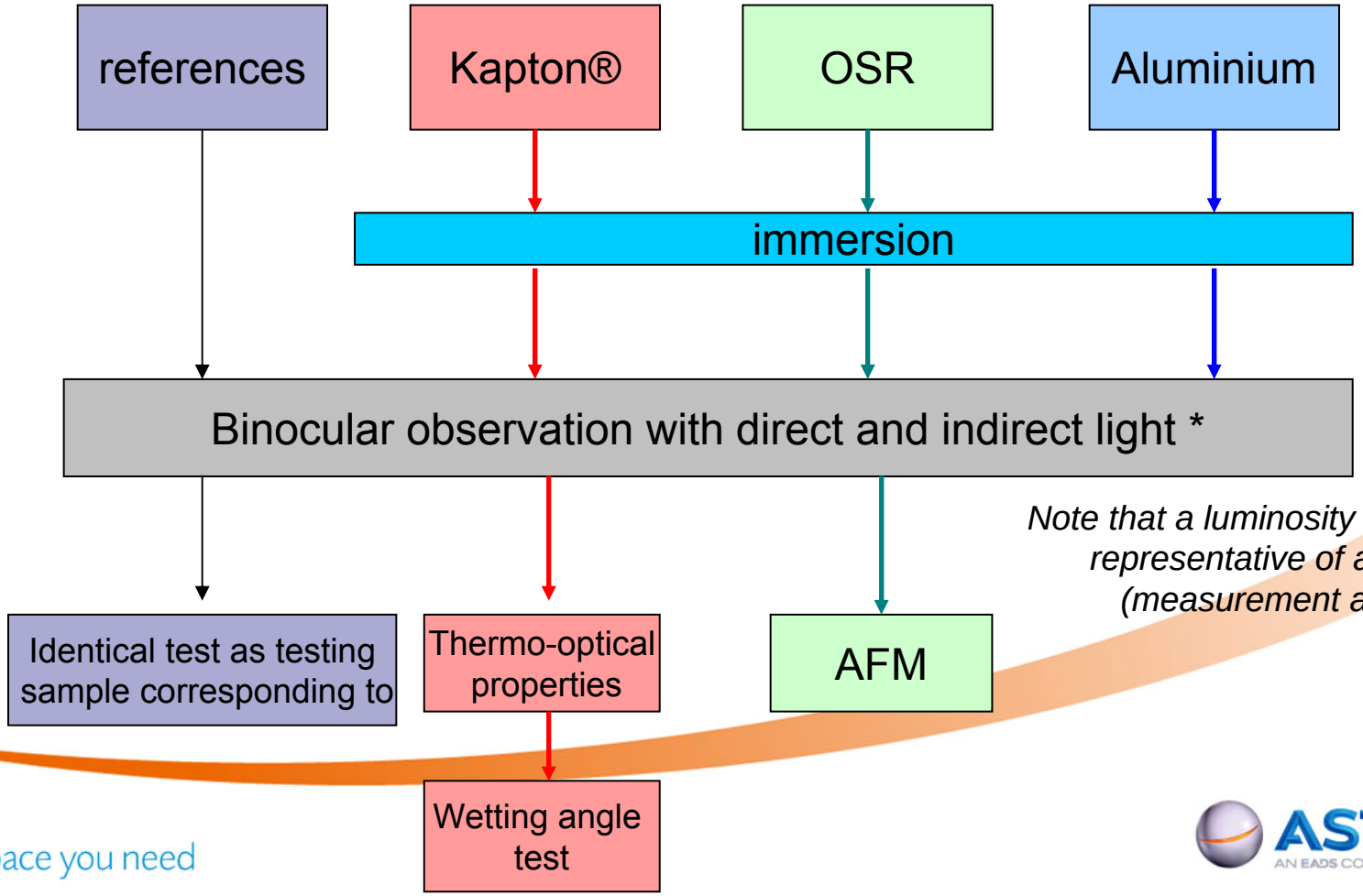




- Substrates:
  - Organic: kapton® VDA 1 side
  - Metallic: Aluminium alloy AG 5754
  - Glass : Optical solar reflector (OSR)
- Test protocol:
  - In accordance with annex H of the ECSS-Q-ST-70-05C
  - Immerse substrates during 15 minutes in 3ml of solvent and then rinse with 1ml of solvent.

Phase 1: Substrates and solvents compatibility Test protocol

- Tests realized to detect a damage depend on substrate



Note that a luminosity change is not representative of a damage (measurement artefact)

Phase 1 tests results

- Visual inspection ➔ no damage observed
- Kapton :
  - Thermo-optical properties ➔ no damage detected
  - Wetting angle study ➔ no damage detected
- OSR :
  - Roughness study (AFM) ➔same damages for trichloromethane as for others solvents

All candidates have succeeded in the protocol phase 1

None of them damage substrates more than trichloromethane

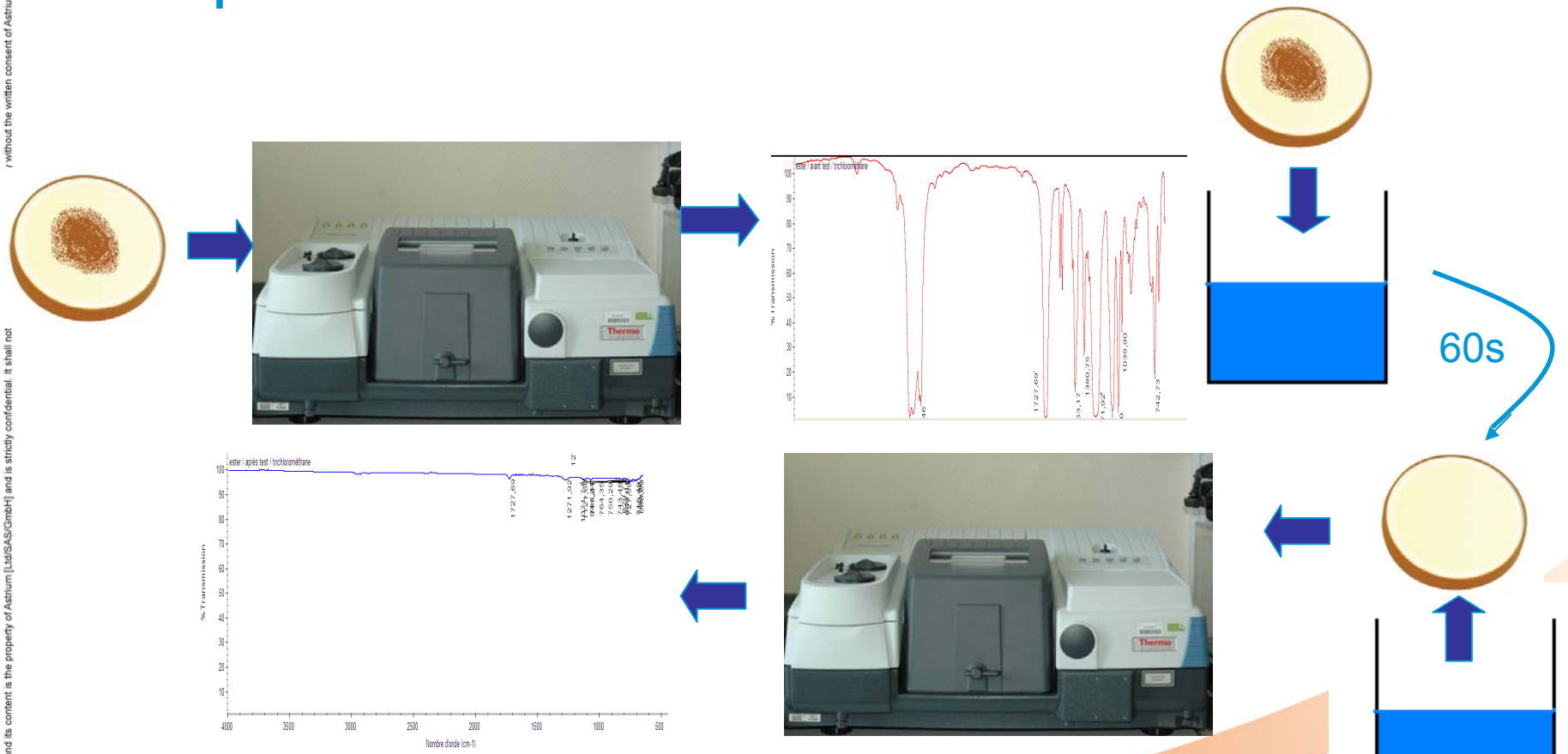
Phase 2: Solvent contaminant transport capacity Test protocol

- Simulated contaminants
  - Should represent 4 contaminant families most observed as contaminants.
  - Should have a well known IR spectrum.
  - Should be easy to supply.

= components used for FTIR Spectrometer calibration

Contaminant	Component used	Formula
Hydrocarbures	paraffine liquide pour spectroscopie	C_nH_{2n+2}
Esters	bis(2-ethylhexyl)phtalate	RCOOR’
Methylsilicones	poly(dimethylsiloxane)	CH_3-$(SiO)_n$-CH_3
Methylphenylsilicones	poly(methylphenylsiloxane)	C_6H_5-$(SiO)_n$-CH_3

Phase 2: Solvent contaminant transport capacity Test protocol



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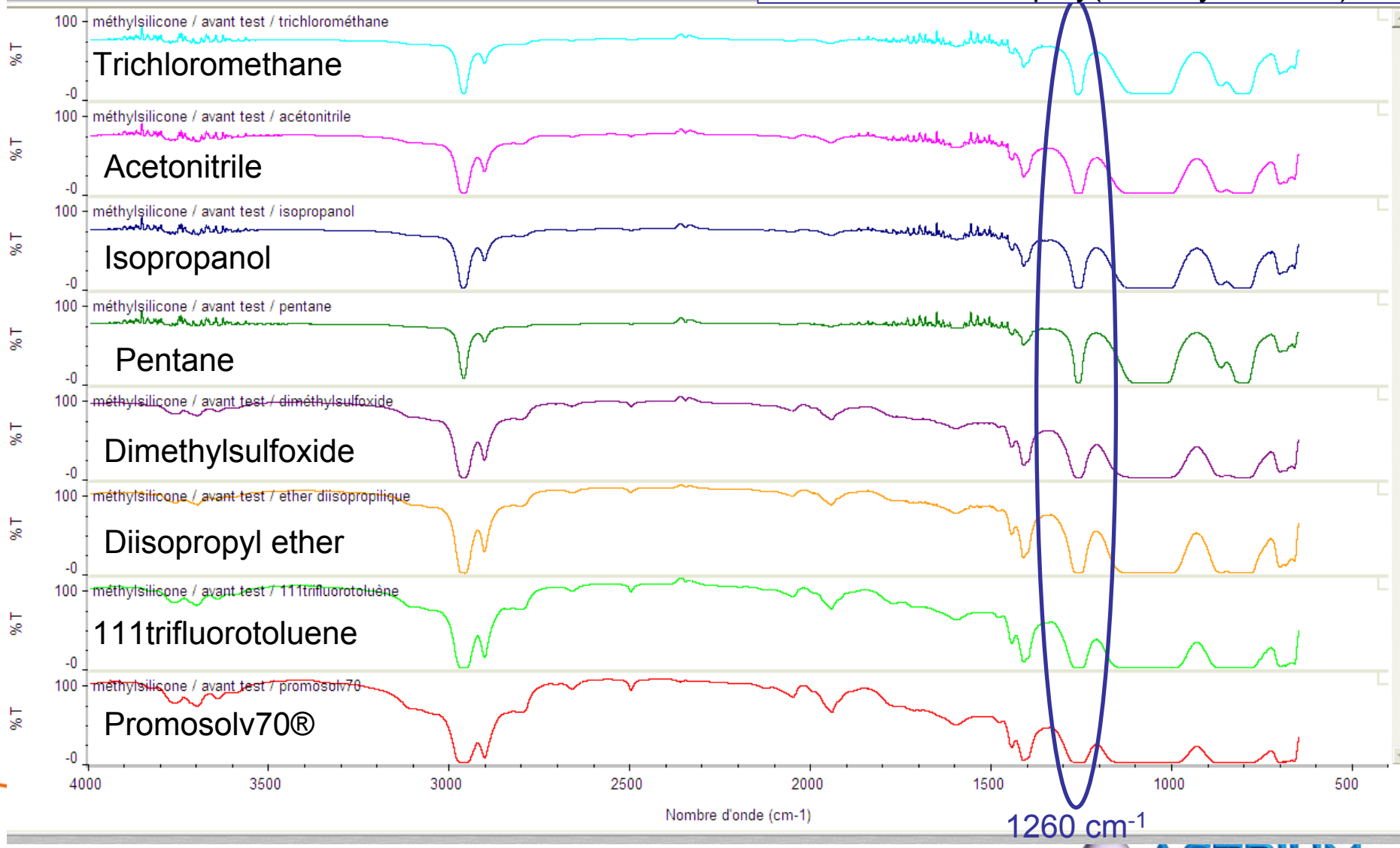
Phase 2 tests results

Before immersion in solvent

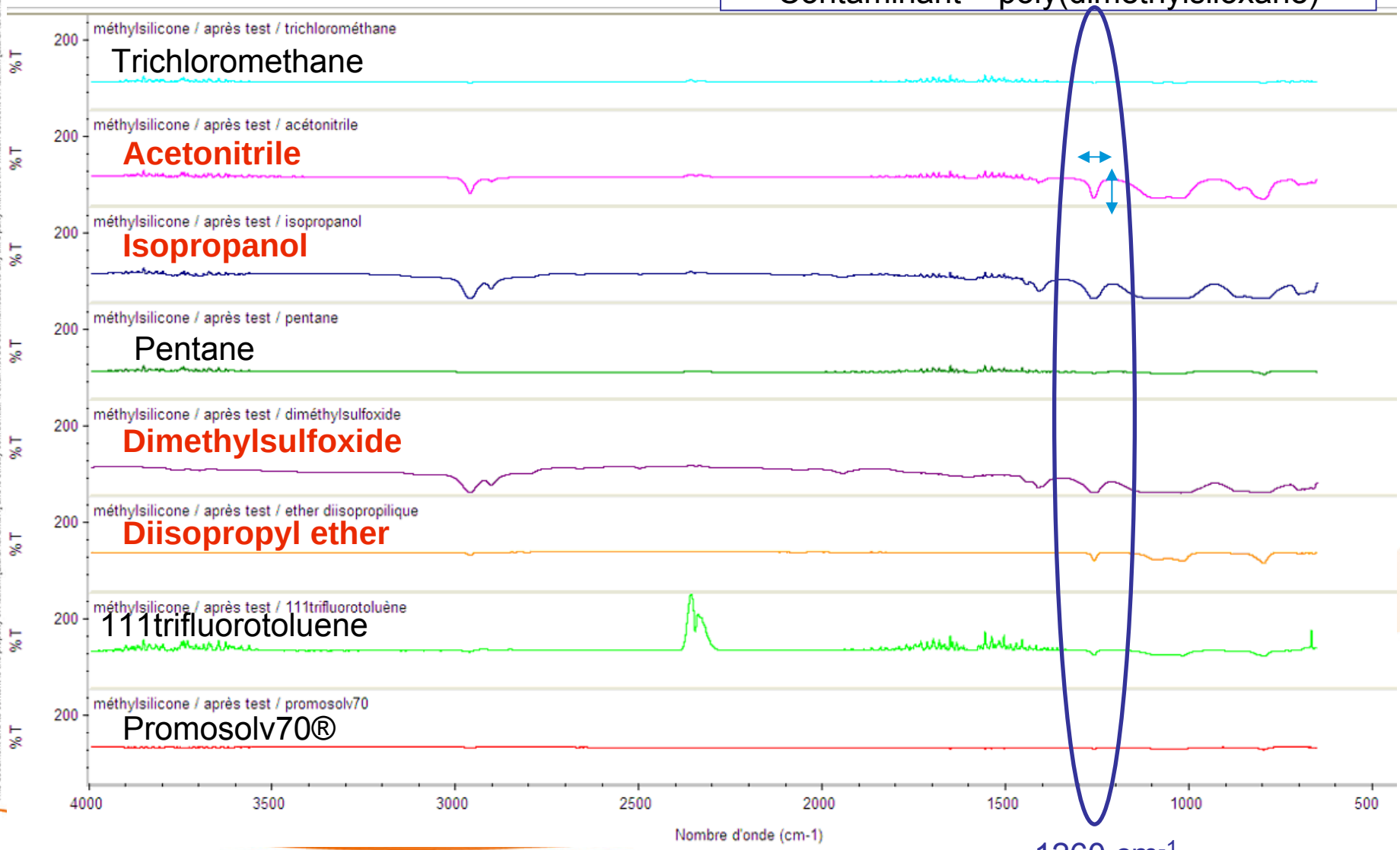
Contaminant = poly(dimethylsiloxane)



Phase 2 tests results

After immersion in solvent

Contaminant = poly(dimethylsiloxane)



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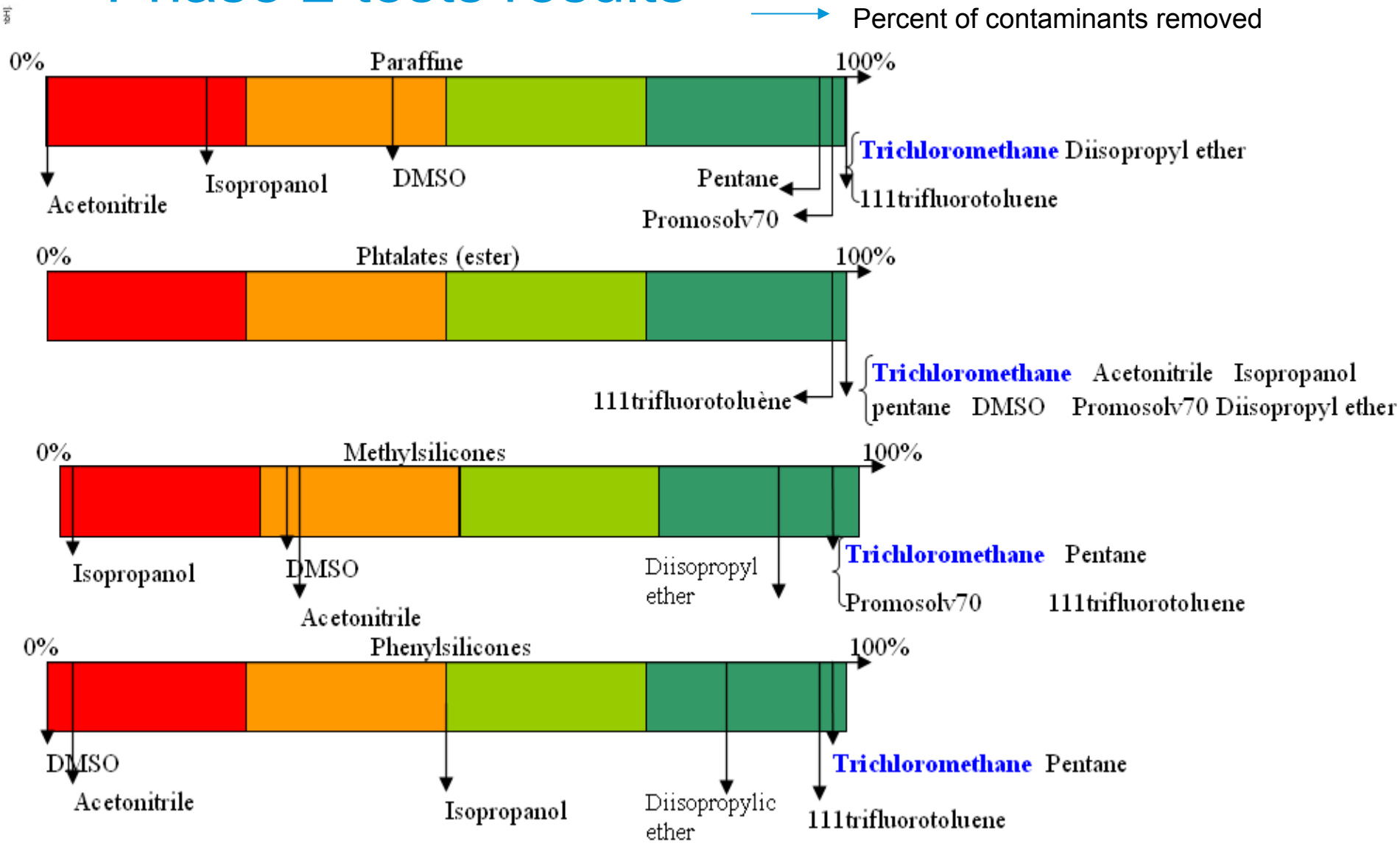
Phase 2 tests results



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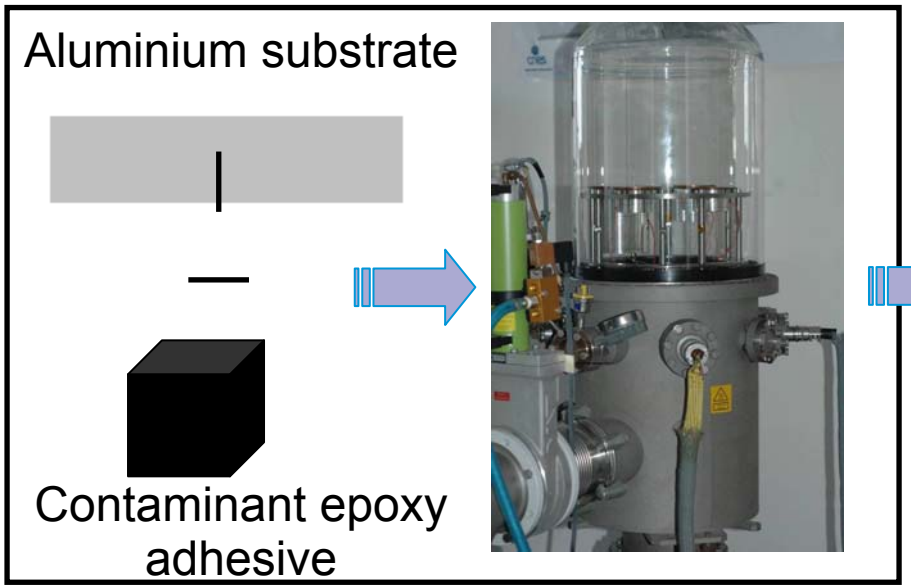
Phase 2 tests results

- None of selected solvent IR absorption peak appears on spectrum after immersion:
  - ➔ All candidate solvents are compatible with this technical requirement
- Acetonitrile, isopropanol dimethylsulfoxide and diisopropyl ether
  - ➔ Low efficiency

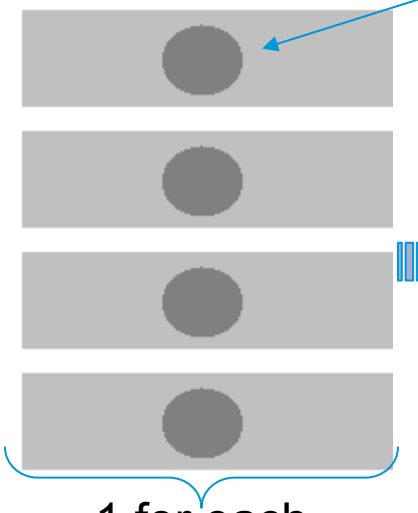
➔ they are deleted from the solvents test list

- 3 solvents left: **pentane; 111 trifluorotoluène; Promosolv70®**

Phase 3: Contamination test
Test protocol



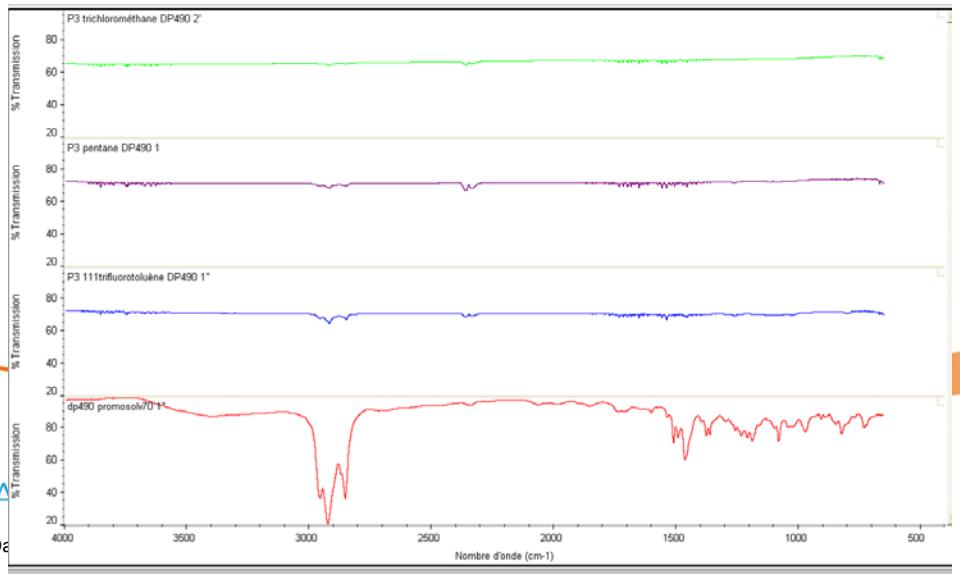
X 4



Deposit of contaminant after outgassing

1 for each solvent

Wiping process with solvents



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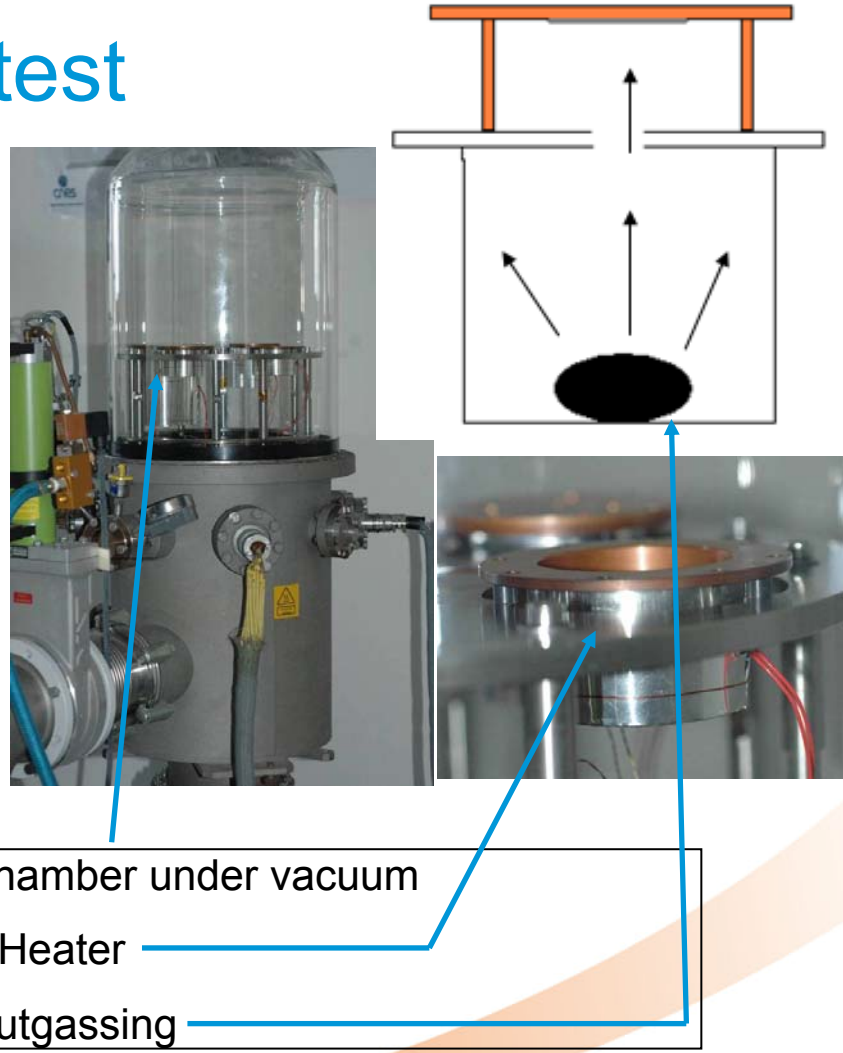
Phase 3: Contamination test
Test protocol

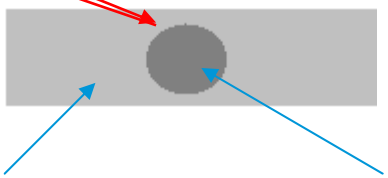
- Purpose:
  - Does the solvent allow to study a contamination?
  - Not quantitative study
  - Not a cleaning of aluminium sample
  - Be close to outgassing phenomenon

- Outgassing:
  - Contaminants: 1g of epoxy adhesive
  - Substrates: aluminium samples
  - Secondary vacuum (10^{-5} mbar)
  - Temperature 125 °C
  - 24h
  - Facility = test facility (not qualified facility)



Phase 3 test results

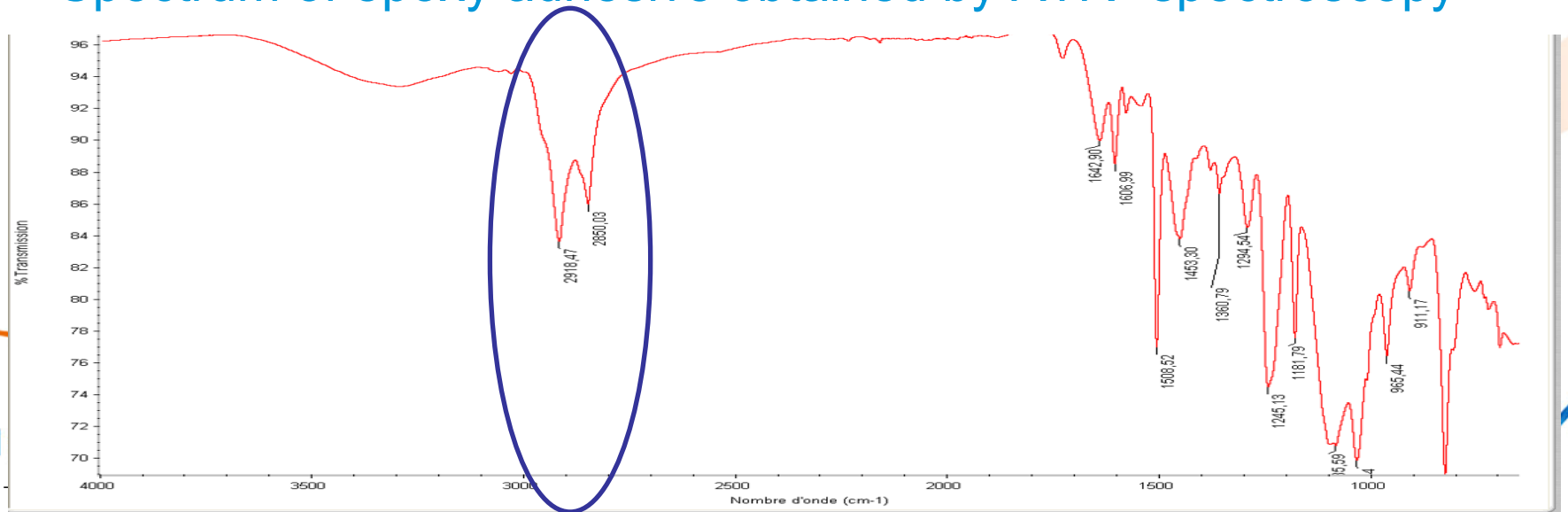
- Mass deposited on aluminium substrates after outgassing adhesive epoxy:
  - Trichloromethane: m = 0.167 mg
  - Pentane: m = 0.058 mg
  - 111trifluorotoluène: m= 0.064 mg
  - Promosolv70®: m = 1.696 mg



aluminium

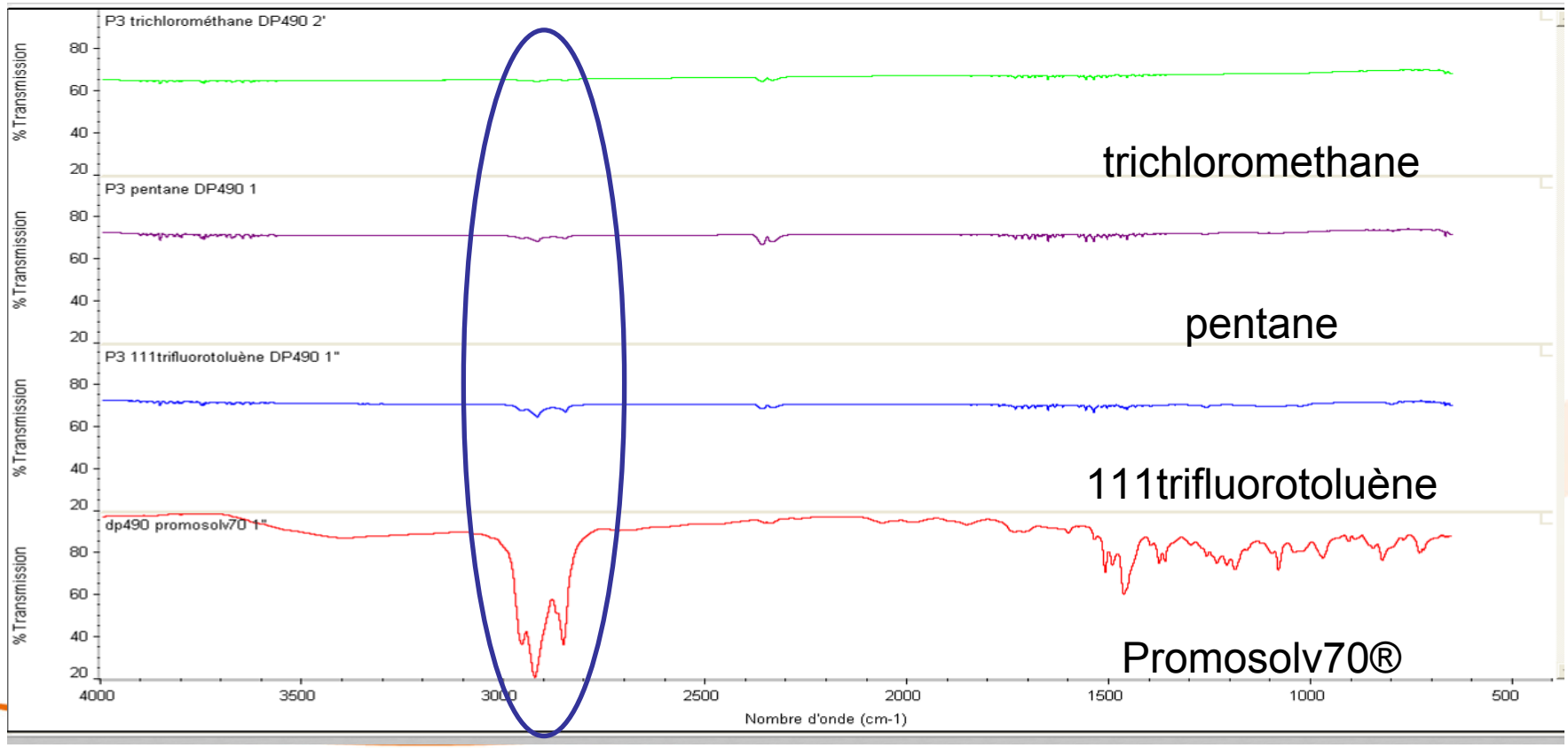
Deposit of contaminant after outgassing

- Spectrum of epoxy adhesive obtained by ATR* spectroscopy



Phase 3 test results

- Spectra obtained by wipe with tested solvents:
  - Same absorbance peak visible
  - Not the same intensity of absorbance peaks



Phase 3 test results

✓ All of these 3 solvents could be used to analyse a condensed contamination with a wiping process.

2 problems:

✗ Mass difference between these four tests

✗ Only one test per solvent has been realized

➔ Impossible to conclude that one of these solvents better than the others

Conclusion

Study purpose:

- ✓ Methodology to select a solvent of replacement has been developed
- ✓ Technical specification for our specific use has been determined
- ✓ A test protocol has been developed and realised on several solvents candidates

Key points:

→ 3 solvents are able to realise a contamination test

- ✘ Promosolv70® seems to be the most promising (less toxic and non inflammable)
- ✘ Tests on solvents have to be thorough to have a clear answer on which one is the most efficient:

→ **Pentane**
111trifluorotoluène
Promosolv70®