Supramolecular Solvent-based Extraction Method for the Determination of a Wide Range of Legacy and Emerging Environmental Contaminants in Indoor Dust

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INTRODUCTION

- Conventional extraction methods for organic pollutants are labour-intensive, time-consuming, and consume large quantities of solvent
- Most conventional methods are tailored to specific pollutants and not suitable for extraction of pollutants with a broad range of physio-chemical properties
- Supramolecular solvents (SUPRAS) are nanostructured liquids from the self-assembly and coacervation of amphiphiles in colloidal suspensions[1,2] and are an alternative extraction method applicable to a broad range of compounds with reduced clean-up
- Despite having the potential to extract a wide range of contaminants, to date SUPRAS are used for the extraction of a single group of contaminants that share similar physio-chemical properties [3, 5, 6, 7]

Why SUPRAS?

- A solvent rich in amphiphiles has a higher abundance of hydrophilic and hydrophobic binding sites (amphiphile concentration ~0.1-1 mg/μL) [2]
- The large number of binding sites facilitates the efficient extraction of compounds at very low solvent volumes
- The multiple extraction mechanisms offered by SUPRAS, including dispersion, hydrogen bonding, polar, ionic, dipole-dipole interactions and others, further enhance the extraction efficiency [1,3]
- SUPRAS have many different polarity microenvironments, which enables them to extract a wide range of pollutants that are both polar and nonpolar, particularly useful for suspect screening or non-targeted analyses [1,3]
- SUPRAS eliminate key matrix components, such as proteins, carbohydrates, and lipids, during extraction, thereby eliminating the need for additional clean-up steps [2,4]

SUPRAS Synthesis

- The process consists of two steps:

1. a colloidal suspension of amphiphiles is spontaneously formed on a molecular level, which contains supramolecular aggregates such as aqueous or reverse micelles or vesicles
2. a coacervation-inducing agent is introduced to alter the environmental conditions of the colloidal suspension, resulting in liquid-liquid phase separation on a nanoscale level[1] (Figure 1)
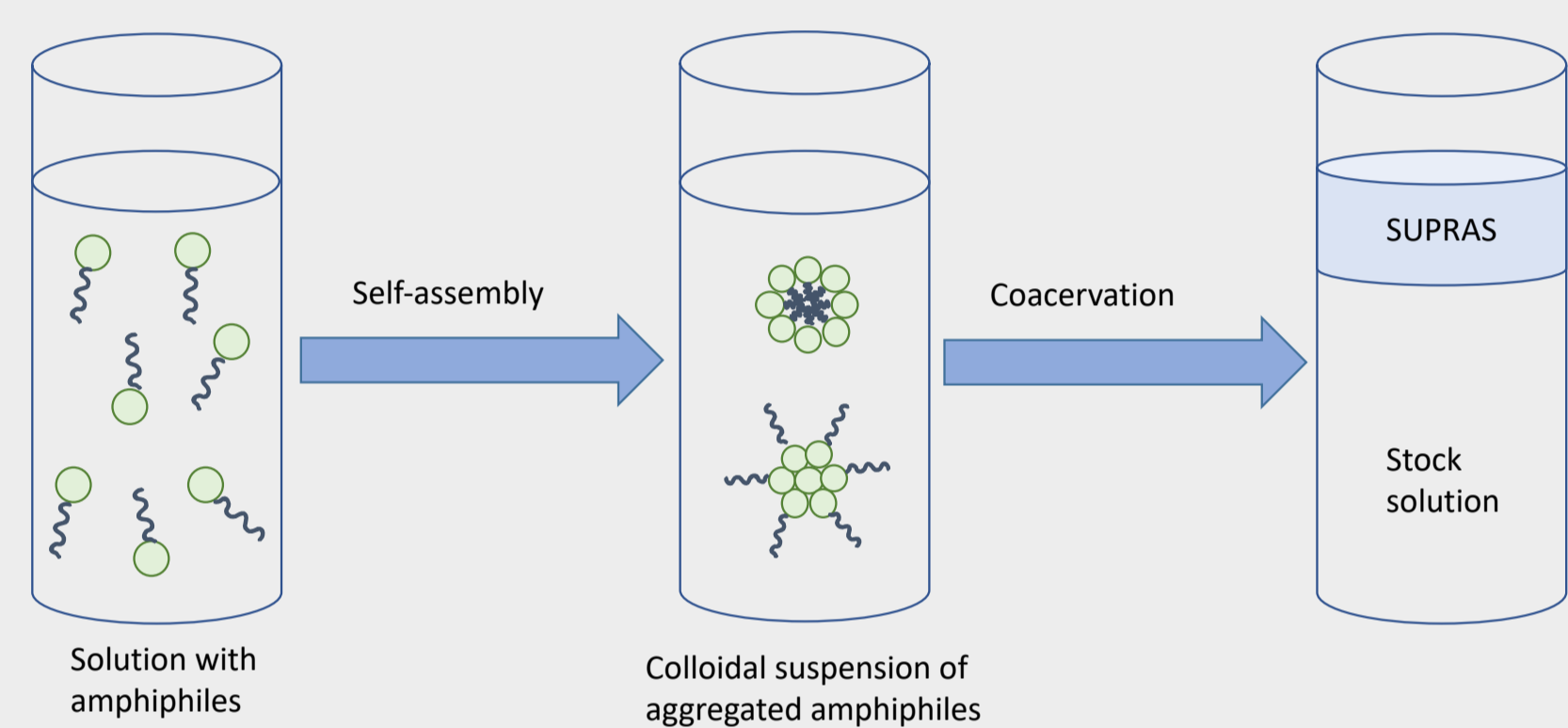

Figure 1: Self-assembly and coacervation of SUPRAS

RESULTS

- Results indicate that SUPRAS Mix 1 was the optimal mixture for extracting a wide range of environmental contaminants (Table 1)
- The extraction efficiency of SUPRAS was either equivalent or inferior to that of conventional extraction methods for many groups of contaminants (Figure 5)
- To extract various groups of pollutants, both conventional and SUPRAS extraction approaches were employed, and their respective concentrations were compared against the certified values of NIST SRM 2585. While SUPRAS recoveries were typically lower than conventional extraction, when values were adjusted for recoveries, SUPRAS exhibited greater accuracy compared to conventional extraction (Figure 6).

Table 1: Average recoveries for labelled internal standards of different groups of chemicals

| Sample	Average recovery for different groups of chemicals (%)									
	PAHs	n-PAHs	o-PAHs	Tonalide	NFRs	PCBs	OCPs	PHTHs	CUPs	PFAS
SUPRAS Mix 1 dust	53,3	69,2	116,7	70,8	72,8	83,8	71,2	81,3	37,3	45,9
SUPRAS Mix 2 dust	47,8	54,8	58,1	67,2	77,1	78,5	63,6	69,9	31,8	46,7
SUPRAS Mix 3 dust	46,8	49,9	58,3	76,0	59,4	61,3	52,8	75,6	37,6	41,3
SUPRAS Mix 4 dust	56,2	84,7	82,6	68,7	62,7	74,2	60,8	68,2	38,9	45,4
SUPRAS Mix 5 dust	41,3	61,7	55,9	53,1	82,4	65,2	56,6	60,9	27,6	46,9
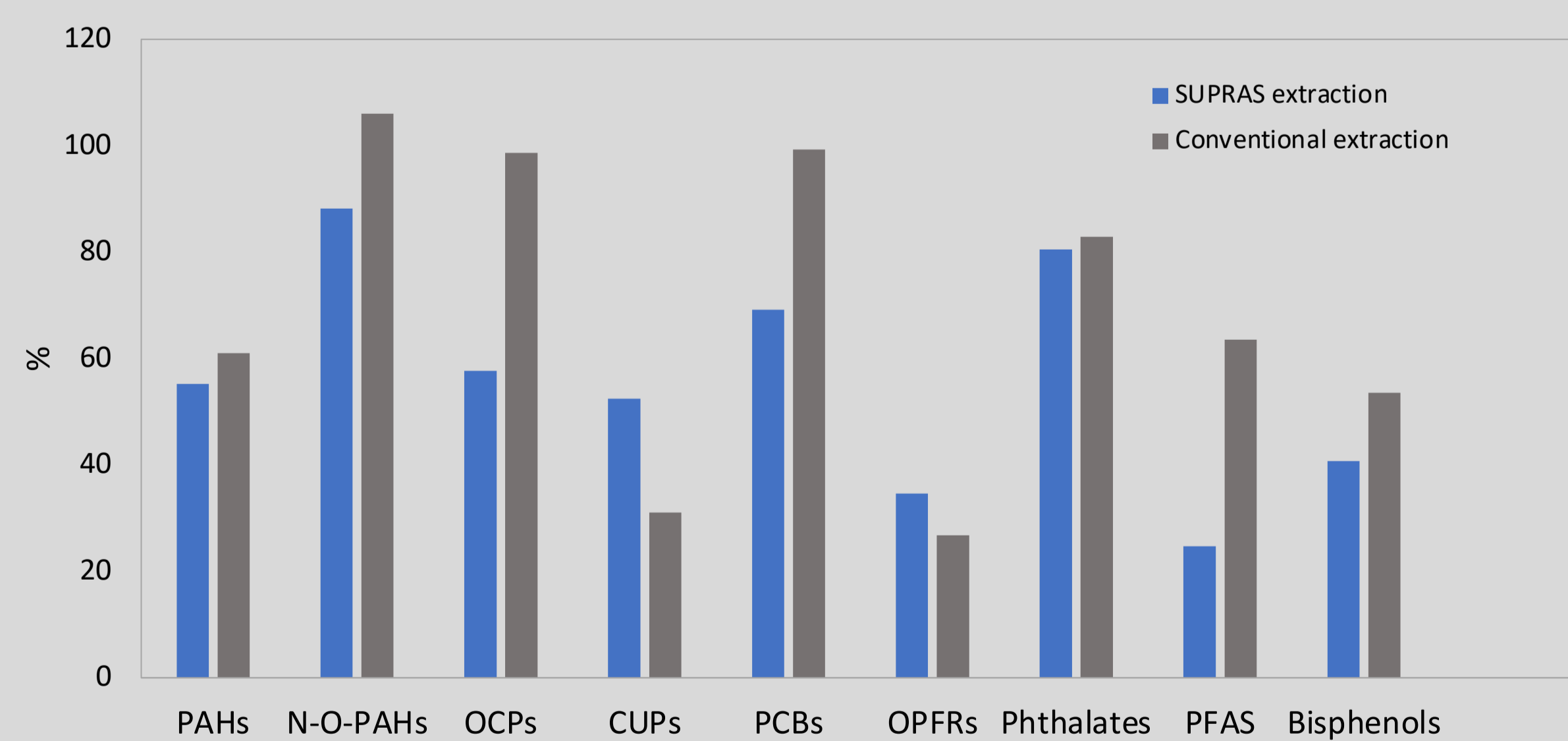
Figure 5: Extraction efficiency (%) of conventional and SUPRAS extraction for different groups of chemicals
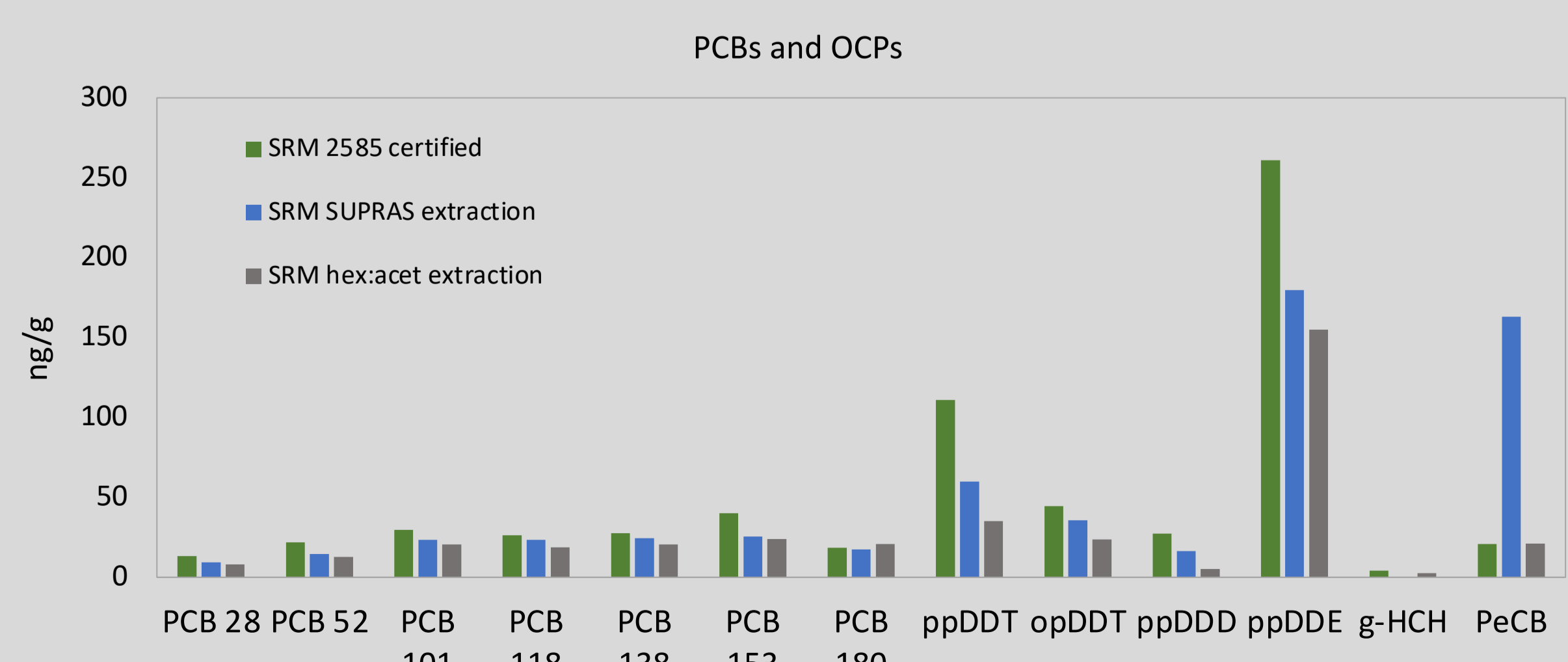

Figure 6: Comparison of hexane:acetone and SUPRAS extraction of SRM 2585 to the NIST certified concentration (ng/g)

AIM

The aim of this study is to employ existing knowledge of supramolecular solvents to develop an extraction method that addresses the challenges inherent in conventional extraction techniques, and subsequently apply this method for extraction of wide range of indoor contaminants from household dust.

METHODS

Sampling

- House dust samples were obtained in the Czech Republic in the summer of 2022
- A household vacuum cleaner equipped with a modified sampling head that allowed for the collection of particles < 1 mm onto the quartz fiber filter was use
- The dust samples, along with the filter were pulverized before processing

SUPRAS Synthesis

- Seven different SUPRAS mixtures were synthetized using Milli-Q water, purified tetrahydrofuran (THF), and an alcohol (Figure 2)
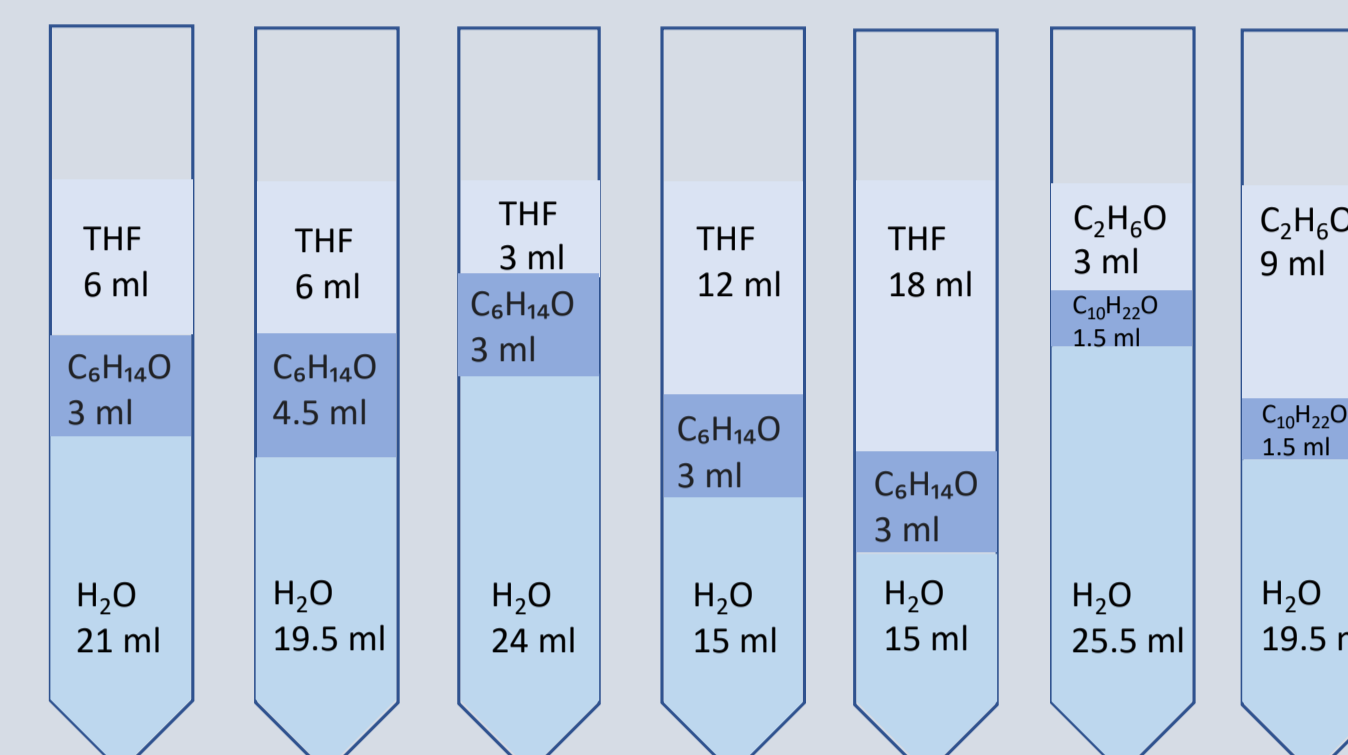

Figure 2: Seven different SUPRAS mixtures synthetized

- The mixtures were prepared by adding all the SUPRAS components into a centrifuge glass and centrifuged for 30 minutes at 2400 rpm (Figure 3)
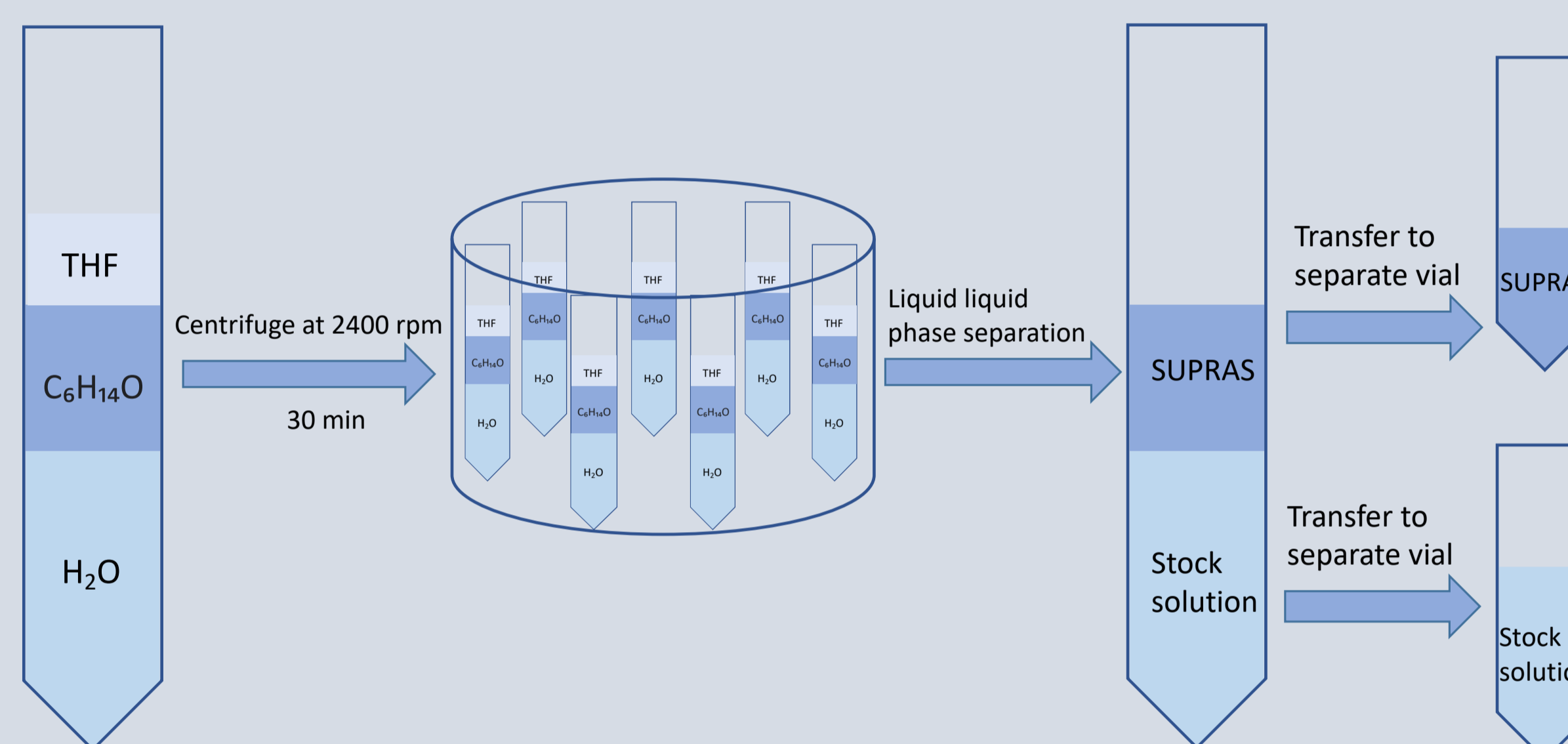

Figure 3: SUPRAS synthesis

Extraction with SUPRAS

- 100 mg of composite dust sample was weighed and spiked with labelled internal standards of targeted contaminants
- The samples were hydrated using 600 μl of SUPRAS stock solution and then extracted with 400 μl of SUPRAS
- The extraction was carried out using ultrasonication for 20 minutes at RT, followed by centrifugation at 11 000 rpm for 15 minutes at RT
- The resulting SUPRAS extracts were evaporated under controlled N_2 flow at 35 °C and dissolved in MeOH (LC-MS) or isooctane/nonane (GC-MS) and analyzed for 9 organic contaminant groups (Figure 4)
- A SUPRAS mixture with best extraction efficiency was identified and used for second round of dust extraction with extended list of organic contaminants
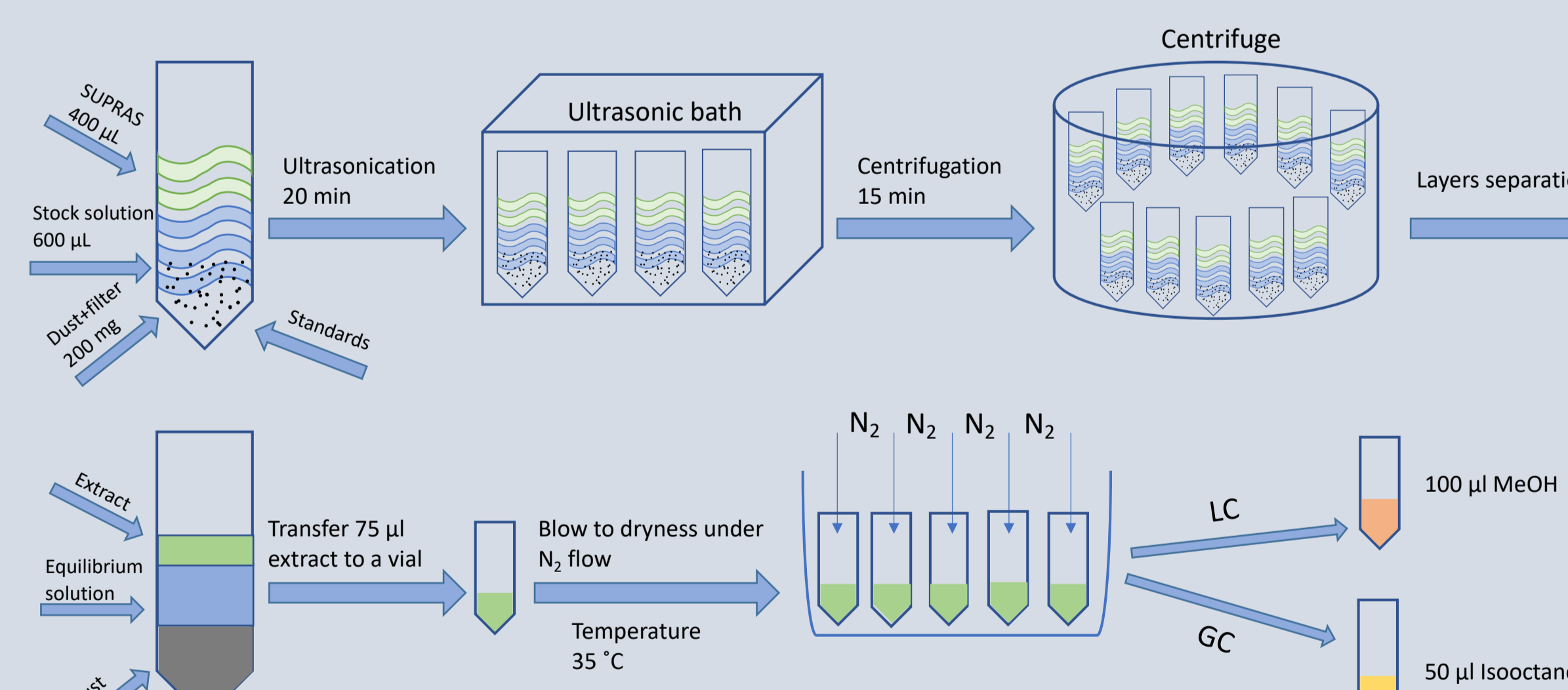

Figure 4: Extraction of a dust sample with SUPRAS

- Alongside the SUPRAS extraction, conventional extractions were performed - hexane:acetone (1:1) for non-polar contaminants, MeOH extraction for polar contaminants
- NIST standard reference material (SRM) 2585 was subjected to both conventional extractions and SUPRAS extraction

CONCLUSION

- Effective extraction method
  - 60-90% recovery for least volatile contaminants
  - 40-60% for more volatile contaminants
- Easy to perform
- Cheap
- Environmentally friendly
- Suitable for broad range of chemicals

- Most volatile compounds evaporated during extraction and not detected
- Matrix effect
- Additional clean-up needed for some contaminant groups

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