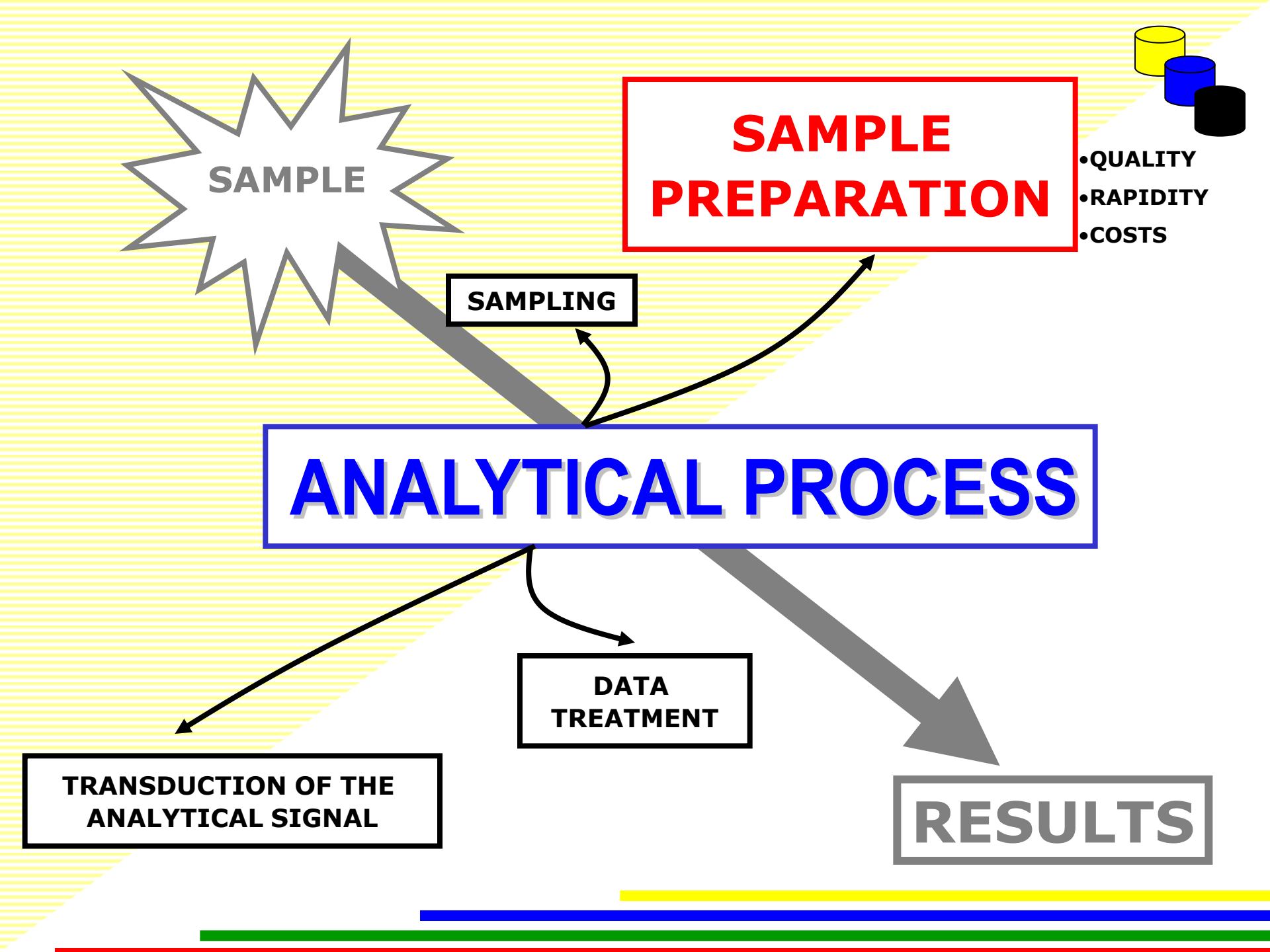
Departamento de Química Inorgánica y Analítica

Facultad de Ciencias Químicas y Farmacéuticas

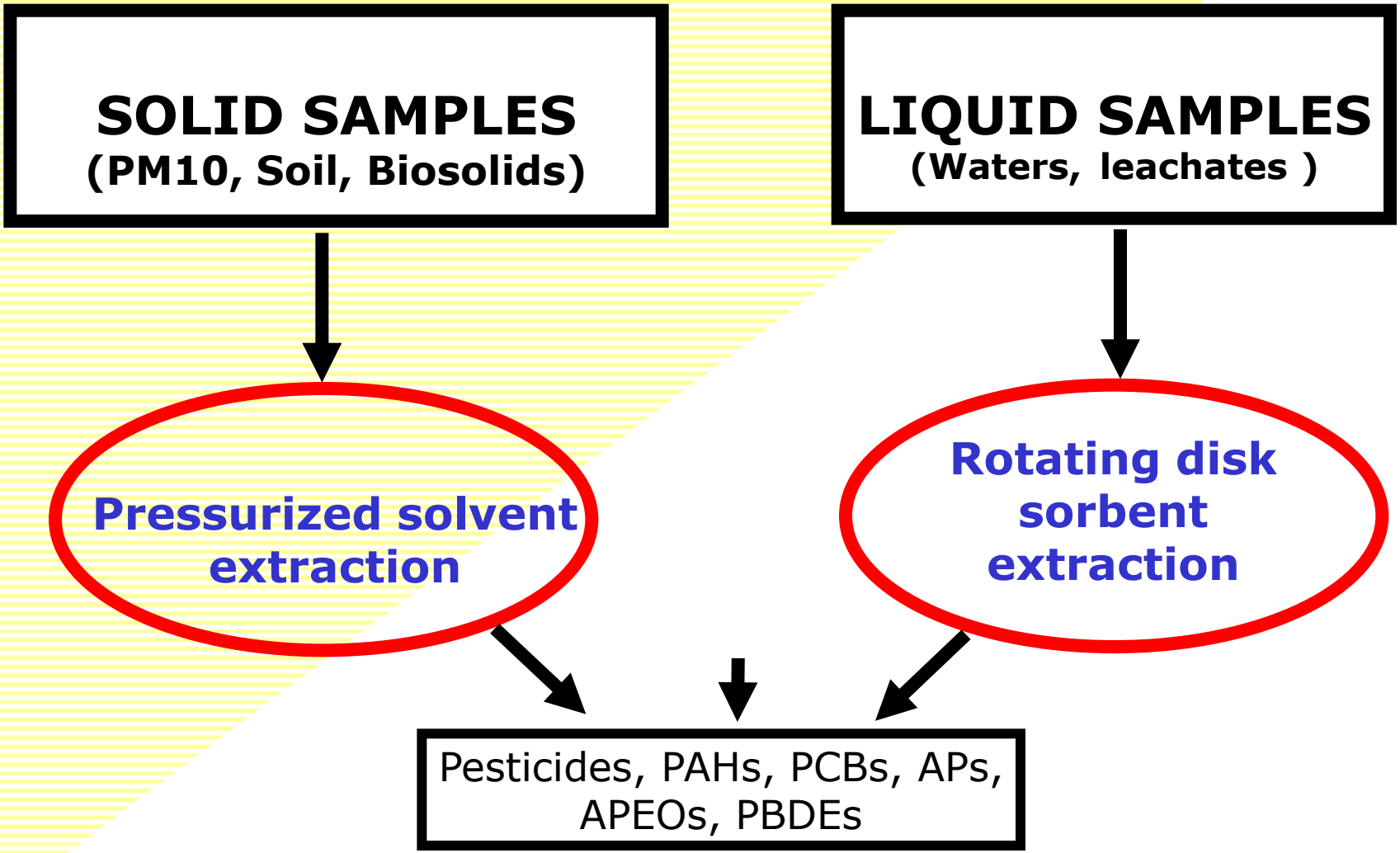
Universidad de Chile

Microextraction of organic pollutants from liquid samples by using rotating-disk sorbent extraction

Pablo Richter


SAMPLE
SAMPLE PREPARATION
•QUALITY
•RAPIDITY
•COSTS
SAMPLING
ANALYTICAL PROCESS
DATA TREATMENT
TRANSDUCTION OF THE ANALYTICAL SIGNAL
RESULTS

Sample preparation



Traditional methods of extraction in solid samples

Why is important the development of new extraction methods?

- Organic solvent use (Green chemistry)
- Low efficiency: Lack of accuracy (quality)
- Heating: slow and no homogeneous.
- Use of open systems: higher contamination, higher reagent use, no pressure advantages.
- High level of human participation.

Advances in sample extraction

- To increase the efficiency
- To increase rapidity
- To reduce (or ELIMINATE) use of organic solvents
- Automation
- To improve quality of results

Solid samples

TRADITIONAL

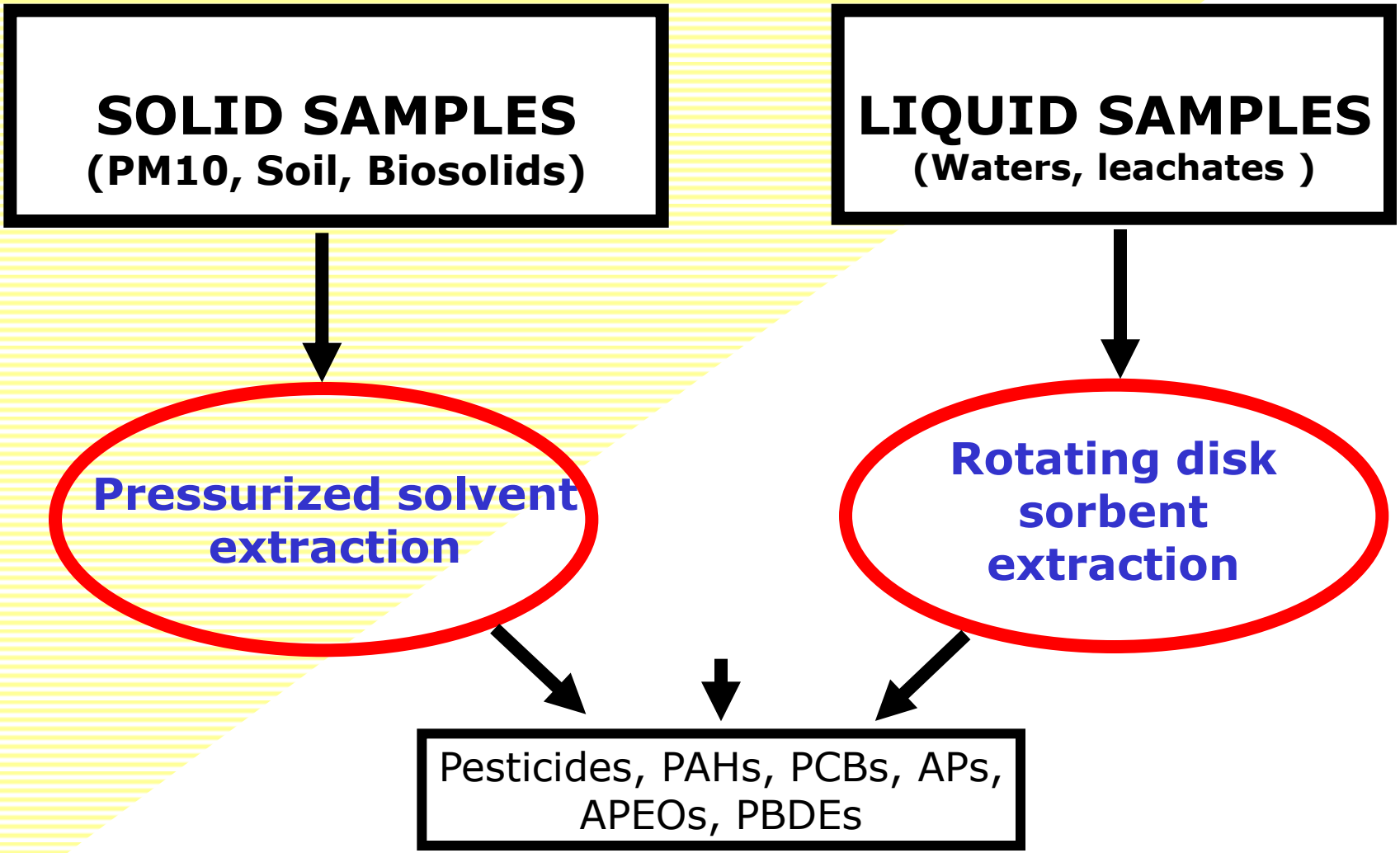
SOXHLET EXTRACTION

Year 1879

MODERN TECHNIQUES

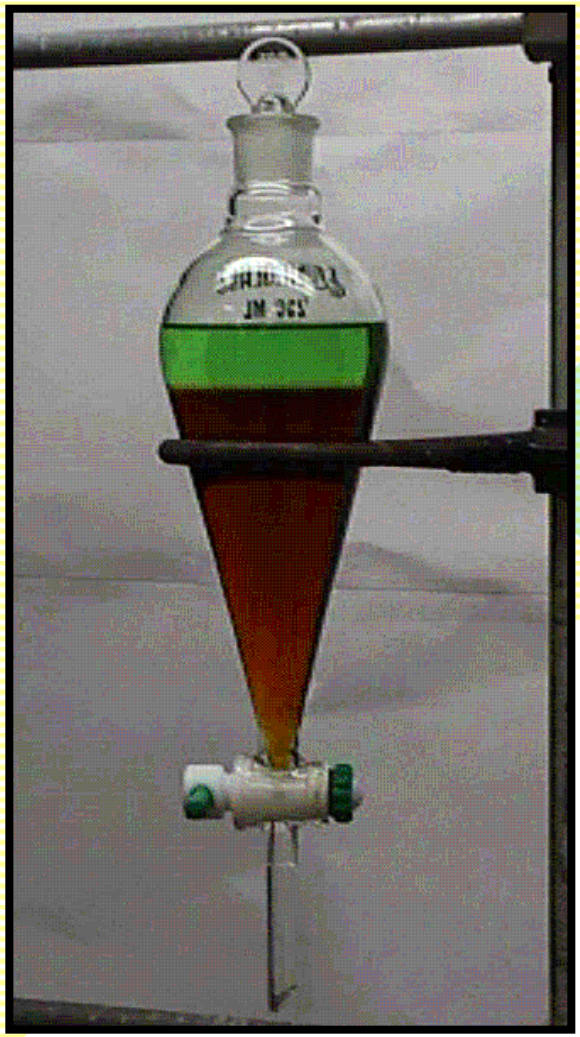
- ULTRASOUND
- MICROWAVES
- SUPERCRITICAL FLUIDS
- PRESSURIZED SOLVENT

Sample preparation



Liquid samples

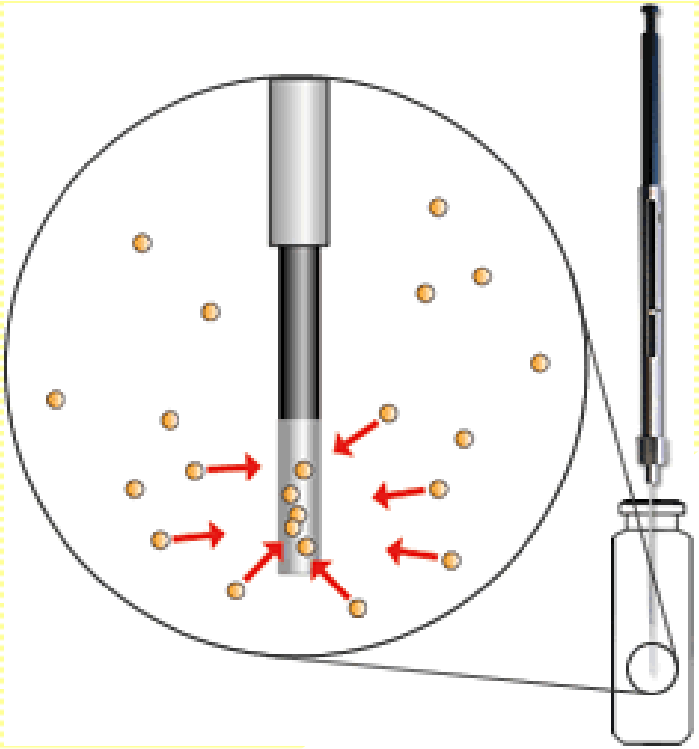
LIQUID-LIQUID EXTRACTION



MODERN TECHNIQUES

- SOLID PHASE EXTRACTION(SPE)
- SOLID PHASE MICROEXTRACTION (SPME)
- SBSE (TWISTER)
- SILICON ROD

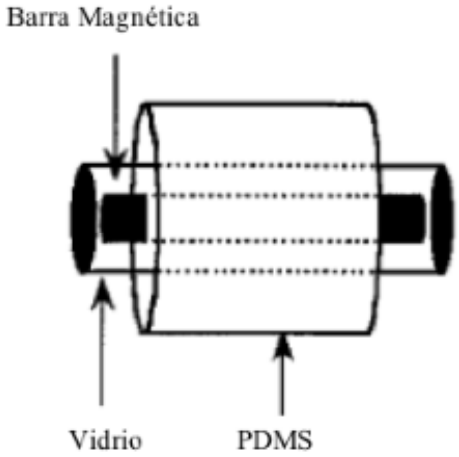
Solid phase microextraction(SPME)
(Pawliszyn, 1989)



- SPME involves the use of a fiber coated with an extracting phase, that can be a liquid or a solid, which extracts different kinds of analytes (including both volatile and non-volatile) from different kinds of media, that can be in liquid or gas phase.

- After extraction, the SPME fiber is transferred to the injection port of separating instruments, such as a Gas Chromatograph, where desorption of the analyte takes place.

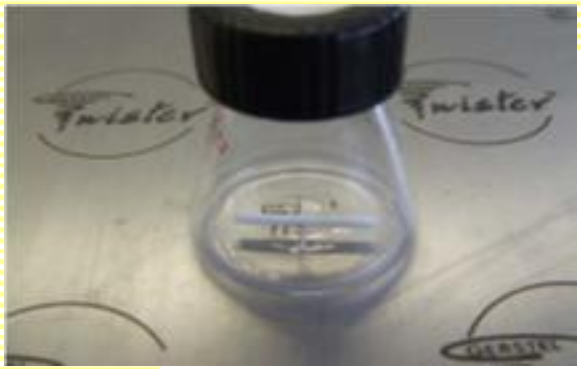
Stir bar sorptive extraction, SBSE (Twister)



- Twister is a new solventless sample preparation method for the extraction and enrichment of organic compounds from aqueous matrices.
- The method is based on the same principles as solid-phase microextraction (SPME).
- Compared with SPME (0.5 µl) , a relatively large amount of extracting phase (100 µl) is coated on a stir bar.
- The technique has been applied successfully to trace analysis in environmental, biomedical and food applications.
- Extremely low detection limits.

E. Baltussen, P. Sandra, F. David, C. Cramers. J. Microcolumn Separations, 11(10) 737-747 (1999)

Silicon rod extraction, SRE



- Silicone rod extraction (SRE) is a not commercial technology, which employ silicone materials in form of rods and tubes for the enrichment of organic compounds.
- SRE is similar to SPME and SBSE but with the advantage of being inexpensive, flexible and robust.
- SRE with different sizes and phase volumes (8–635 µL) have been applied for the extraction of a large variety of organic micropollutants.

P. Popp, C. Bauer, A. Paschke and L. Montero, Anal. Chim. Acta 504 (2004), p. 307

Thin-Film Microextraction

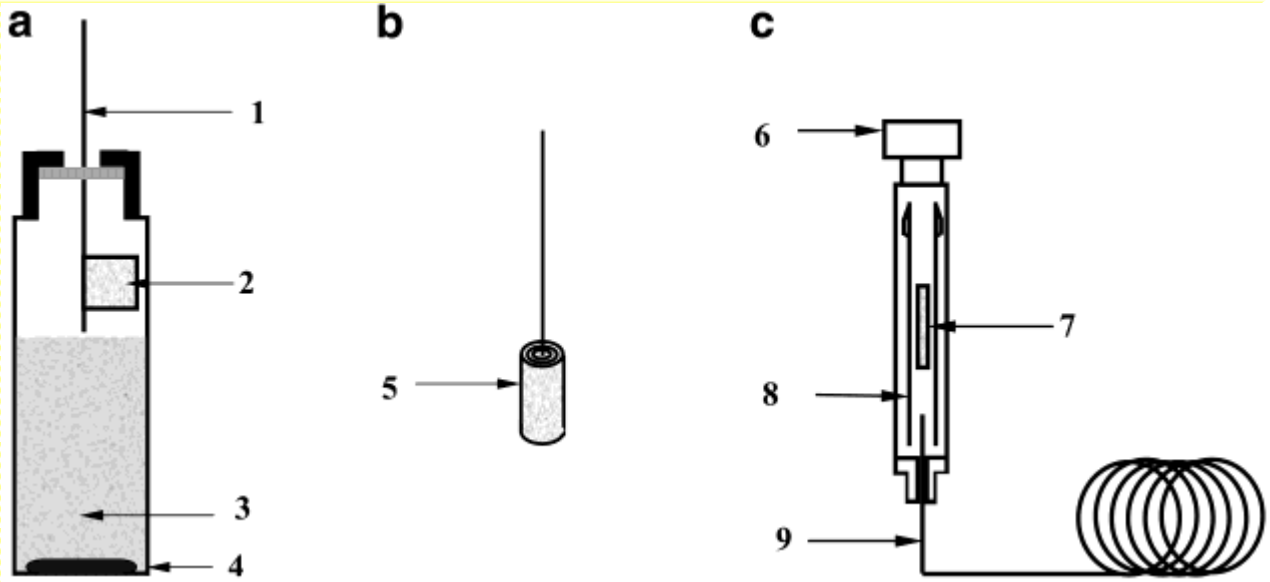


Figure 1. Drawing of the headspace membrane SPME system. 1. Deactivated stainless steel rod. 2. Flat sheet membrane. 3. Sample solution. 4. Teflon-coated stirring bar. 5. Rolled membrane. 6. Injector nut. 7. Rolled membrane. 8. Glass liner. 9. Capillary column.

- A thin sheet of polydimethylsiloxane (PDMS) membrane is employed as an extraction phase.
- This PDMS extraction approach showed much higher extraction rates because of the larger surface area to extraction-phase volume ratio of the thin film.

I. Bruheim, X.C. Liu and J. Pawliszyn, Anal. Chem. 75 (2003), p. 1002.

Extraction in PDMS

- Partition coefficient PDMS-water

$$K_{O/W} \approx K_{PDMS/W} = \frac{C_{PDMS}}{C_W} = \frac{m_{PDMS}}{m_W} \times \frac{V_W}{V_{PDMS}}$$

$$\frac{K_{O/W}}{\beta} = \frac{m_{PDMS}}{m_W} = \frac{m_{PDMS}}{m_0 - m_{PDMS}}$$

- Analyte recovery

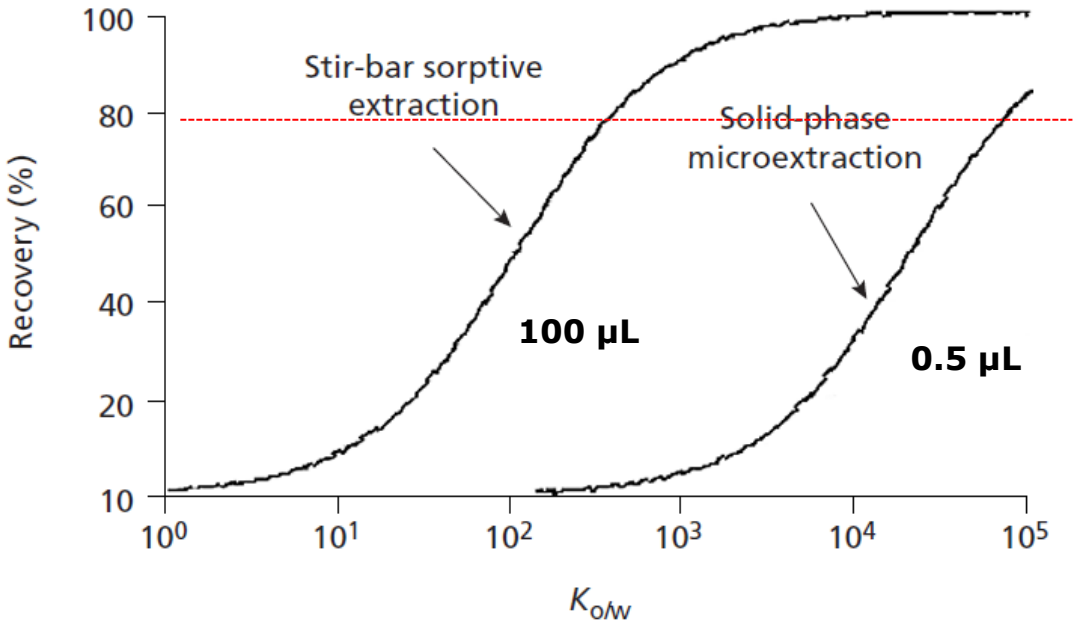
$$\frac{m_{PDMS}}{m_0} = \frac{\left(\frac{K_{O/W}}{\beta}\right)}{1+\left(\frac{K_{O/W}}{\beta}\right)}$$

Same Ko/w, recovery in SBSE is higher than in SPME

Extraction in PDMS

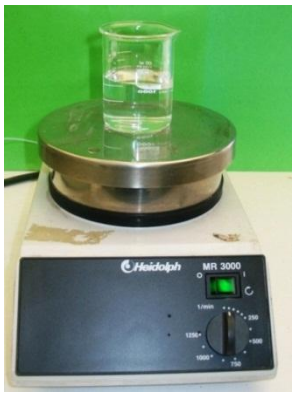
Theoretical comparison between SBSE and SPME

Figure 1: Recovery for solutes in function of the octanol–water partitioning coefficient $K_{o/w}$ for SPME (10 mL sample, 100 µm polydimethylsiloxane fibre) and for stir-bar sorptive extraction (10 mL sample, 10 mm × 0.5 mm polydimethylsiloxane-coated stir bar)

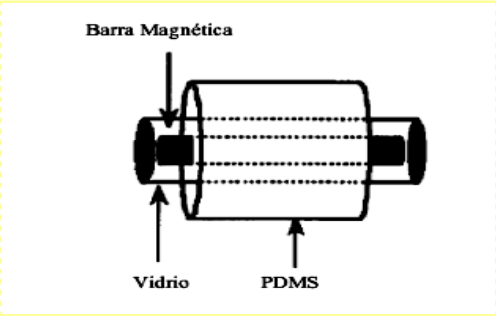


Drawbacks observed in SBSE

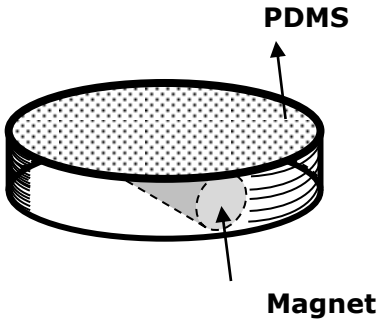
- Increasing stirring rate may cause physical damage in the extraction phase due to direct contact with the sample vial bottom.
- Surface area to extraction-phase volume ratio
- High cost.



Rotating disk sorbent extraction (RDSE)



SBSE



RDSE

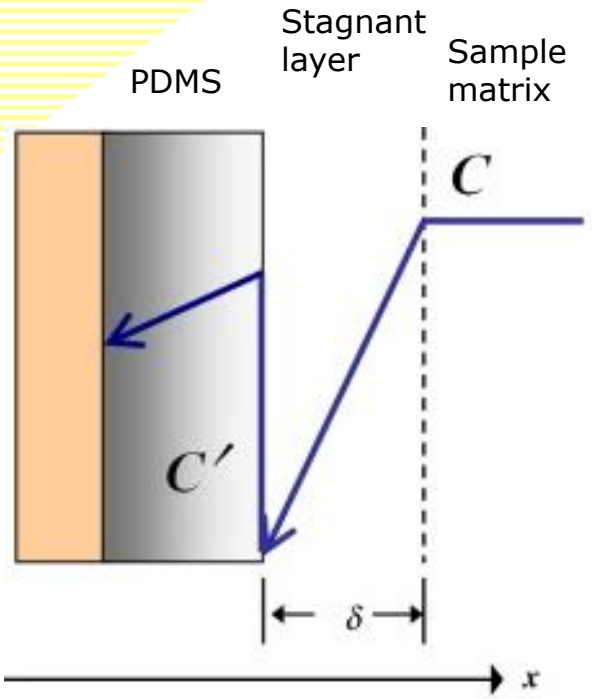
- **> Higher rotation velocity**
- **> A/V ratio**
- **< Cost**
- **> Automation capability**

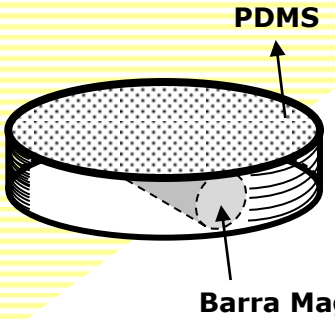
P. Richter, C. Leiva, C. Choque, A. Giordano, B. Sepúlveda, J. Chromatogr. A, 2009, 1216, 8598-8602.

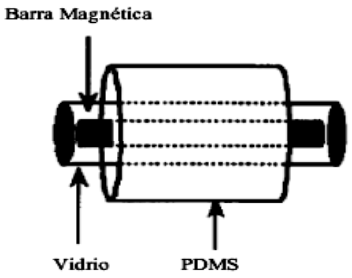
Extraction efficiency

$$t_e = \frac{3 \cdot \delta \cdot K_d \cdot P_f}{D} \quad (2)$$

$$\frac{dn}{dt} = \left(\frac{D \cdot A}{\delta}\right) \cdot C \quad (3)$$

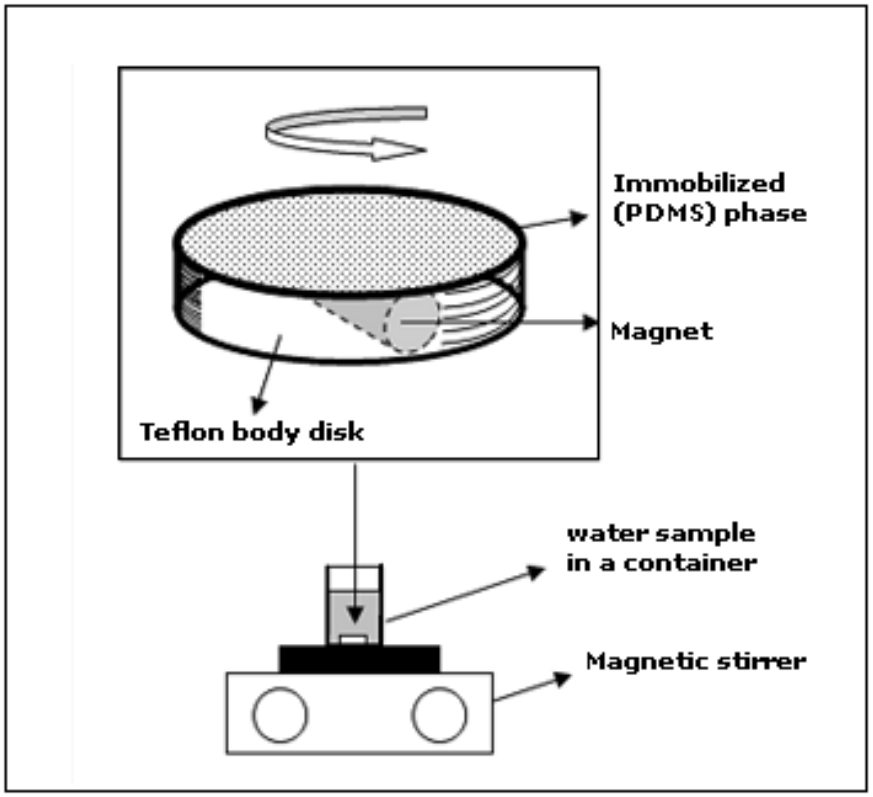


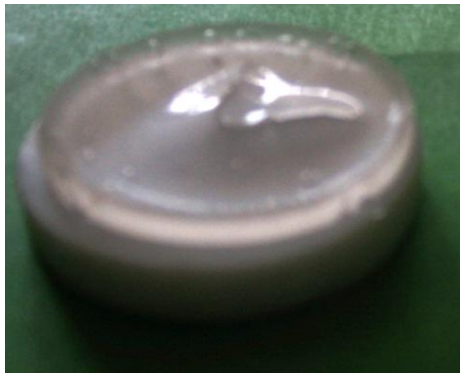




Rotating disk sorbent extraction (RDSE)

Batch system

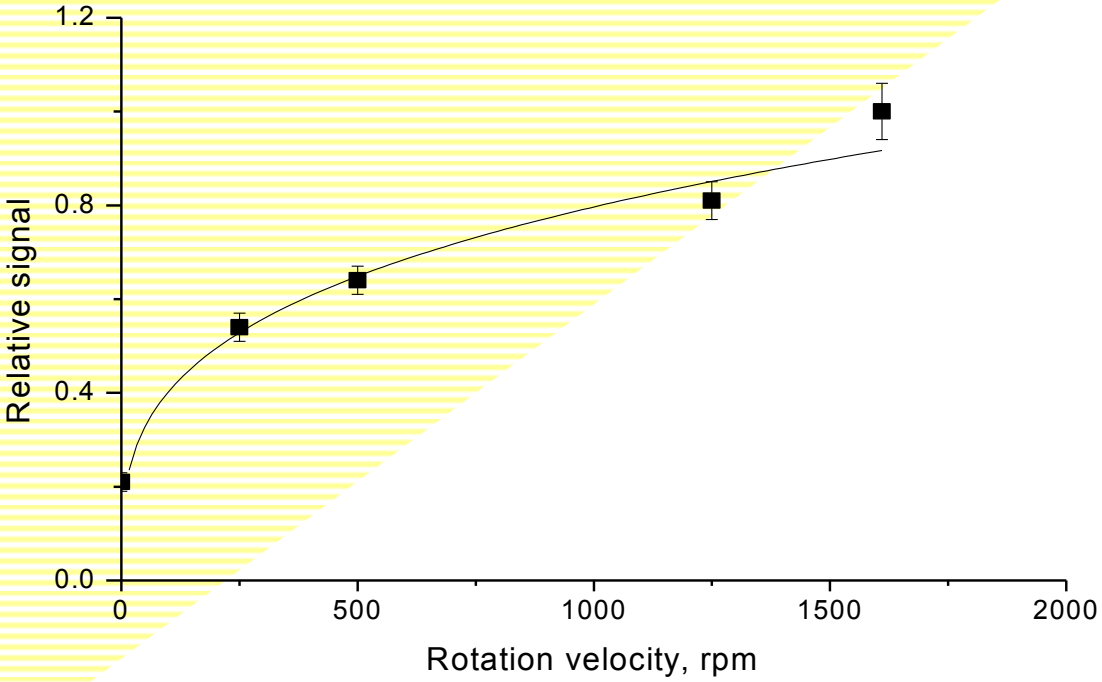




Analyte desorption:

- **Solvent (methanol)**
- **Thermal**

Nonylphenol extraction from water



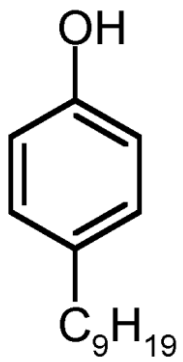
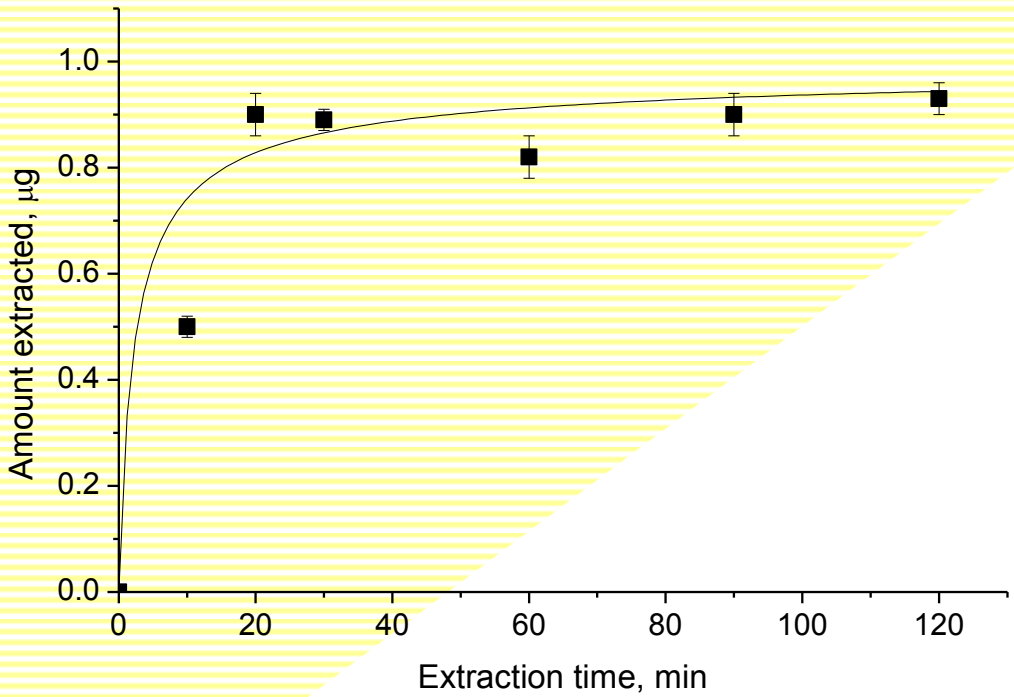


Figure 2. Rotation velocity effect on the extracted amount of NP. Extractions were made from a 250 mL water sample solution spiked with analyte at 10 µg/L. Extraction time, 20 min.

P. Richter, C. Leiva, C. Choque, A. Giordano, B. Sepúlveda, J. Chromatogr. A, 2009, 1216, 8598-8602.

Nonylphenol extraction from water



T_e = 20 min (RDSE)

T_e = 60 min (SBSE)

Figure 3. Effect of extraction time on the extracted amount of NP. Extractions were made from a 250 mL water sample solution spiked with analyte at 10 µg/L. Rotation velocity, 1250 rpm.

Table 3. Recovery and precision of the method at different concentration level of analytes.

Concentration, µg/l	Recovery (RSD), %[a]	
	4-NP	4-OPEO
3	103 (3)	97 (4)
12	95 (2)	92 (4)
30	106 (1)	104 (3)
60	104 (3)	104 (2)
120	97 (2)	94 (2)

[a] Relative standard deviation, n = 3

Precision of the analytical response was determined by using both the same disk (n = 6) and different disks (n = 3) at a concentration of 10 µg/L, showing RSD of 3.7% and 10% for the analyte, respectively.

Table 4. Alkylphenols and alkylphenol etoxylates determination in a real water sample by RDSE and by SBSE.[12]

Analyte	Concentration found, µg/L (SD) [a]		Recovery, %[b]	
	RDSE	**SBSE**	**RDSE**	**SBSE**
4-t-OP	3.4 (0.2)	3.1 (0.1)	99.8	82.6
4-NP	3.7 (0.2)	2.3 (0.2)	97.6	79.0
4-n-OP	3.9 (0.1)	4.1 (0.3)	80.2	88.4
4-OPEO	5.9 (0.3)	5.1 (0.3)	98.1	89.2
4-NPEO	1.9 (0.2)	2.3 (0.1)	50.4	45.0

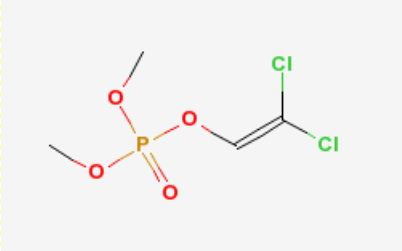
[a] Standard deviation, n = 3

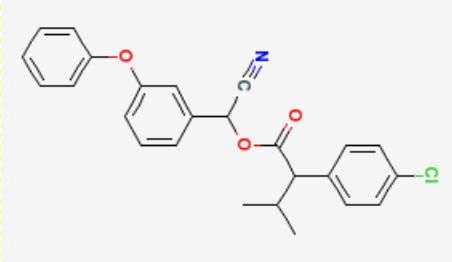
[b]Recovery was calculated after spiking of the sample with 12 µg/l concentration.

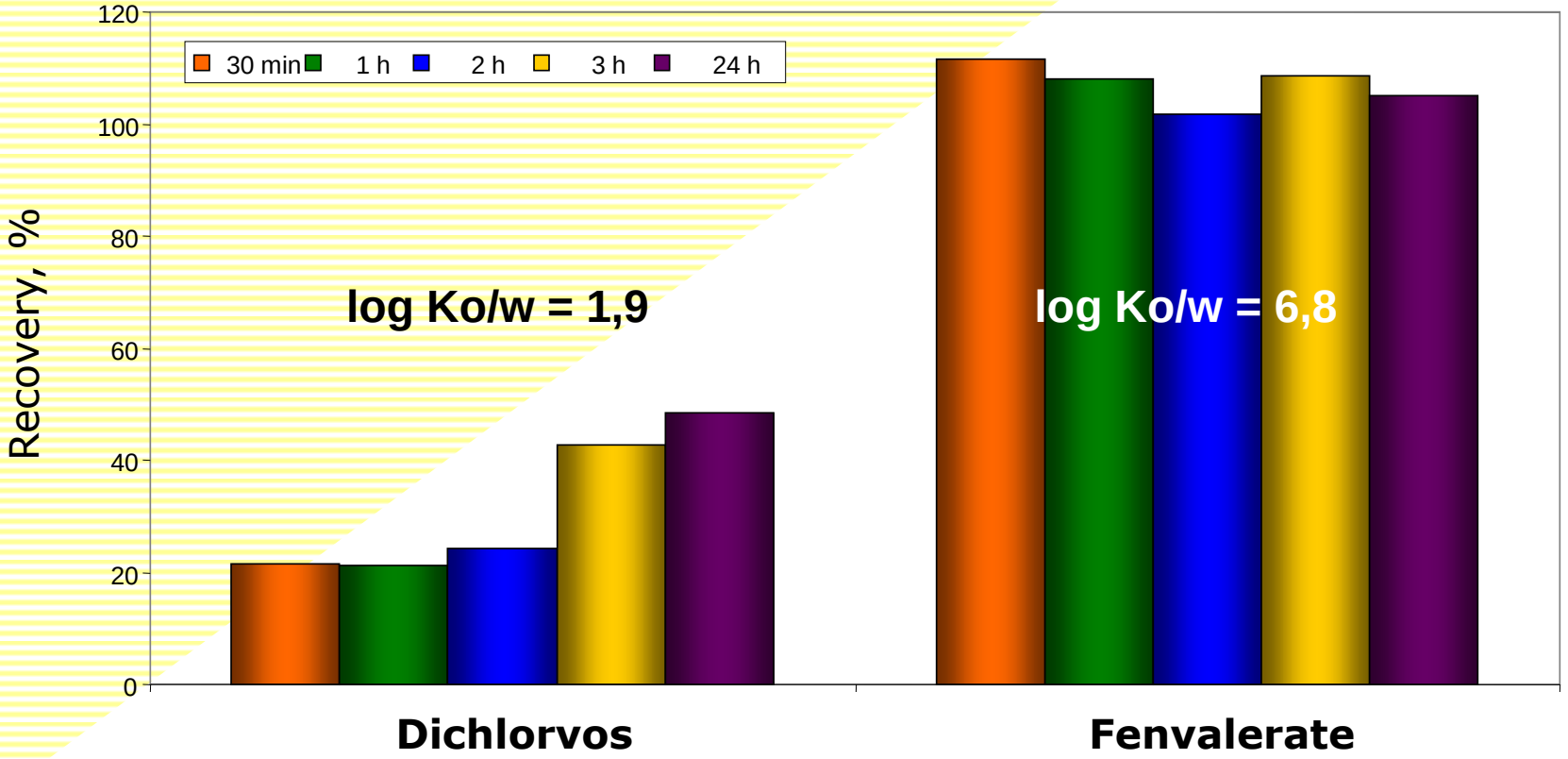
Extraction of pesticides from water

PESTICIDE	log $K_{o/w}$
Pirimicarb	1,7
Dichlorvos	1,9
Malathion	2,75
Diazinon	3,86
Tebuconazole	3,89
Lindane	4,25
Chlorpyrifos	5,27
Cypermethrin	6,38
Fenvalerate	6,76
Cyhalothrin	6,85

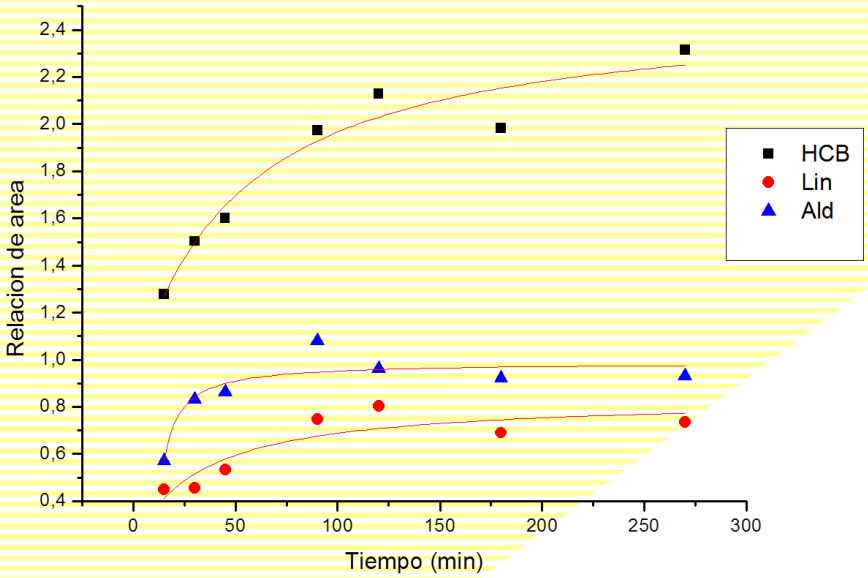
Extraction of Pesticides from water







Extraction of organochlorine pesticides and PCBs from water



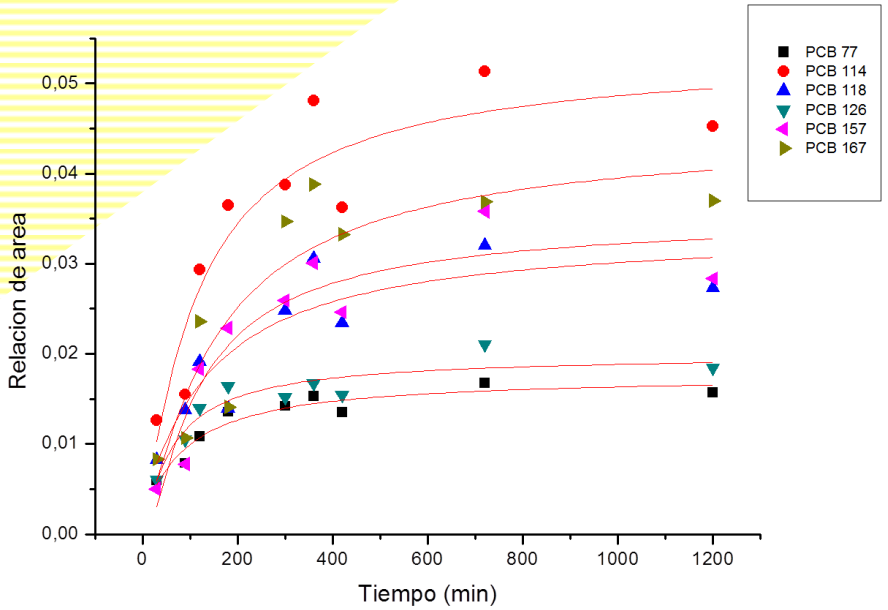
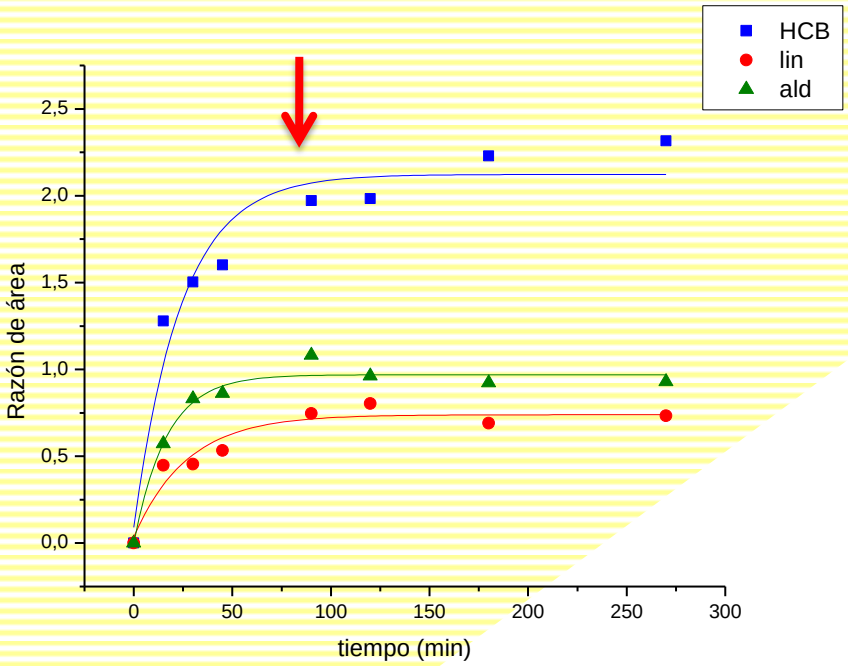
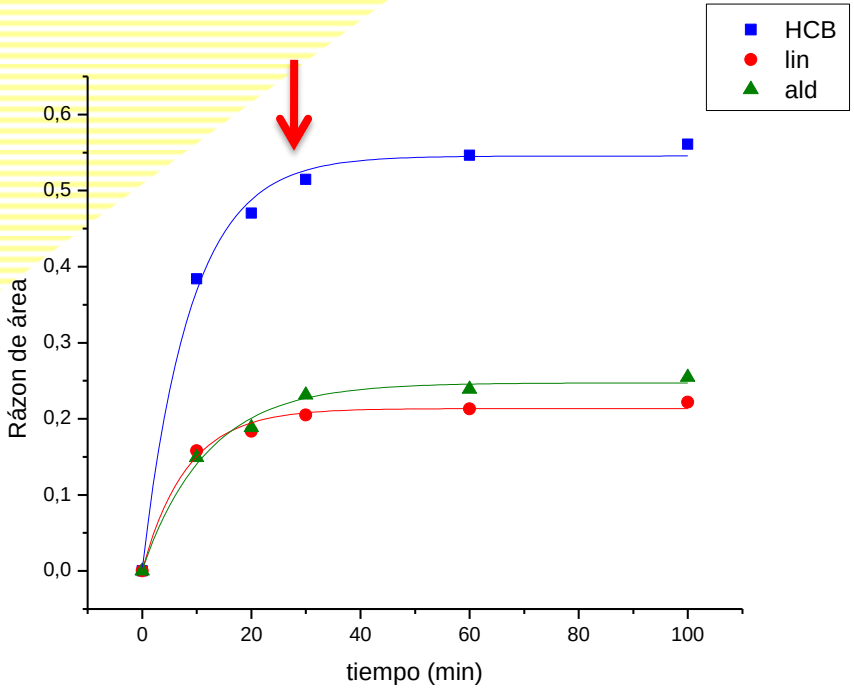


Figura Nº1 gráficos de curvas de extracción para distintos tiempos de: (a) Lin, HCB y Ald y (b) PCBs

Extraction of organochlorine pesticides

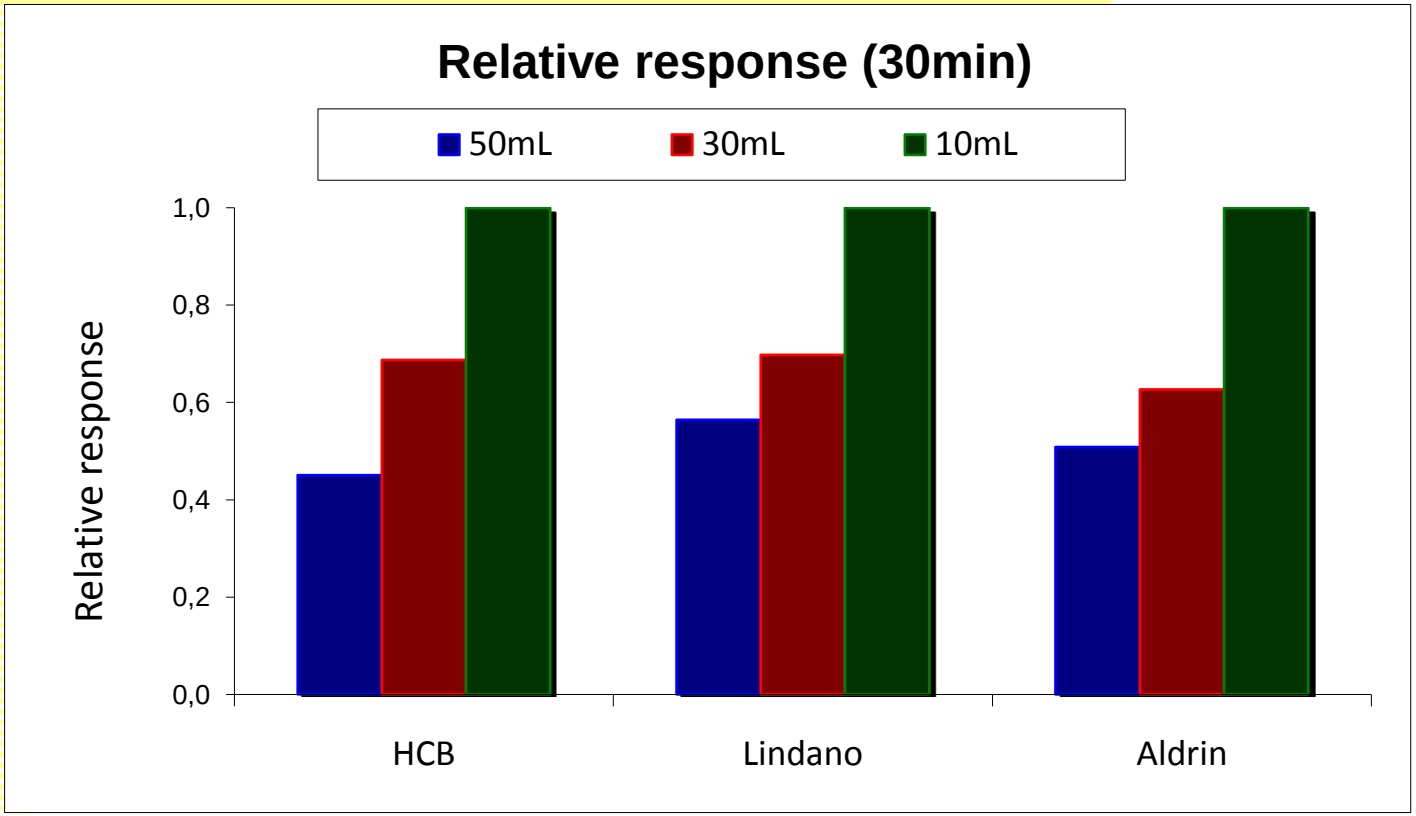




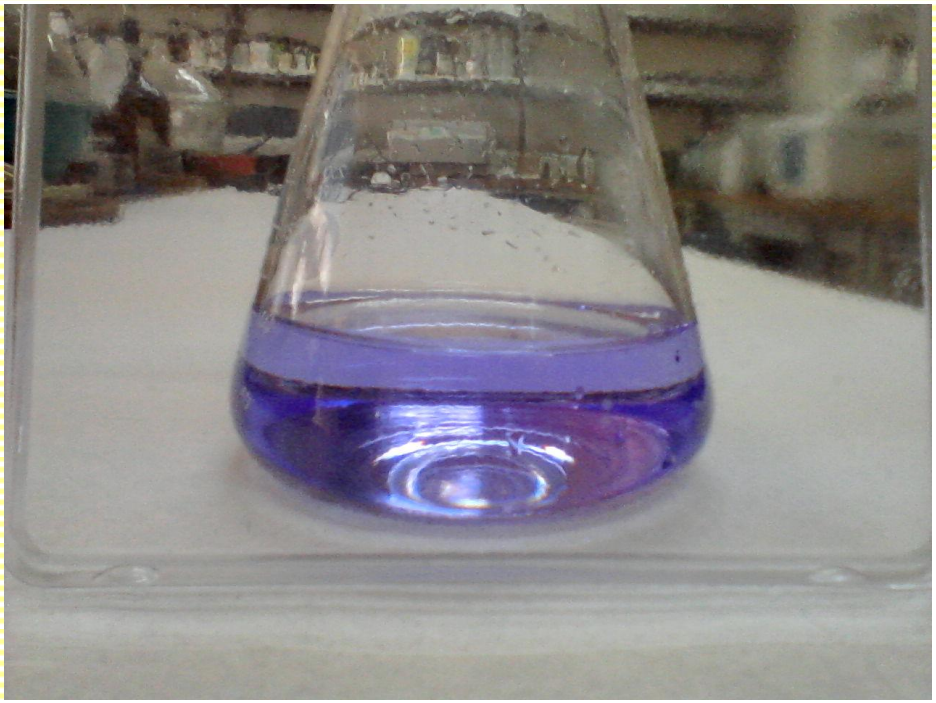
SAMPLE VOLUME: 50 ml

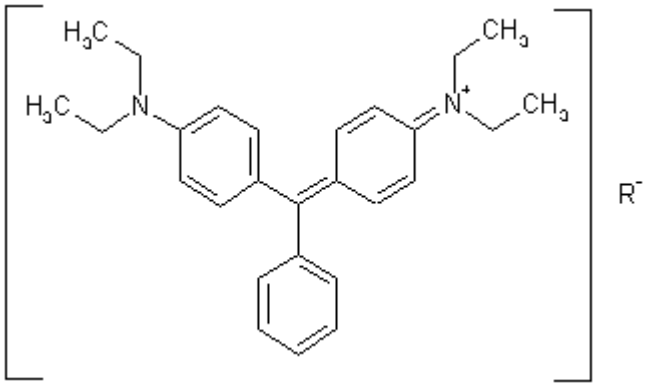
SAMPLE VOLUME: 10 ml

Extraction of organochlorine pesticides: Effect of the sample volume



Pre-concentration of chromogenic organic compounds and direct determination by solid phase spectrophotometry (RDSE)



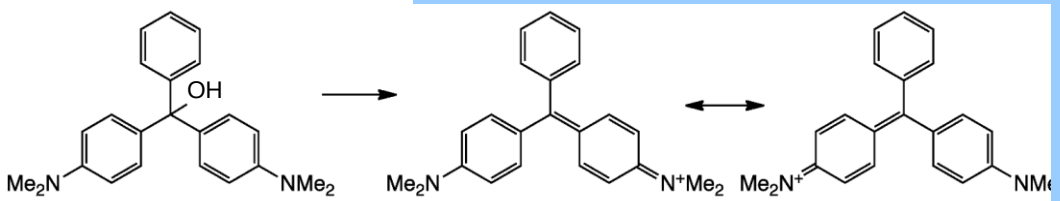


Ex:

- MALACHITE GREEN
- CRYSTAL VIOLET

P. Richter, A. Cañas, C. Muñoz, C. Leiva. Anal. Chim. Acta, 2011, in press.

Extraction of chromogenic organic compounds (RDSE)



Extraction of chromogenic organic compounds

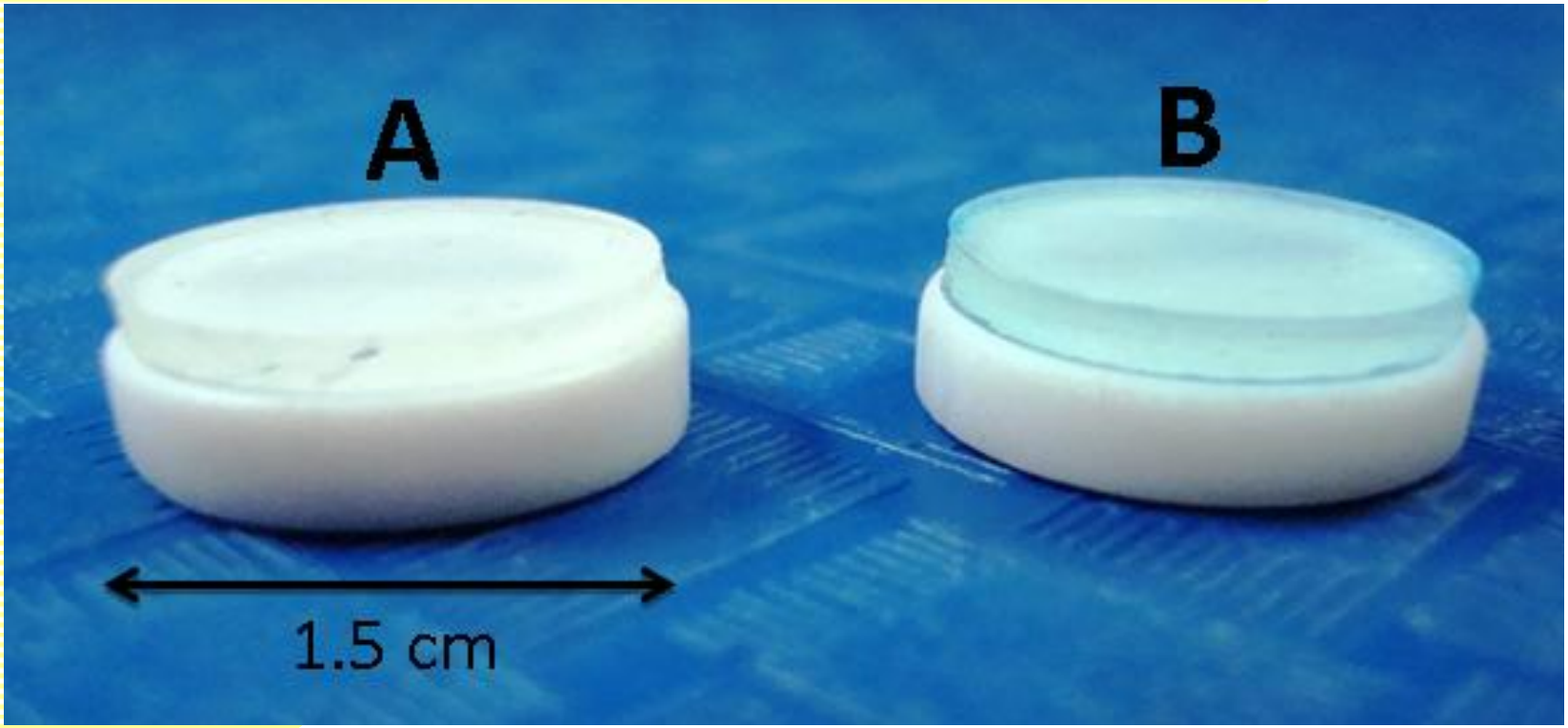


Figure 1. Photograph of the Teflon rotating disk containing the PDMS phase. (A) Before and (B) after extraction of a 100 mL water sample containing 40 µg L^{-1} MG.

Extraction of chromogenic organic compounds

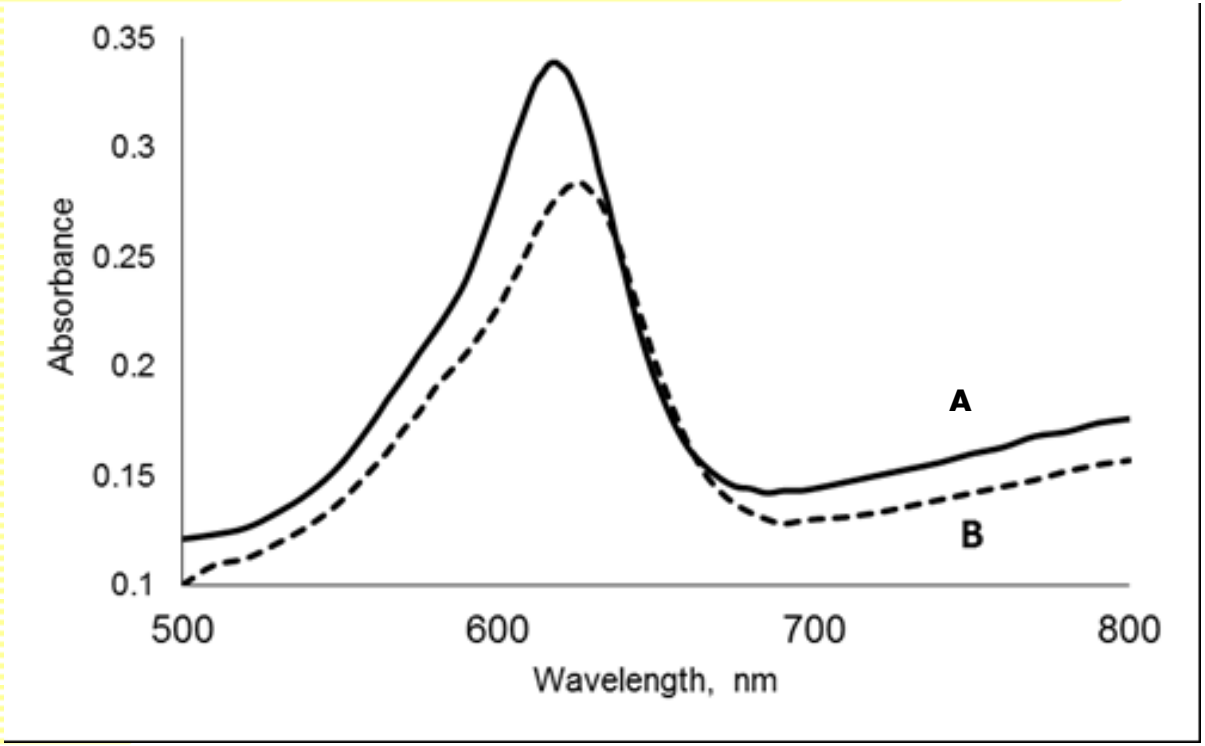


Figure 2. Absorption spectra of MG in (A) aqueous solution at a concentration of 2 mg L^{-1}, using a typical 1 cm cell, and in (B) PDMS disk phase after concentration from a solution of 0.2 mg L^{-1}, using a path length of 0.1 cm (phase thickness).

Extraction of chromogenic organic compounds

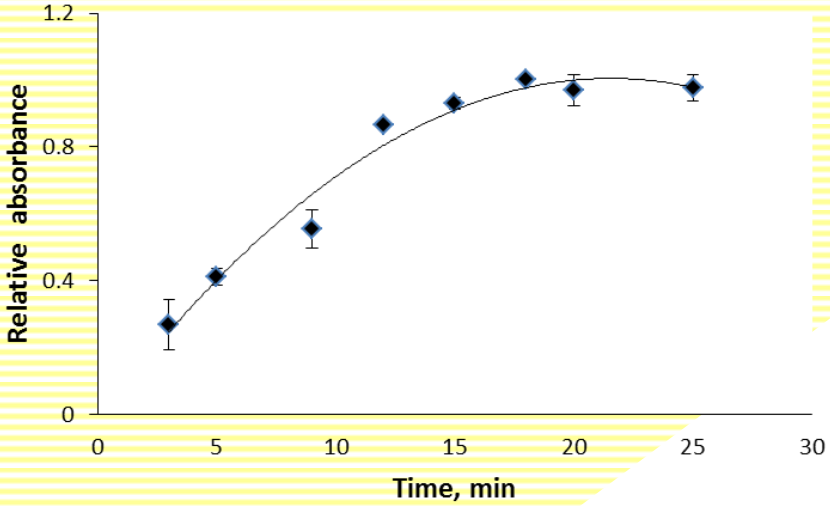


Figure 4. Effect of the extraction time on the absorbance in PDMS disk phase. MG was concentrated at 1000 rpm from 100 mL of aqueous solutions containing 0.5 mg L^{-1} MG and 10% sodium sulfate at 75ºC.

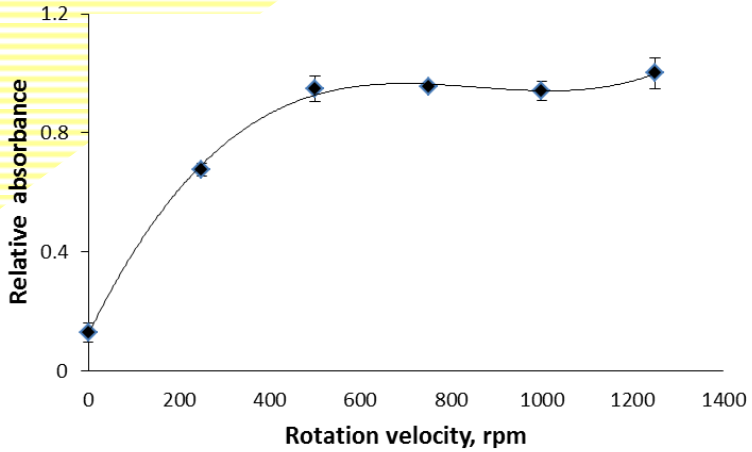


Figure 5. Effect of the rotation velocity of the disk on the absorbance. MG was concentrated for 18 min from 100 mL of aqueous solutions containing 0.5 mg L^{-1} MG and 10% sodium sulfate at 75ºC.

Extraction of chromogenic organic compounds

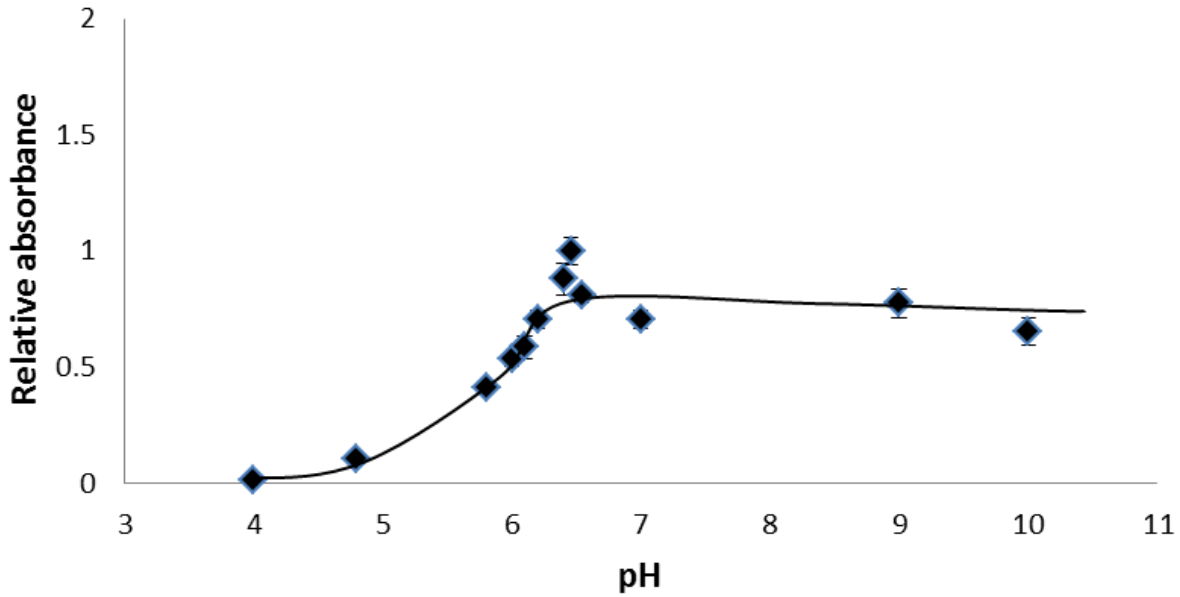


Figure 6. Effect of pH on the absorbance in PDMS disk phase. MG was concentrated for 18 min at 1000 rpm from 100 mL of aqueous solutions containing 0.5 mg L^{-1} MG and 10% sodium sulfate at 75ºC.

Conclusions

- The extraction capability of a rotating disk containing a PDMS film has been demonstrated. In this method, the disk, with a large surface area, can be stirred at higher velocity than the stir bar used in SBSE, without damaging the phase because it does not contact the sample vial bottom; thus, analyte mass transfer to the PDMS surface is facilitated.
- PDMS phase on the disk could be used for at least 50 experiments. In any case, replacement of the PDMS film on the disk is very easy and inexpensive, as compared to the stir bar used in SBSE.
- Another possible variant of the present RDSE technique is to use another solid phase instead of the PDMS film to extract more polar analytes.
- The extraction capability of chromogenic compounds from water samples on a rotating disk containing a PDMS film has been demonstrated. After extraction, the PDMS phase was used directly in the solid phase spectrophotometric determination of the analyte.
- PDMS phases on the disk could be reused after desorption of MG. After a batch of 50 determinations, all phases were cleaned simultaneously for 1 h by desorption of MG with methanol. Additionally, replacement of the PDMS film on the disk is simple and low cost.

Agradecimientos

- Muchas gracias a ustedes por la atención

- Financiamiento: Proyectos FONDECYT Regulares y Proyectos CONICYT de doctorado.

- Integrantes del Laboratorio de Química Analítica y Ambiental

Agradecimientos

CELDA DE EXTRACCIÓN