Polymer treatment procedures for its elemental analysis by Atomic Spectrometry techniques

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Elemental analysis of polymers

- Sample characterization
- Toxicological studies

European Union Directives

General use	**91/388/CEE** (June, 18th 1991) **94/62/CEE** (December, 20th 1994)
Toys	**88/378/CEE** (May, 3rd 1988)

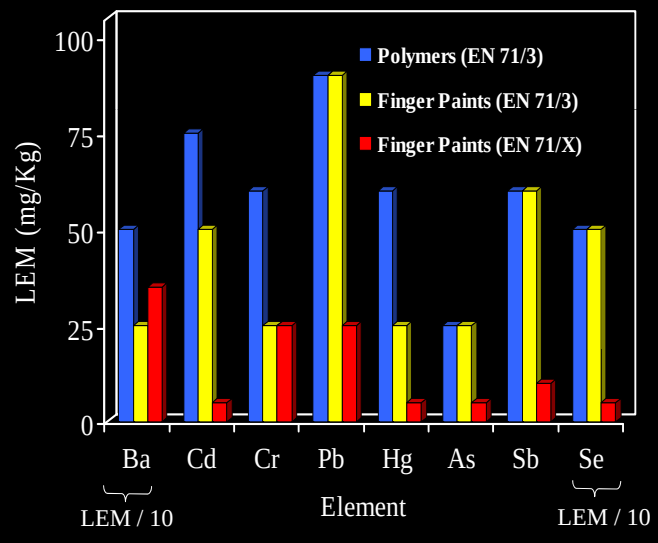
Daily bioavailability levels of toxic elements resulting from the use of toys (88/378/CEE)

Element	Amount (μg)
Ba	25.0
Cd	0.6
Cr	0.3
Pb	0.7
Hg	0.5
As	0.1
Sb	0.2
Se	5.0

European normative for safety of toys

EN 71 /3

Limits of element migration (LEM) from toy material (EN 71/3)



Migration analysis

Principle

Soluble elements are EXTRACTED from materials under the condition which simulate the material remaining in contact with stomach acid for a period of time after swallowing. The concentrations of these elements are ANALYSED.

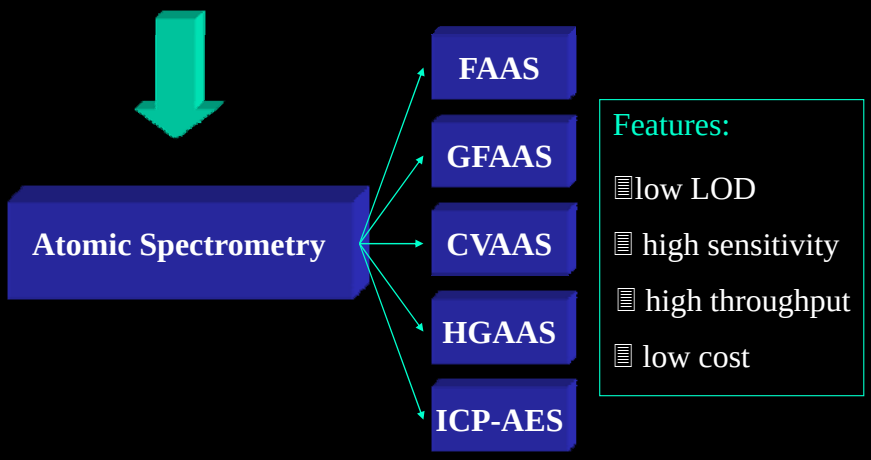
Procedure

1. Cut out test portions (< 6 mm) of polymeric material
2. Take a test portion > 100 mg
3. Add HCl 0.07 M
   (volume equal to 50 times the mass of the test portion)
4. Add HCl 2 M up to obtain a pH $\leq$ 1.5
5. Shake the mixture for 1 h
6. Leave the sample to rest for 1 h
7. Analyse

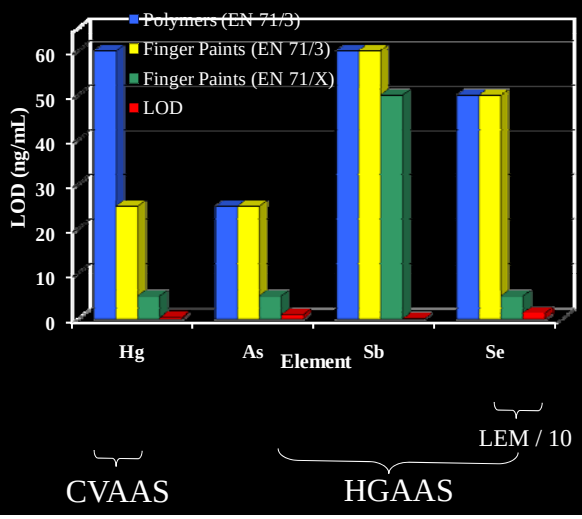
Caution: Keep the mixture away from the light and at 37 $\pm$ 2 ºC

Analytical technique requirements (EN 71/3)

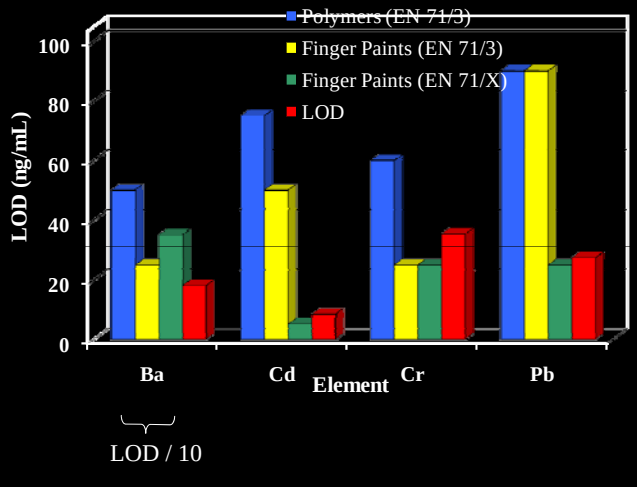
LOD < 1/10 maximum analyte concentration (solution)



Analytical technique requirements (EN 71/3): CVAAS and HGAAS



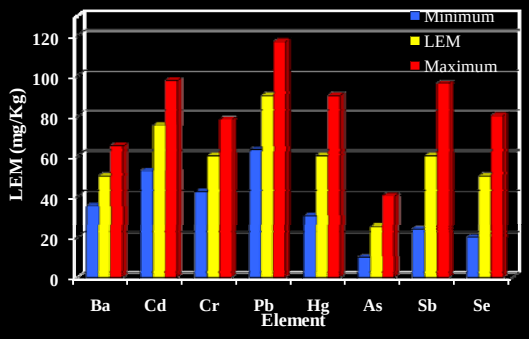
Analytical technique requirements (EN 71/3): ICP-AES



Precision of the method (EN 71/3)

Element	RSD (%)
Ba, Cd, Cr, Pb	30
Hg	50
As, Sb, Se	60

Polymers



LEM / 10 LEM / 10

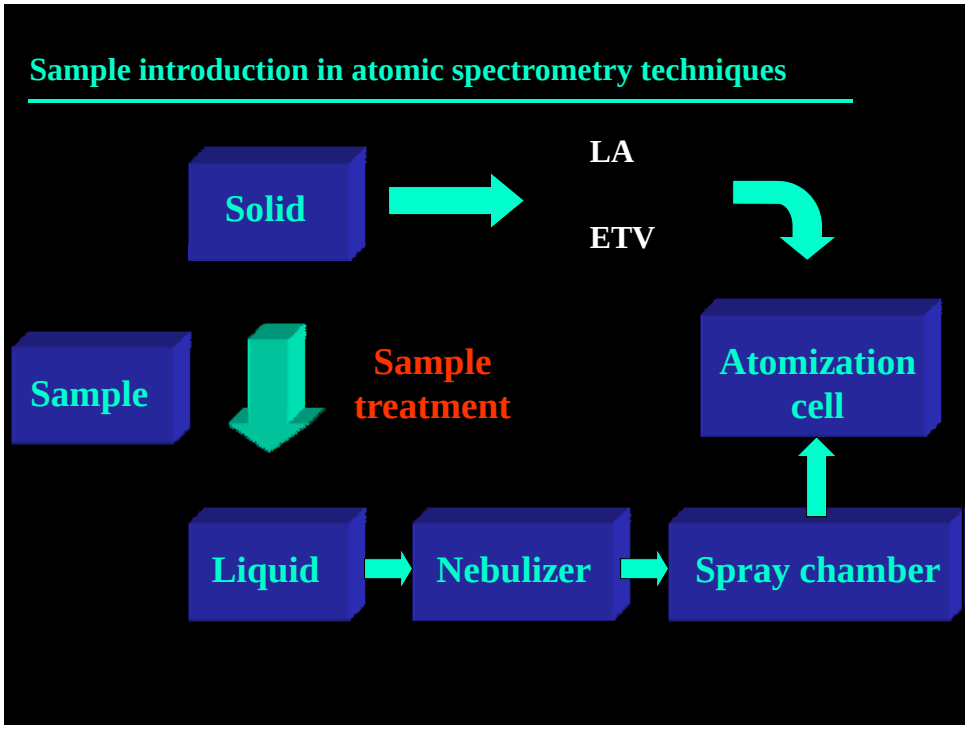
Summary

- LEM sometimes lower than LOD
- Poor precision

- **New analytical methods**
- **Total content**

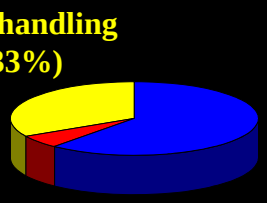
Total content analysis

Sample introduction in atomic spectrometry techniques



Sample treatment

Distribution of the total time of analysis

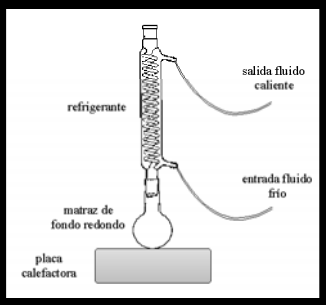


- Drying
- Milling
- Dissolution

Heating methods

- Conductive
- Microwaves

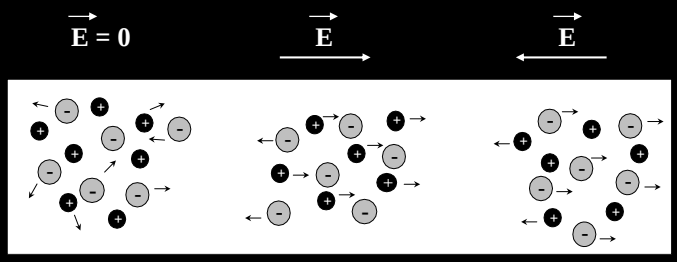
Conductive heating

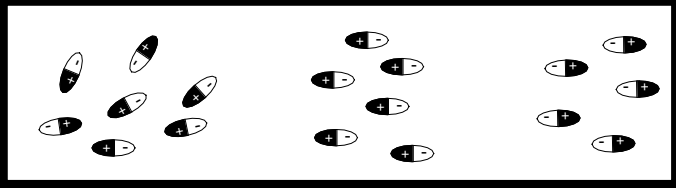


Drawbacks:

- Slow process
- Risk of contamination
- Poor precision
- Loss of volatile
- Incomplete process

Microwaves heating





Microwaves heating

Factors affecting MW heating:

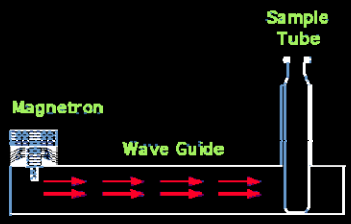
- Ionic concentration
- Ionic mobility
- Physical properties
- Dielectric loss factor (tg δ)

Advantages:

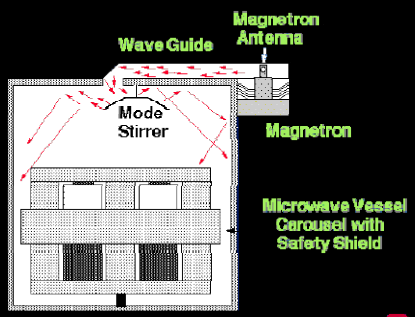
- Faster
- Homogeneous
- More efficient

Microwaves digestion systems

Open vessel



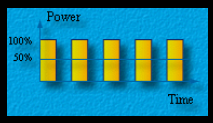
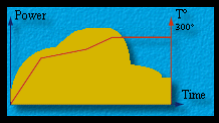
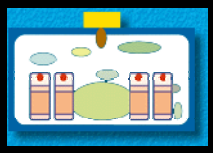
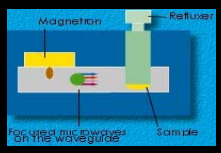
Closed vessel



Microwaves digestion systems

Closed vessel

Open vessel *versus* Closed vessel

Closed vessel	Open vessel
	
	
Higher pressure Higher Temperature Lower time Lower amount of reagents Absence of toxic vapours	Temperature limited (Tb) Loss of volatiles Higher precision

Polymer dissolution procedure

Dissolution procedure

PVC composition

Element	Concentration (mg/Kg)
Cd	4
Cr	2
Pb	10
Hg	0.4

Dissolution procedure

Reagent	Method	Variable
Acid	Conductive	Temperature Time Acid concentration
Organic	Microwave (closed vessel)	Power Time

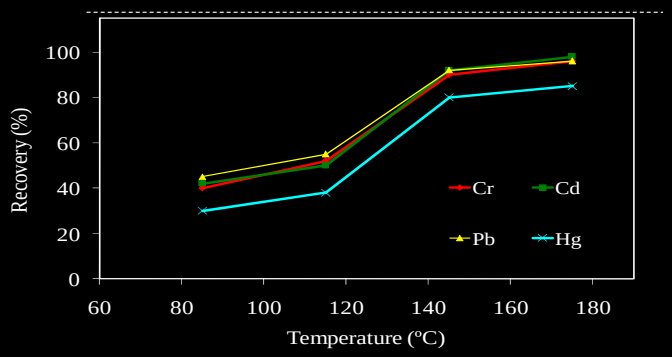
Recovery

ICP-AES

Acid treatment

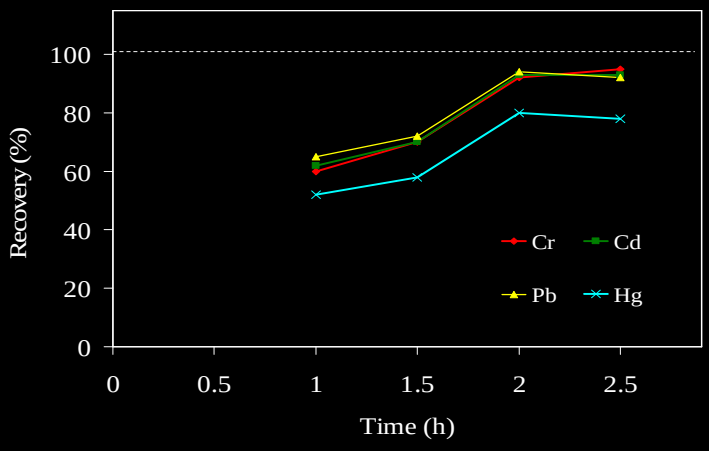
Conductive heating

Effect of the temperature



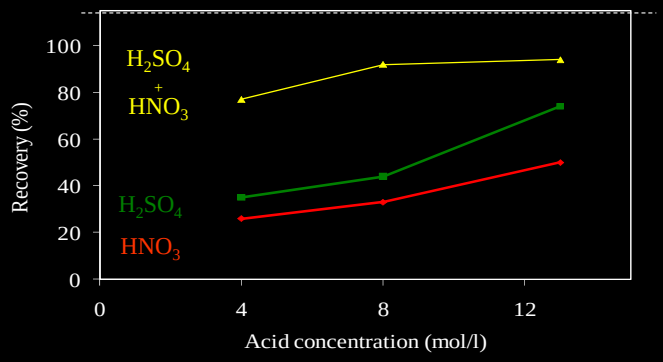
0.4 g PVC
5 mL H2SO4 18M, t =15 min, T = 145 ºC
HNO3 13 M, t = 2 h

Effect of the time



0.4 g PVC
5 mL H2SO4 18M (t =15 min, T = 145 ºC)
HNO3 13 M (T = 145 ºC)

Effect of the acid

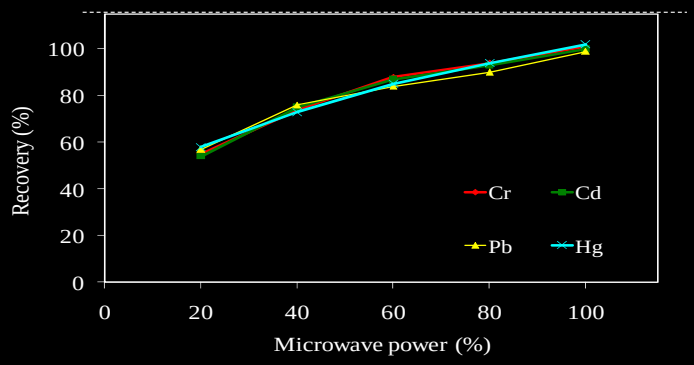


Cd
0.4 g PVC
HNO_3, t = 2 h, T = 145 °C
H_2SO_4, t = 15 min, T = 145 °C
H_2SO_4 18 M, t =15 min, T = 145 °C + HNO_3, t = 2 h, T = 145 °C

Acid treatment

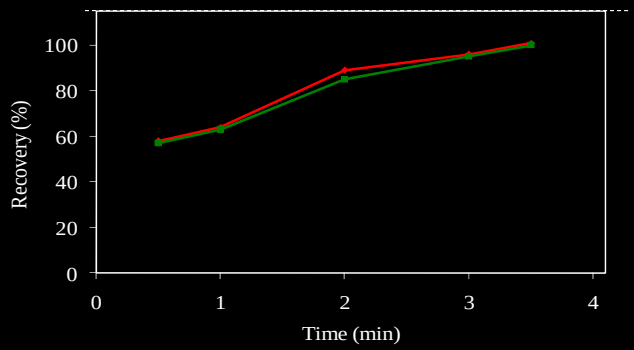
Microwave heating

Effect of the MW power



0.4 g PVC
5 mL H2SO4 18M, t = 2.5 min, P = 70%
HNO3 13 M, t = 3.5 min

Effect of the time



Cd
0.4 g PVC
H2SO4 18 M, t = 2.5 min, P = 100% +
HNO_3 13 M + H_2O_2, P = 100%
HNO_3 13 M, P = 100%

Organic treatment

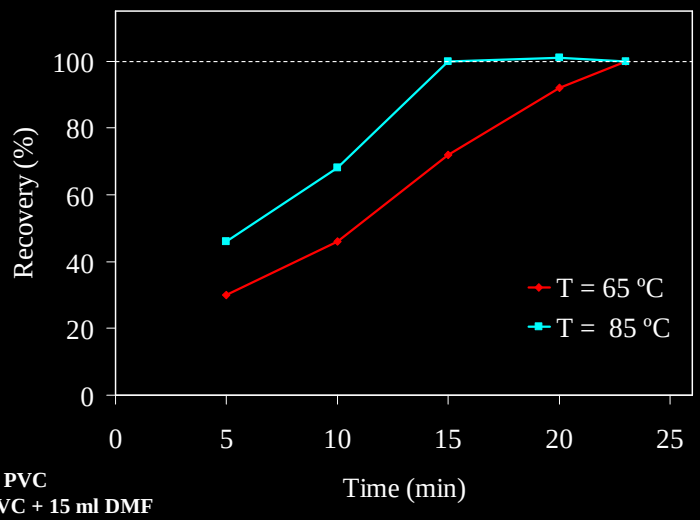
Polymer dissolution using organic solvents

Polymer	Solvent
Polyvinyl chloride	Acetone
	N,N-dimethylformamide (DMF)
	N,N-dimethylacetamide
Polyethilene terephtalate	Trifluoroacetic acid
	o-Chlorophenol
	Hexafluoro iso propanol
Polyethylene	1,2,4, trichlorobenzene
Ethyl vinyl acetate	ODCB

Organic treatment

Conductive heating

Effect of the time and temperature

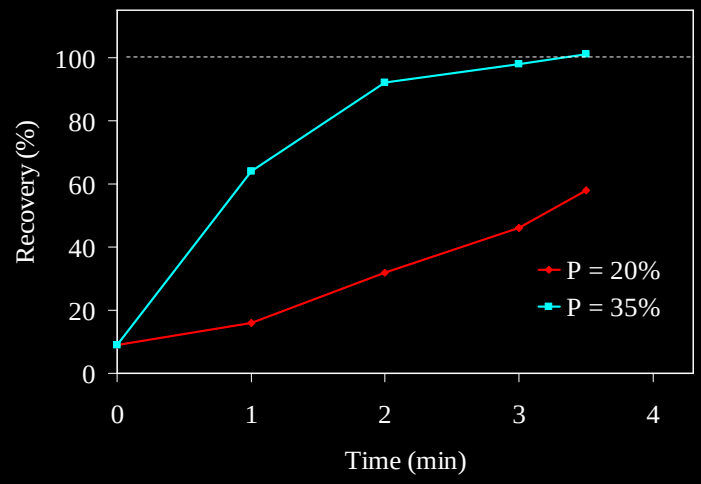


Pb in PVC
1 g PVC + 15 ml DMF

Organic treatment

Microwave heating

Effect of the time and MW power



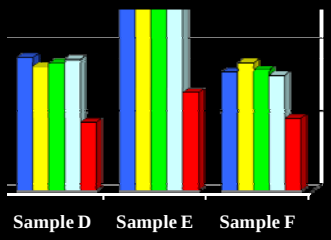
Cd in PVC
1 g PVC + 15 ml DMF

Summary

- MW *versus* conductive heating
  - Lower digestion time
  - No loss of volatiles
  - Higher efficiency
- Organic *versus* acid treatment
  - Simplest (one step)
  - Faster (lower digestion time)
- Interferences
  - Additional sample treatment procedure
  - Alternative sample introduction system

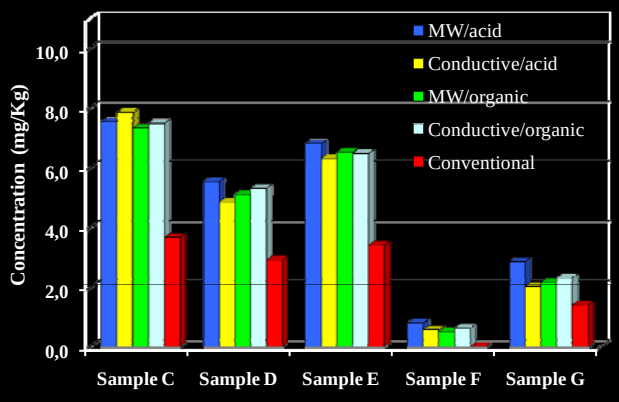
Analysis of real samples

Cd in PVC samples



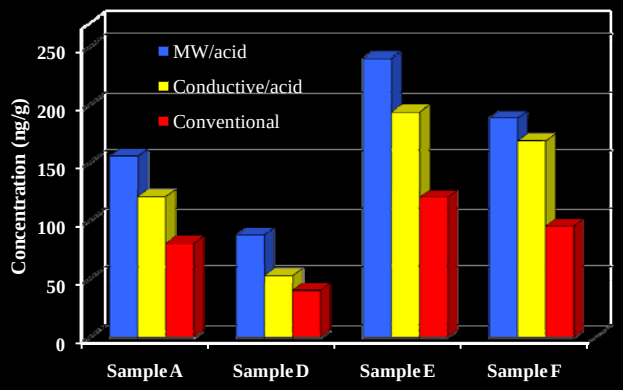
LEM = 75 mg/Kg

Cr in PVC samples



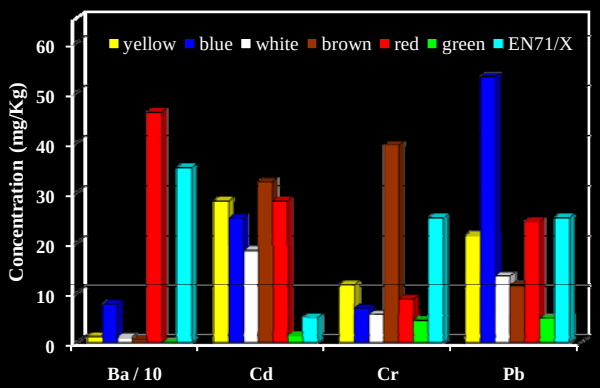
LEM = 60 mg/Kg

Hg in PVC samples



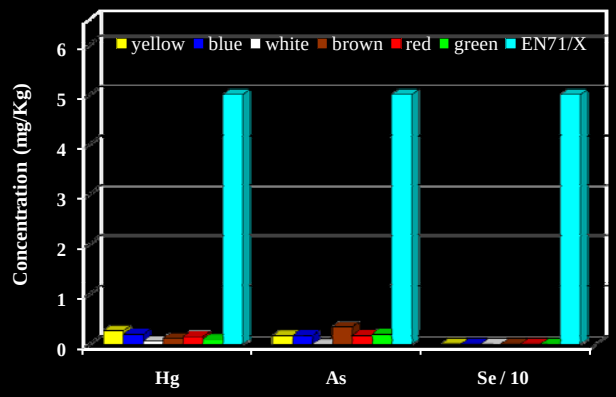
LEM = 60 mg/Kg

Ba, Cd, Cr, Pb in finger paints



MW acid digestion

Hg, As, Se in finger paints



MW acid digestion

Conclusions

Sample treatment:

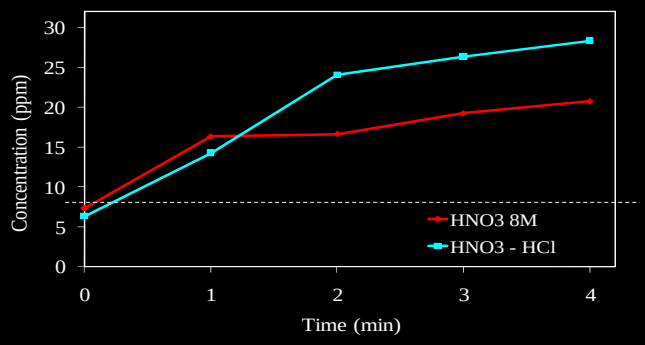
- **Determine analytical results**
- **Not universal**
- **Optimised for each sample**

Comparison between atomic spectrometry techniques

Parameter	Technique		
	FAAS	GFAAS	ICP-AES
LOD	1	4	3
Precision	4	1	3
Interferences	3	1	4
Linear range	2	1	4
Analysis throughput	2	1	4
Easy to use	4	1	2
Cost	4	4	1

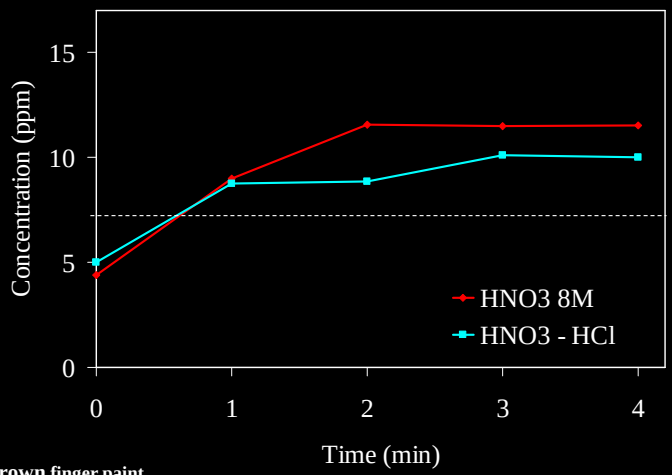
Score from 1 to 4

Microwave heating: effect of the acid



Cd in red finger paint
P = 770 W

Microwave heating: effect of the acid



Pb in brown finger paint
P = 770 W

Microwave heating