University of Vigo

Sono-induced vapor generation for Mercury determination by Atomic Spectrometry

2006 Workshop COST D32WG5. Plovdiv 17-19 December

Degradation reactions induced by ultrasound

Sonochemical effects take place either due to the pyrolytic decomposition inside the bubbles, or by the reaction with radicals at the gas–liquid interface, and to lesser extent in bulk solution

Advanced oxidation processes (AOPs)

Removal of organic pollutants

Production of oxidizing radicals by Ultrasound

$$H_2O \rightarrow H\bullet + OH\bullet$$
$$O_2 \rightarrow 2O\bullet$$
$$H\bullet + H_2O \rightarrow OH\bullet + H_2$$
$$O\bullet + H_2O \rightarrow 2OH\bullet$$
$$H\bullet + O_2 \rightarrow HOO\bullet$$
$$2OH\bullet \rightarrow H_2O_2$$
$$2HOO\bullet \rightarrow H_2O_2 + O_2$$

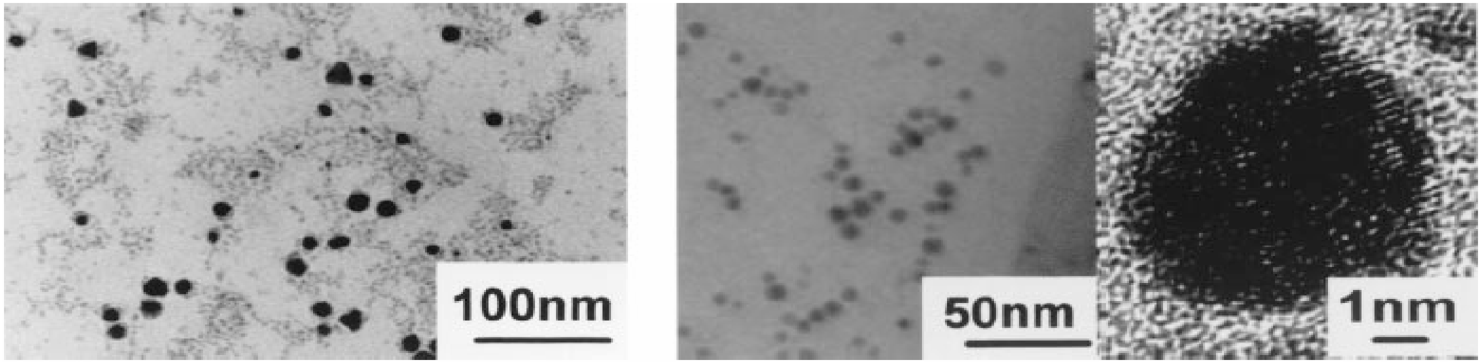
$E^0 = +2.8$ V

Can ultrasound induce reduction processes?

Synthesis of metal nanoparticles by ultrasound

$Pd(II)$	$E^0 = 0.62$	V
$Au(III)$	$E^0 = 1.002$	V
$Pt(IV)$	$E^0 = 0.758$	V
$Ag(I)$	$E^0 = 0.799$	V
$Rh(III)$	$E^0 = 0.758$	V

$$M^{n+} \quad + \quad Organic \quad additive \xrightarrow{Ultrasound} M^0$$



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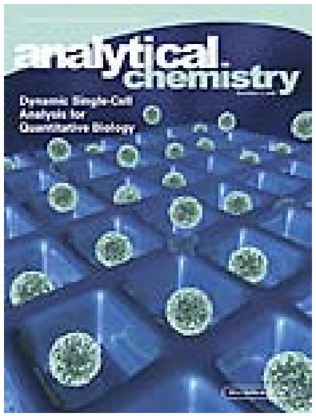

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Ultrasound-Promoted Cold Vapor Generation in the Presence of Formic Acid for Determination of Mercury by Atomic Absorption Spectrometry

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Cold vapor generation was accomplished in a sonoreactor by reduction of Hg(II) to Hg(0) owing to the reducing gases and radicals formed upon sonolysis of formic acid added to the sample solution. An efficient and fast release of the Hg(0) occurred as a result of the degassing effect caused by cavitation.

Conventional cold vapor generation

Cold vapor generation with atomic absorption spectrometry detection (AAS) Is the most extended technique for Hg determination in most application areas. This technique is accomplished by conversion of Hg(II) to Hg(0) volatile using a chemical reducing agent such as sodium tetrahydroborate (III) or stannous chloride in batch or continuous mode.

$$Hg^{2+} + 2NaBH_4 + 6H_2O \leftrightarrow Hg^0 + 7H_2 + 2H_3BO_3 + 2Na^+$$

$$HgCl_2 + SnCl_2 \leftrightarrow Hg^0 + SnCl_4$$

Conventional reduction agents for CVG: limitations

- Expensive reagents, moderate-high environmental impact
- Unstable reagents
- Problems with blanks
- Strong matrix effects by transition metals
- Problems with the H_2 excess
- Problems with foam formation, vigorous reactions

Proposal of a reaction pathway for Sono-induced cold vapor generation (SI-CVG)

(1) $H_2O \xrightarrow{US} OH\bullet + H\bullet$

(2) $HCOOH + OH\bullet(H\bullet) \xrightarrow{US} COOH\bullet + H_2O(H_2)$

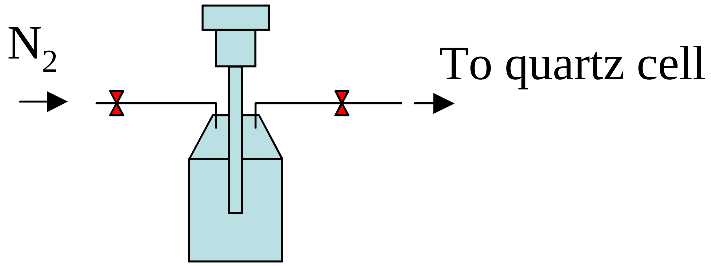
(3) $2HCOOH \xrightarrow{US} CO + CO_2 + H_2O + H_2$

(4) $Hg(II) + reducing \quad species \longrightarrow Hg(0)_{dis}$

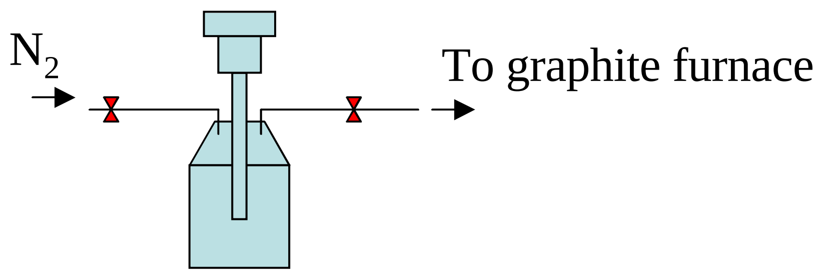
(5) $Hg(0)_{dis} \longrightarrow \uparrow Hg(0)_{gas}$

$$E^0 = 0.758 \quad V$$

Interface of the sonoreactor with a quartz cell and a graphite furnace

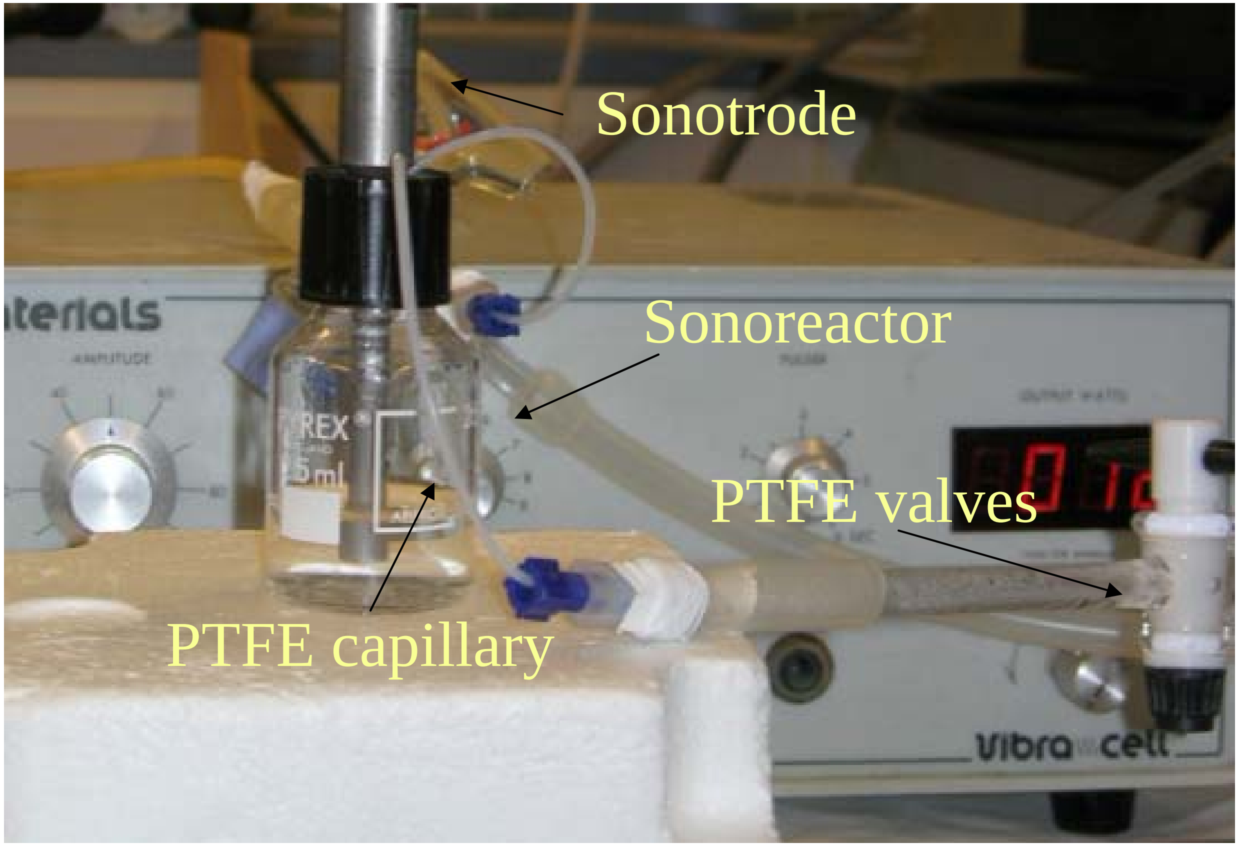


With accumulation of Hg in the headspace

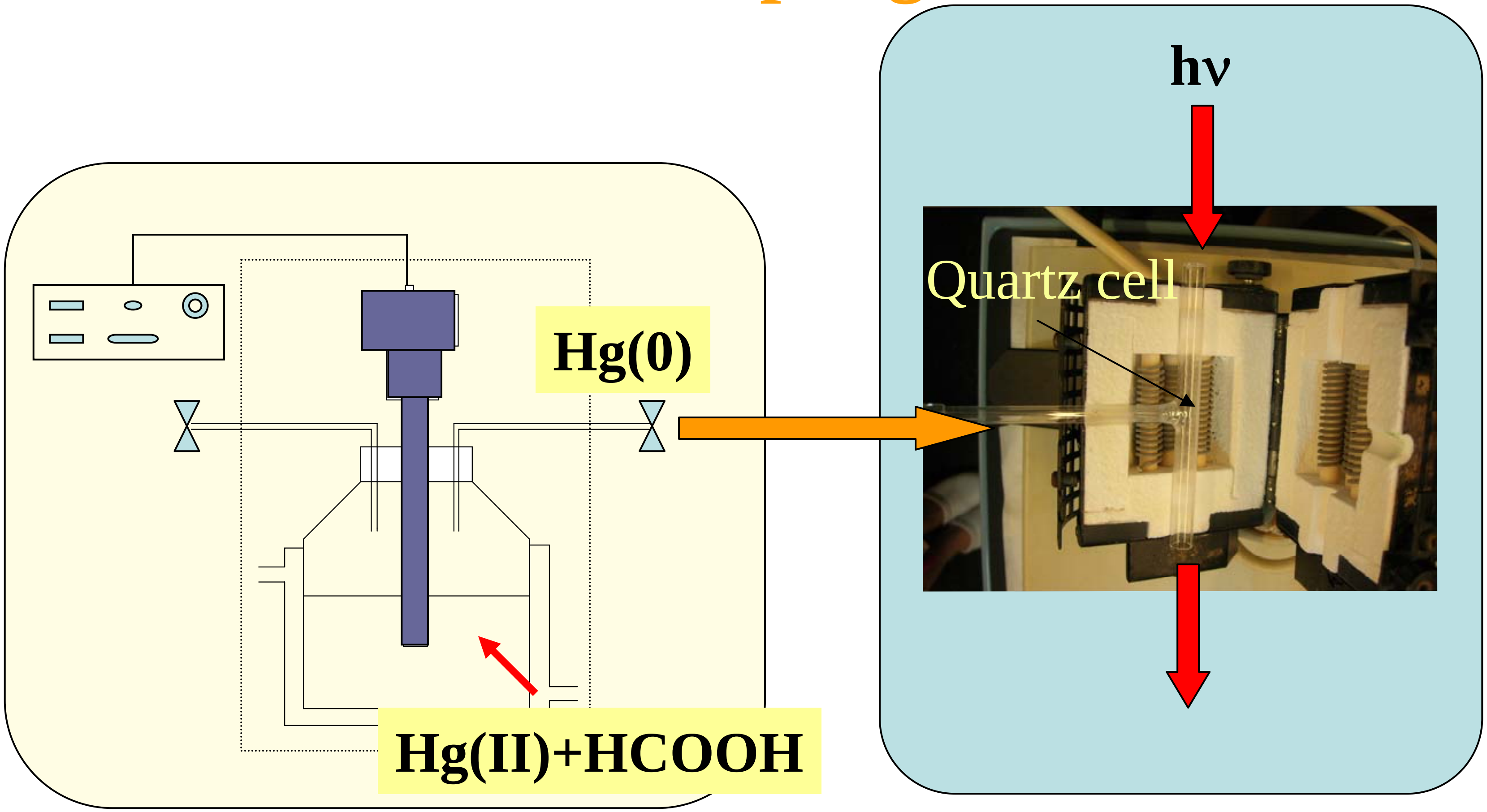


With direct transport and trapping in the atomizer

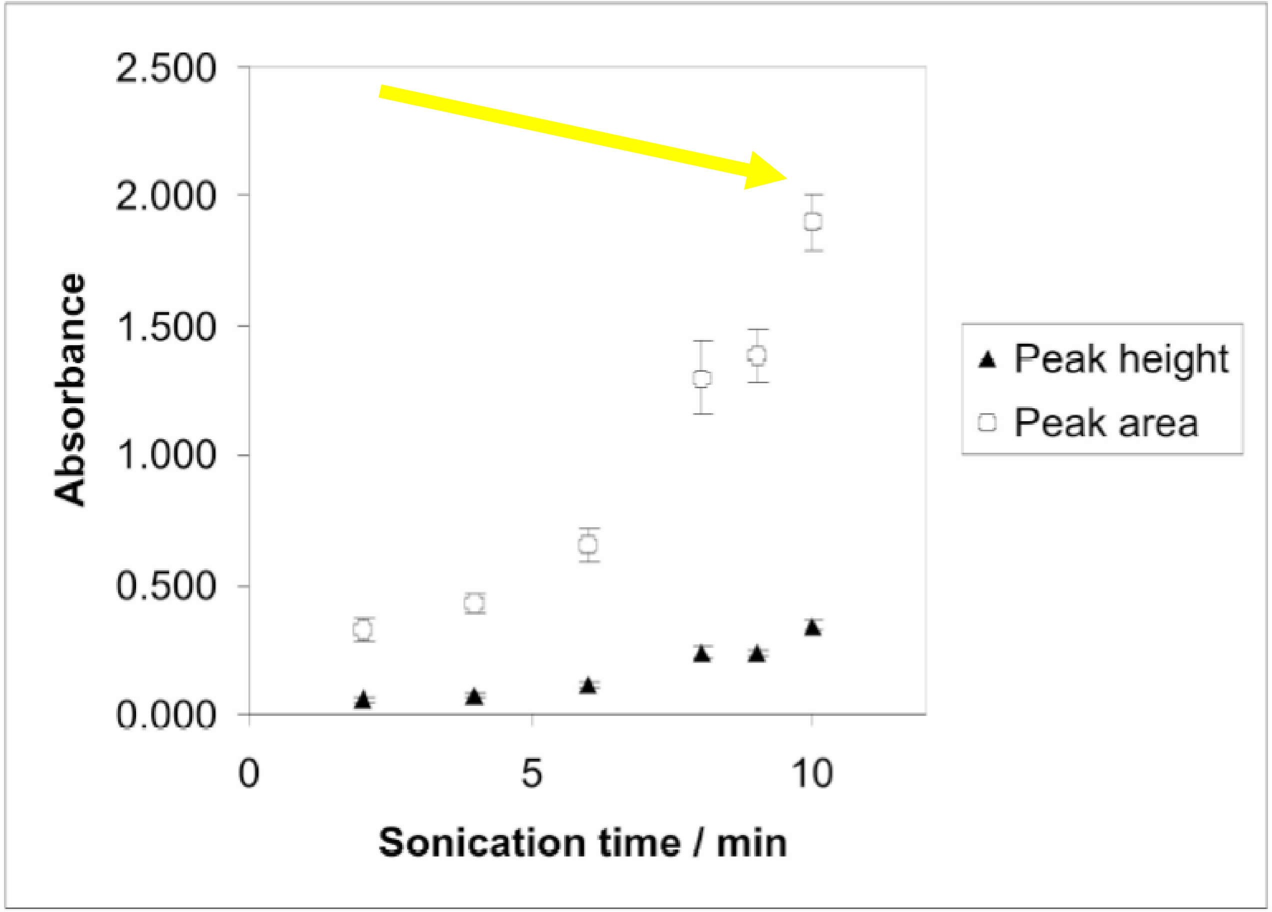
Sonoreactor design



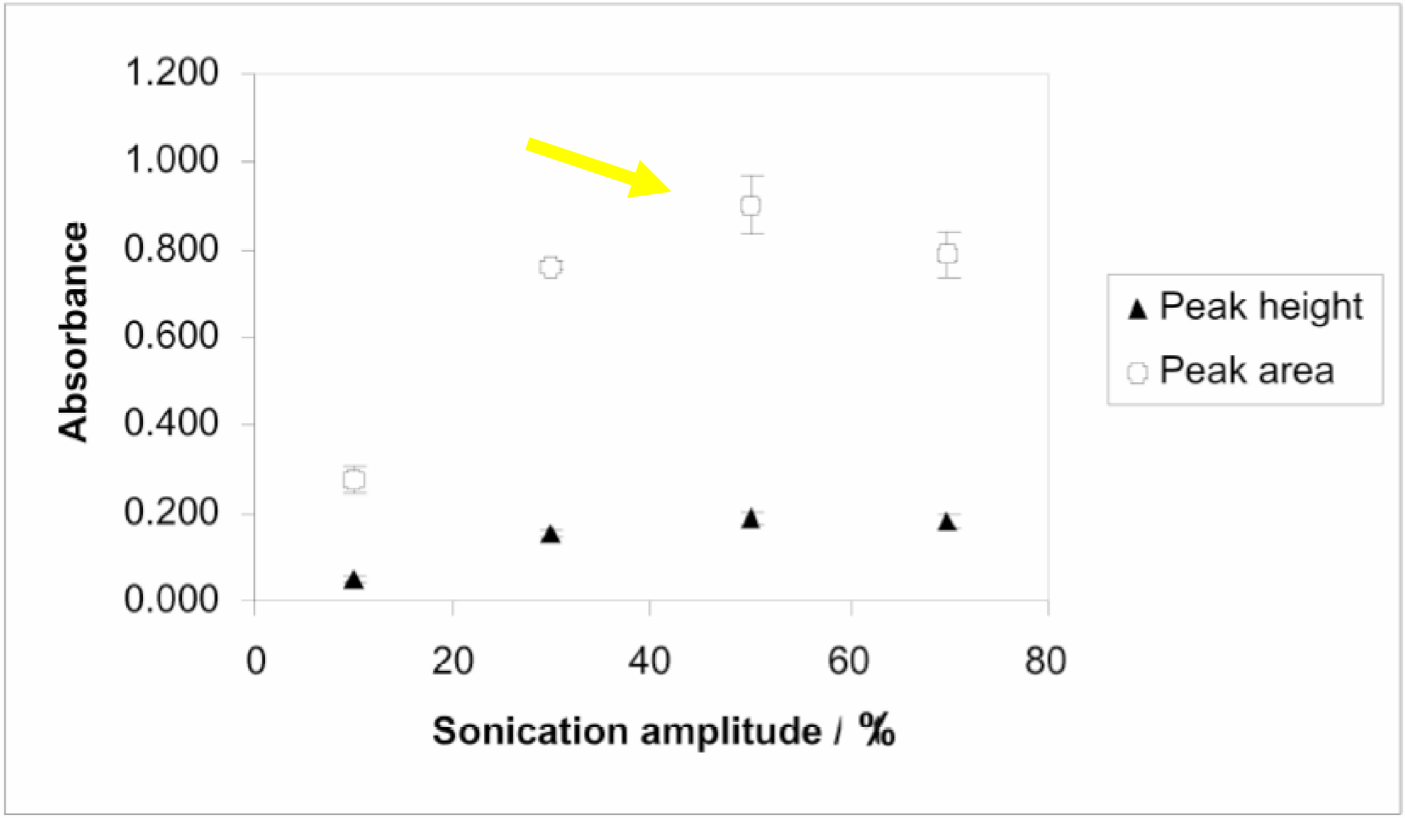
SI-CVG-AAS coupling



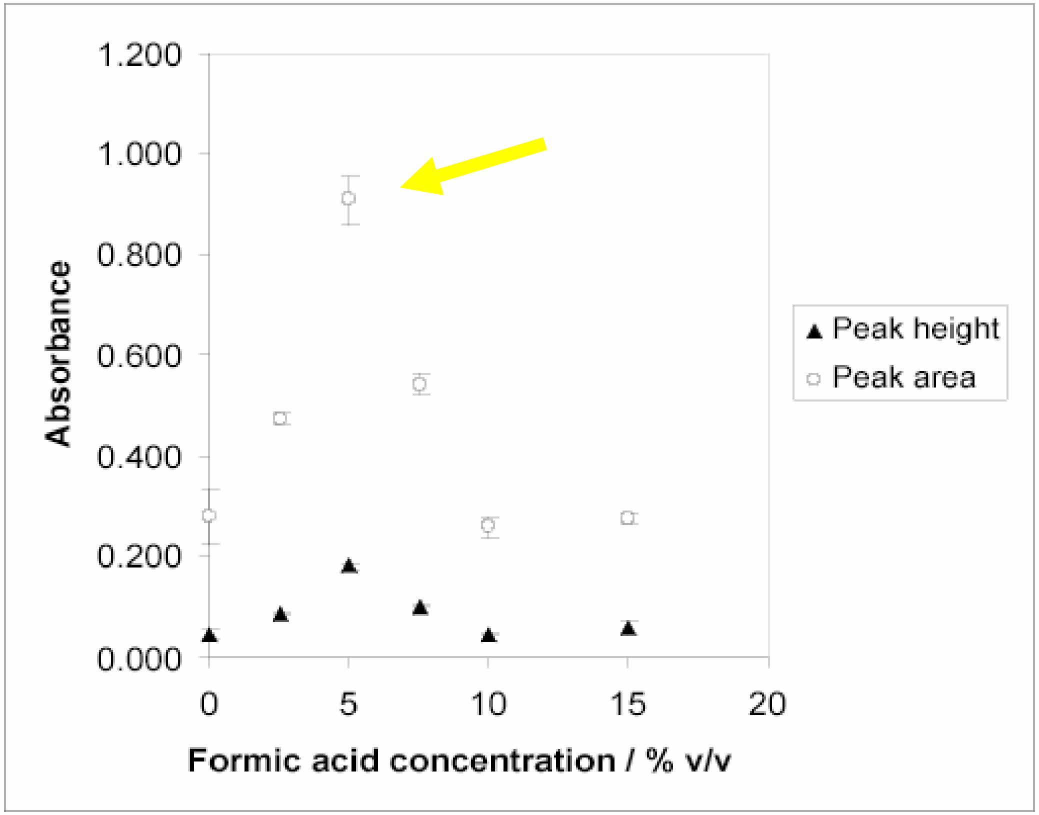
SI-CVG-AAS: effect of sonication time



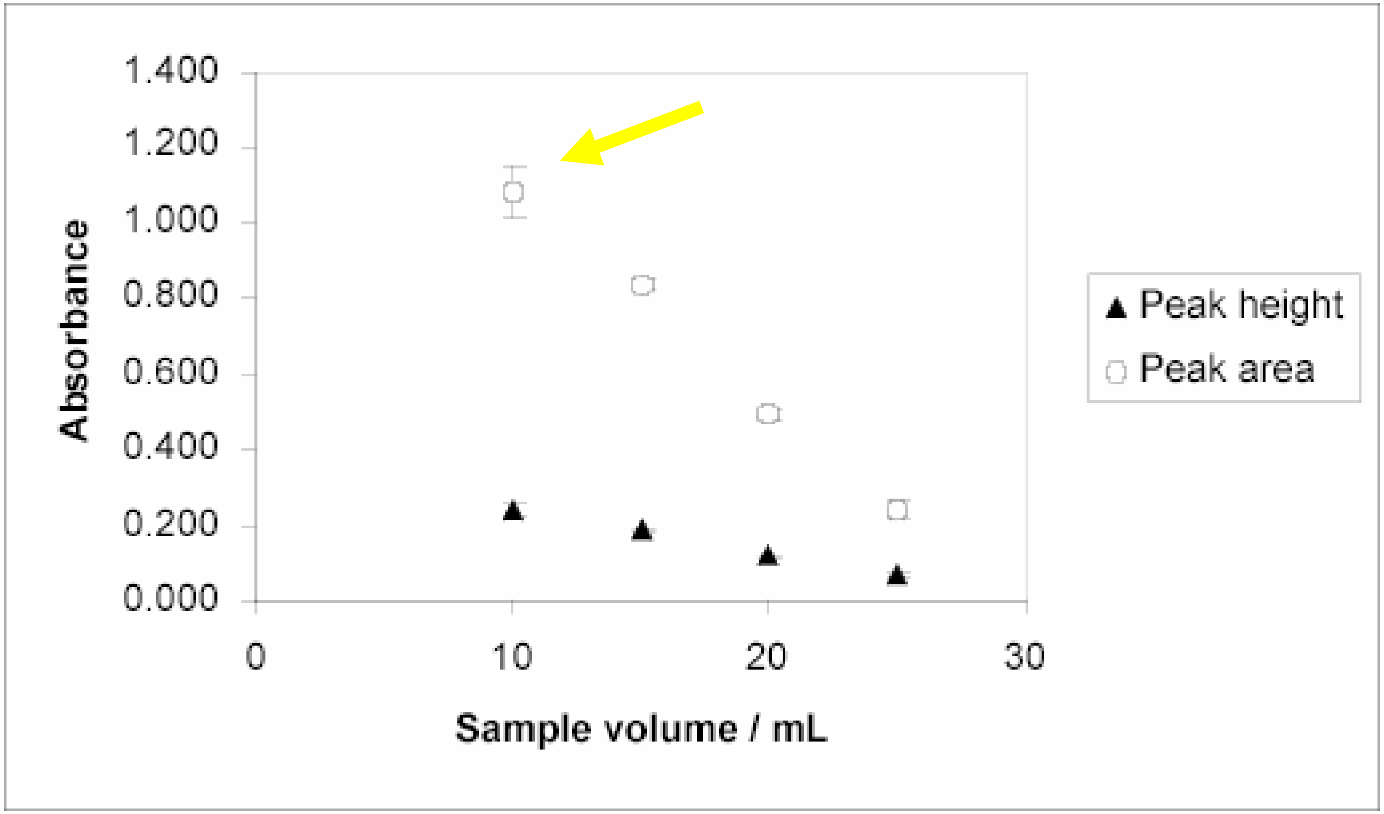
SI-CVG-AAS: effect of sonication power



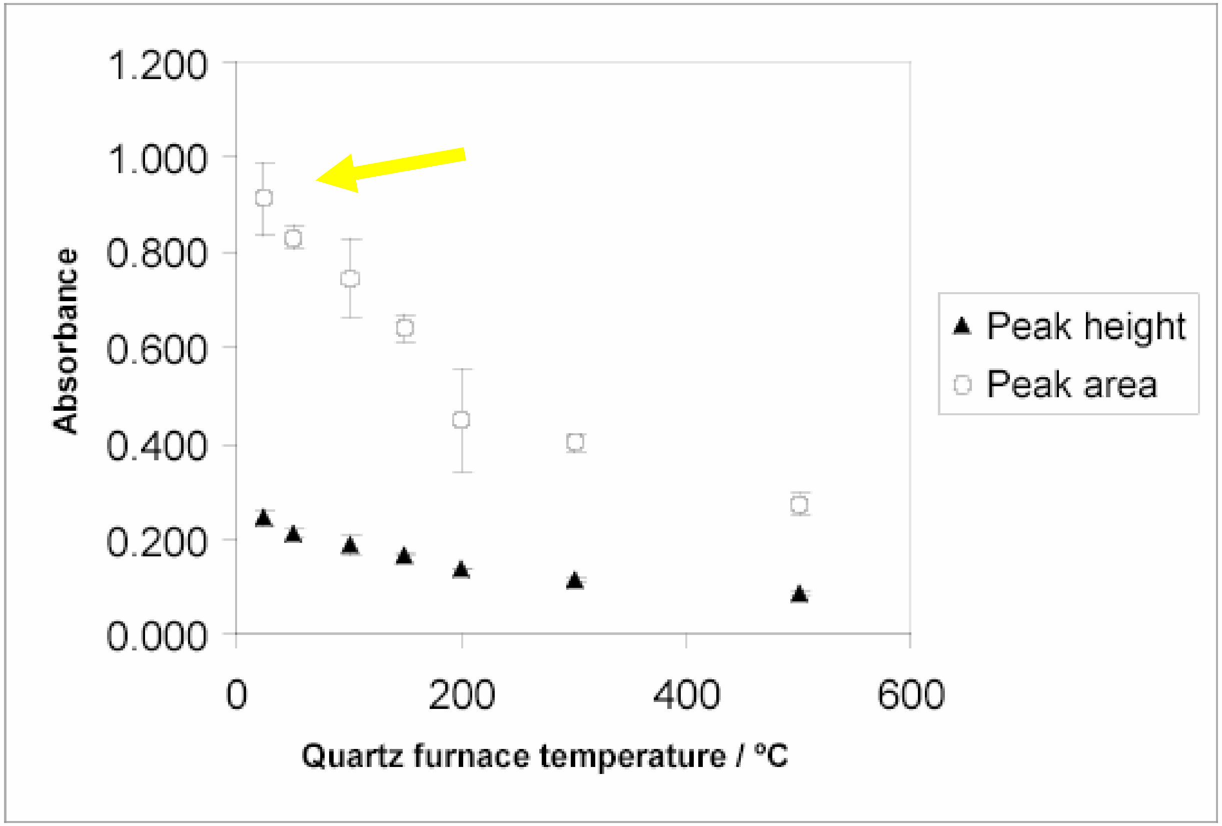
SI-CVG-AAS: effect of HCOOH concentration



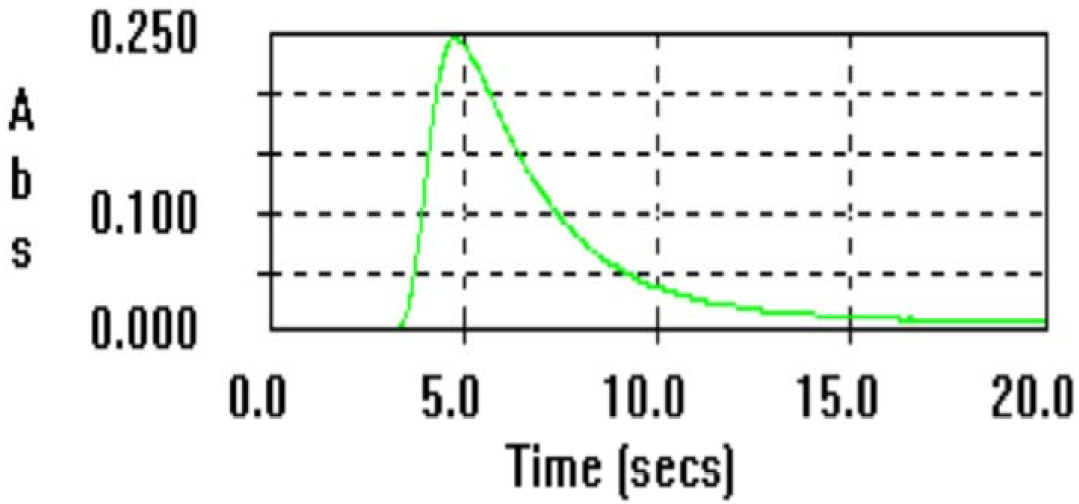
SI-CVG-AAS: effect of sample volume



SI-CVG-AAS: effect of quartz cell temperature



SI-CVG-AAS: analytical characteristics



Calibration line: Y=0,0405×[Hg] + 0,0079
Linearity: 10 ng/mL
Detection limit: 0,1 ng/mL
Repeatability: 4.4% (peak height)

Matrix effects

Interferent	Interferent concentration (mg/L)[a]	Effect (%)
NaCl	10	-7
NaCl	100	-34
NaCl	1000	-57
Na_2CO_3	10	-24
Na_2CO_3	100	-50
$CaCl_2$	100	-54
KCl	100	-50
$MgCl_2$	100	-60
$MgCl_2$	10	-7
KNO_3	100	+1
$MnCl_2$	10	-37
$Pb(NO_3)_2$	10	-6
$CoCl_2$	10	-21
$NiCl_2$	10	-18
$Ni(NO_3)_2$	10	-9
$(SO_4)_2Fe(NH_4)_2$	10	-3
$Cd(NO_3)_2$	10	-3
$CuCl_2$	1	-24
$CuCl_2$	10	-50
$CrCl_3$	10	-18
$Cr(NO_3)_3$	10	-7
$SnCl_2$	10	-37
Humic acid	0.1	-5

Green method for ultrasensitive determination of Hg in natural waters by electrothermal-atomic absorption spectrometry following sono-induced cold vapor generation and 'in-atomiser trapping'

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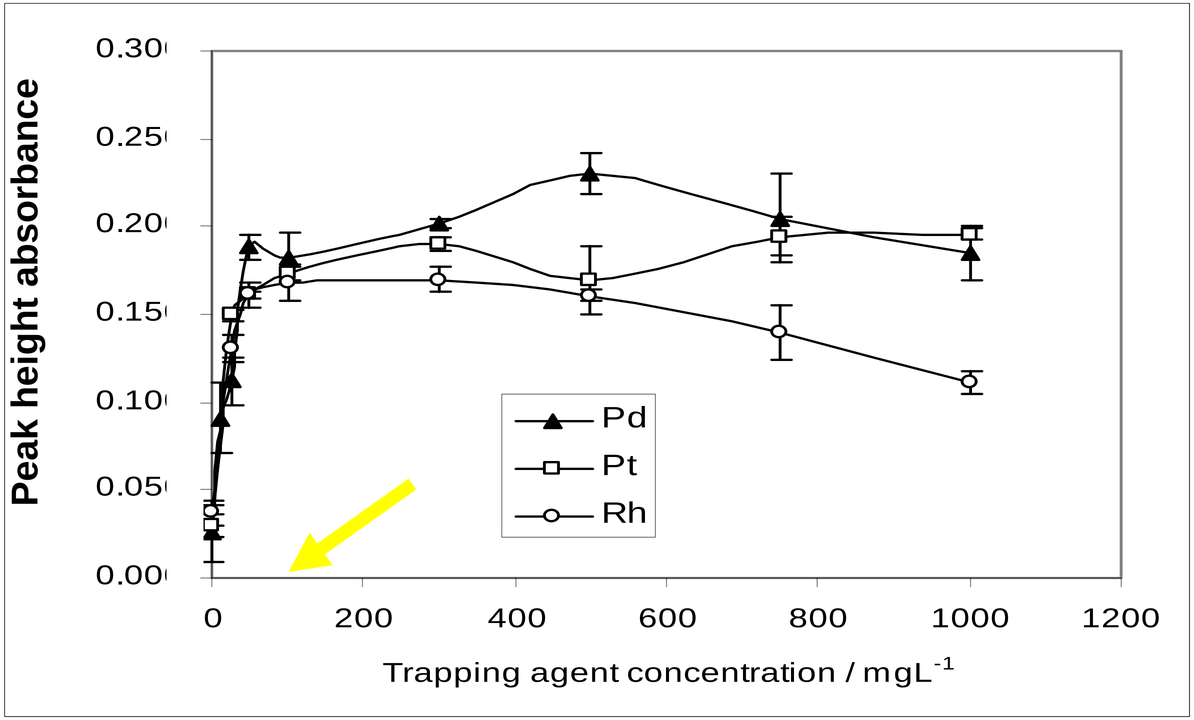
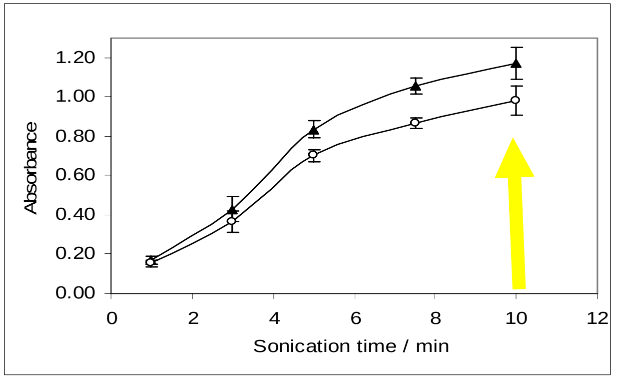
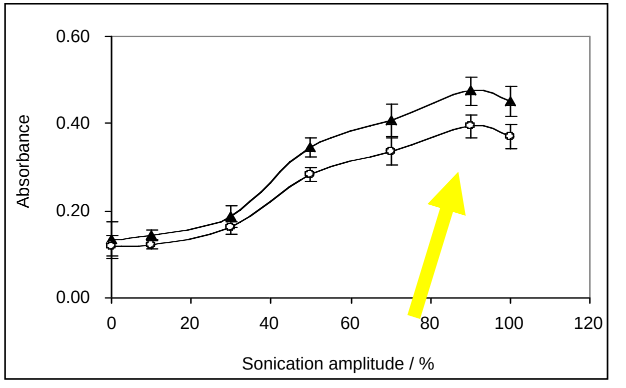
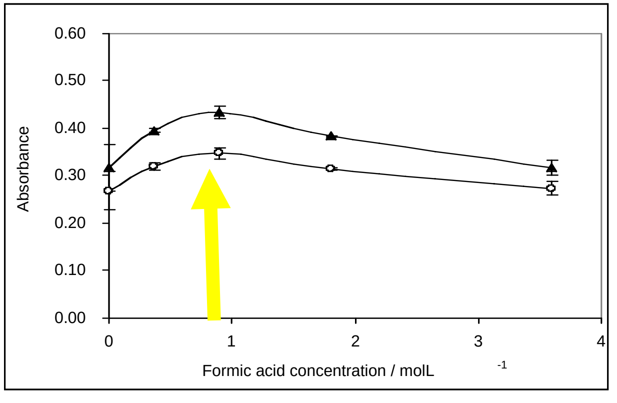
SI-CV-ETAAS: Effect of the noble metal on Hg trapping

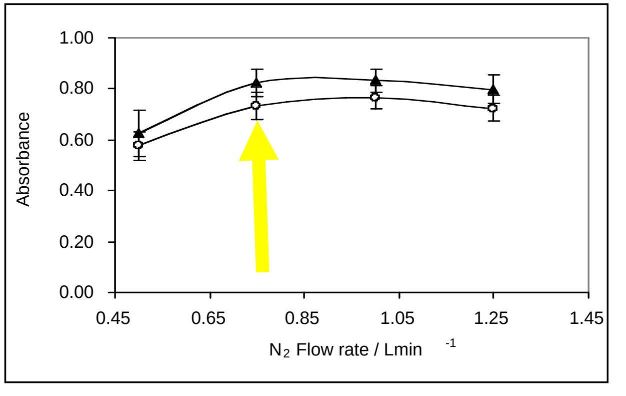


SI-CV-ETAAS: effect of variables









SI-CV-ETAAS: Analytical characteristics

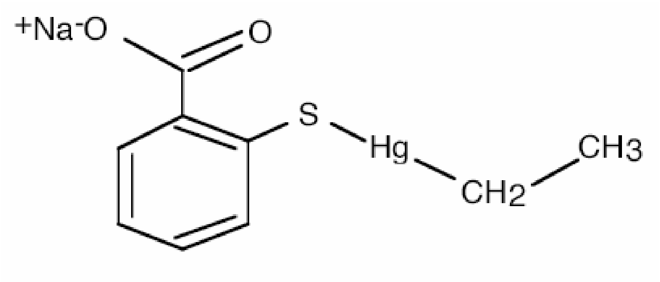
Calibration line: Y=0,176×[Hg] + 0,0138

Linearity: 4 ng/mL

Detection limit: 0,03 ng/mL Hg

Repeatability: 3 % (peak area)

Determination of thiomersal by SI-CVG-AAS



$$\xrightarrow[H_2O_2]{UV} Hg^{2+}$$

(sodium ethylmercurithiosalicylate)

$$Hg^{2+} \xrightarrow[HCOOH]{US} Hg(0)$$

Analysis of ophthalmic solutions

Eye-drop sample	Found concentration (µg/mL)	
Isopto B12	105 ± 3	(100 µg/mL)
Colicursí Cloramfenicol	110 ± 4	
Vitaphakol	45.4 ± 2	
Ocubrax	38.8 ± 2	
Clarvisan	0.30 ± 0.02	
Oftalmowell	<LOD	
Visine	<LOD	

Analysis of natural waters

Sample	Hg spiked ($\mu g\ L^{-1}$)	Hg found ($\mu g\ L^{-1}$)*	Error (%)
Milli-Q water + Humic acid	1	0.97 ± 0.1	-3
MWI (Cabreiroá)	1	1.12 ± 0.2	+12
MWII (Fontecelta)	1	0.96 ± 0.15	-4
MWIII (Mondariz)	1	0.98 ± 0.1	-2
MWIV (Fontvella)	1	1.08 ± 0.15	+8
CRM NWTM-27.2 (Lake water)	1	0.89 ± 0.15	-11

*Average value ± standard deviation (N=4)

Conclusions

☺No use of $NaBH_4$ or $SnCl_2$ for reduction

☺Simplicity, low operation costs

☺Benefits in Green Chemistry: no toxicity due HCOOH

☺Low blanks, improved LOD

☺Enhanced trapping efficiency for "in-atomizer trapping"

Future prospects

- Improvements in the coupling of the sonoreactor and the sample solution
- Implementation of the SI-CVG tecnique in on-line manifolds
- Interface with other atomic detectors (ICP-OES, ICP-MS)
- Sono-induced reduction to other elements

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