Experience with on-line pretreatment in a flow and flow injection hydride generation AAS by means of microwave and UV-assisted oxidation

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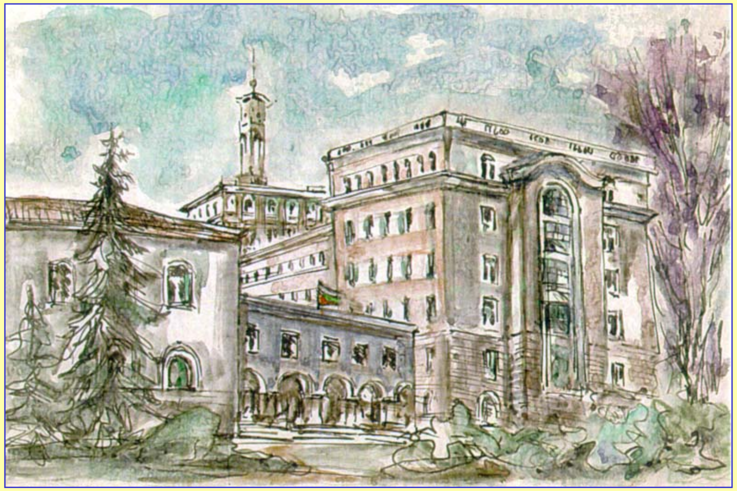

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http://www.chem.uni-sofia.bg/depart/achem/

Topics

Vapor generation AAS (HG and CVT for Hg)

- On-line chemical pretreatments in FI and CF VGAAS by

    microwave digestion

        FI-MWD-CVAAS

        FI-MWD-HGAAS

    UV photooxidation

        FI-UV-HGAAS for org-As and org-Sn

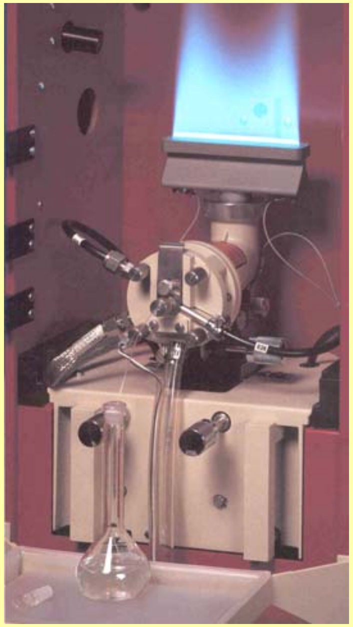
        on-line pre-oxidation

- Examples from speciation analysis

    FI-UV-HGAAS-QTA

    HPLC–UV–HGAAS-QTA

Flame AAS *(FAAS)*



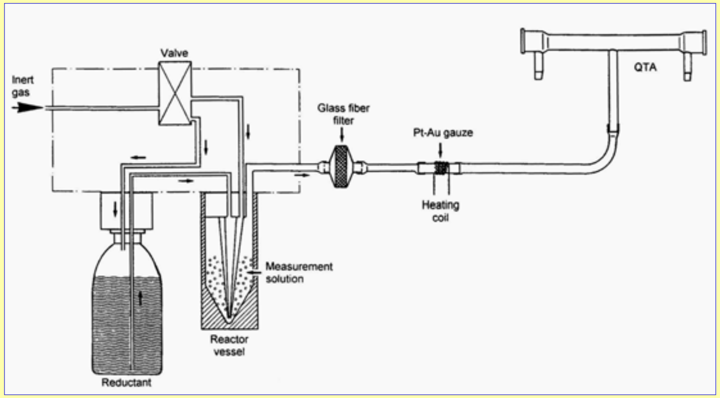
AAS TECHNIQUES

Electrothermal AAS

Hyphenated (coupled) techniques

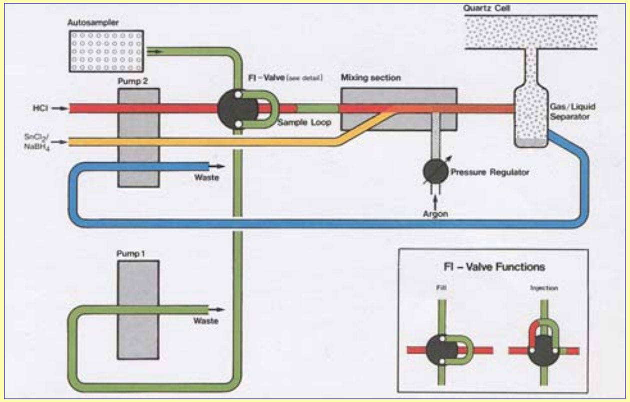
e.g. HG-ETAAS, HPLC-HG-AAS etc.

Vapour generation AAS *(HGAAS)*



Cold vapour AAS *(CVAAS)*

Batch *vs.* FI or CF
with or without intermediate pretreatment and/or enrichment



Hydride generation AAS *(HGAAS)*

CHEMICAL VAPOUR GENERATION in ATOMIC SPECTROMETRY

Hydride generation (HG)	*As*, *Bi*, Cd?, *Ge*, (In?), Pb, *Sb*, *Se*, *Sn*, *Te*, (Tl?)
Cold vapour technique (CV)	Cd?, *Hg*
Atomic vapours or clusters	Cu, noble metals ...
Ethylation	Bi, Cd, Co, *Hg*, *Pb*, *Se*, *Sn*, Tl
Butylation	Be, Ga, *Hg*, *Pb*, *Sn*, Zn
Carbonyl generation	Co, Fe, *Ni*
Chlorides	*As*, Bi, Cd, *Ge*, Mo, Pb, Sn, Tl, Zn
Fluorides	Ge, Mo, Re, U, V, W
Dithiocarbamates	Co, Cr, Cu
β - diketonates	Al, Co, *Cr*, Cu, Fe, Mn, Ni, Pb, Zn
Misc. VG techniques	$B(OCH_3)_3$, OsO_4

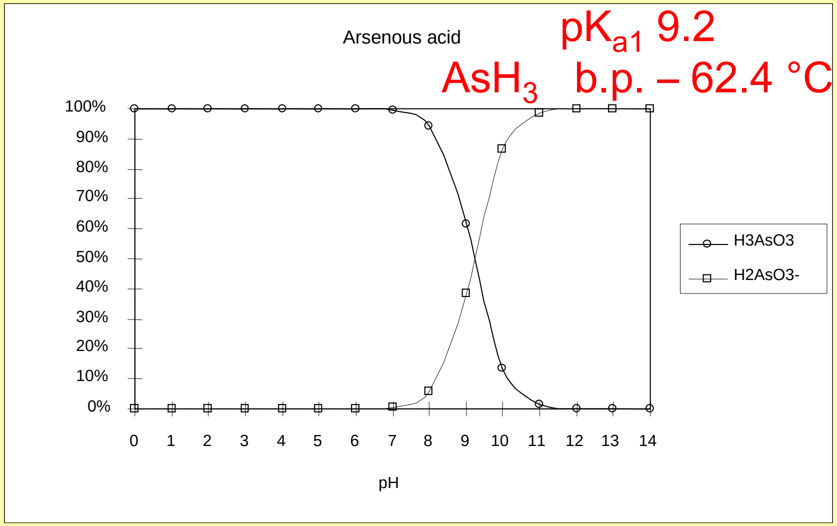
CHEMICAL VAPOUR GENERATION in AAS

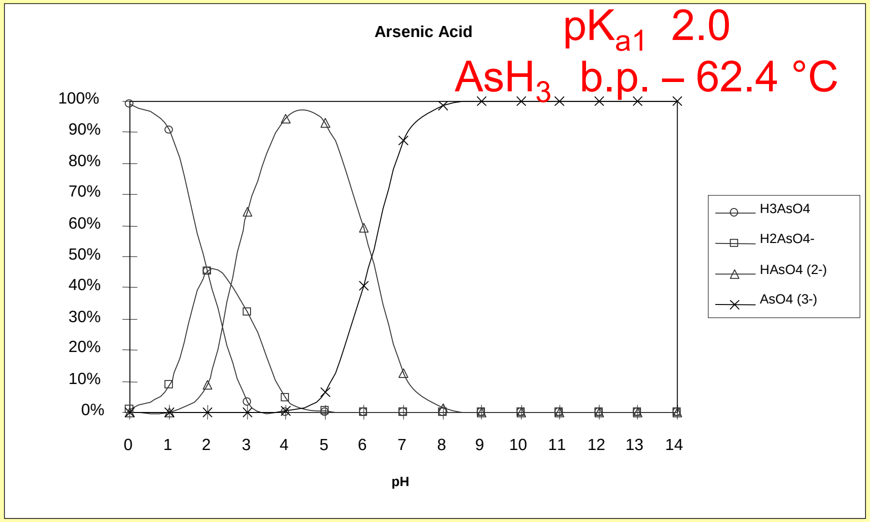
Advantages	*Drawbacks & limitations*
• **High chemical yields & transport efficiencies**	• **Complex, on-line chemistry involved**
• **Separation from troublesome matrices**	• **Specific sample pre-treatment required**
• **Enrichment**	• **Effect of oxidation & binding state of analyte**
• **Automation (in FI and CF mode)**	• **Chemical interferences**
• **Good sample throughput rates**	• **Foaming and aerosol formation**
• **Competitive LODs and RSDs**	• **Numerous instrumental & chem. parameters for optimisation**
• **Commercially available accessories**	• **Applicability to a limited number of analytes**
• **Economically affordable**	• **Limited linear range**
• **Speciation potentialities**	• **Poor multi-element capabilities**

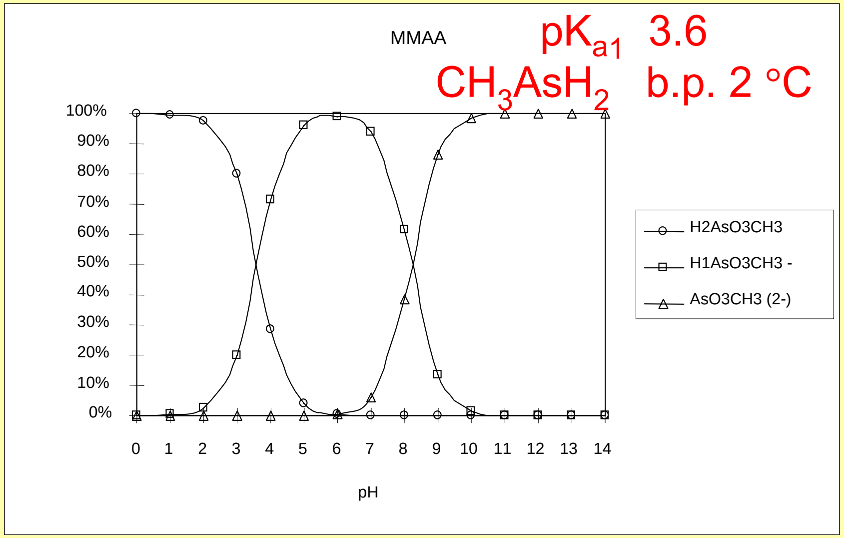
ORGANOARSENIC SPECIES STUDIED

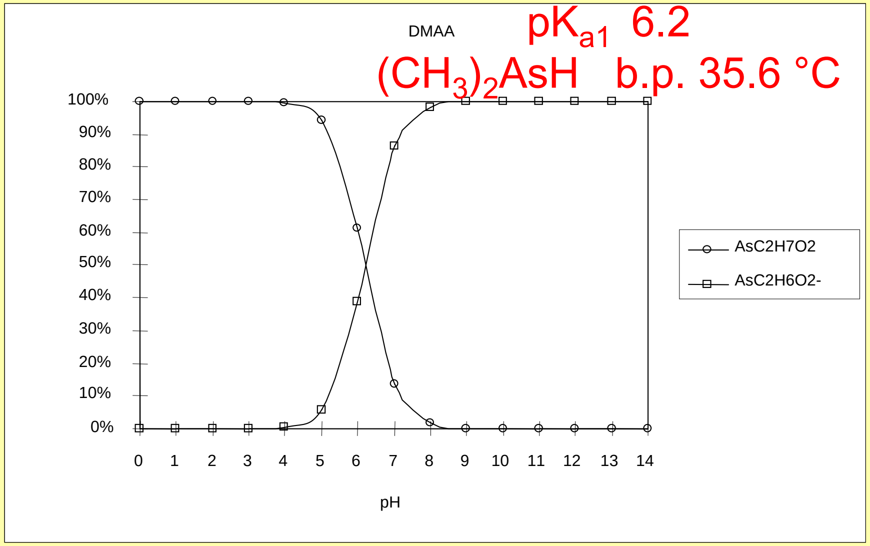
Abb.	Arsenic species	Formula	pK_a
i-As(III)	Arsenic(III)	AsO_3^{3-}	9.2
i-As(V)	Arsenic(V)	AsO_4^{3-}	2.3, 6.8, 11.5
MMA	Methylarsonic acid	$CH_3AsO(OH)_2$	3.6, 8.2
DMA	Dimethylarsinic acid	$(CH_3)_2AsO(OH)$	1.3, 6.2
TMAO	Trimethylarsineoxide	$(CH_3)_3As^+O^-$	3.6
Me_4As	Tetramethylarsonium	$(CH_3)_4As^+$	
AB	Arsenobetaine	$(CH_3)_3As^+CH_2COO^-$	2.2
AC	Arsenocholine	$(CH_3)_3As^+CH_2CH_2OH$	

DISTRIBUTION DIAGRAMS of SOME HYDRIDE-FORMING ARSENIC ACIDS *vs.* pH

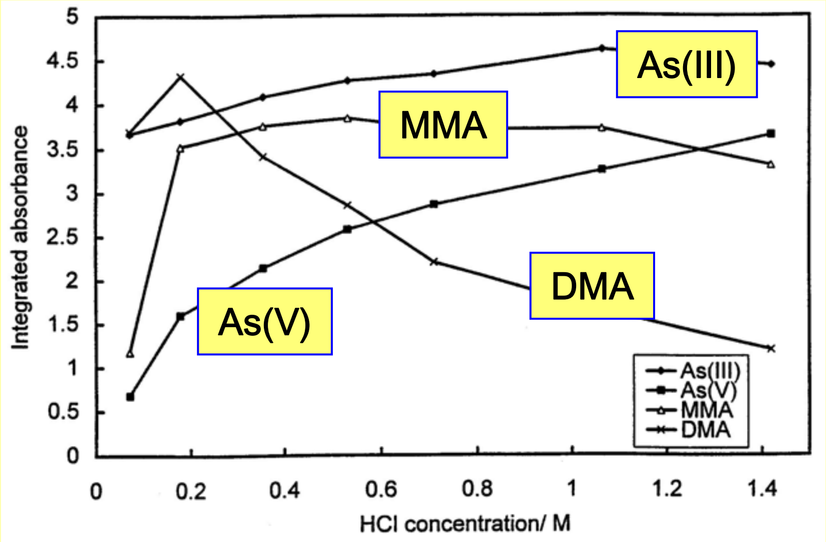


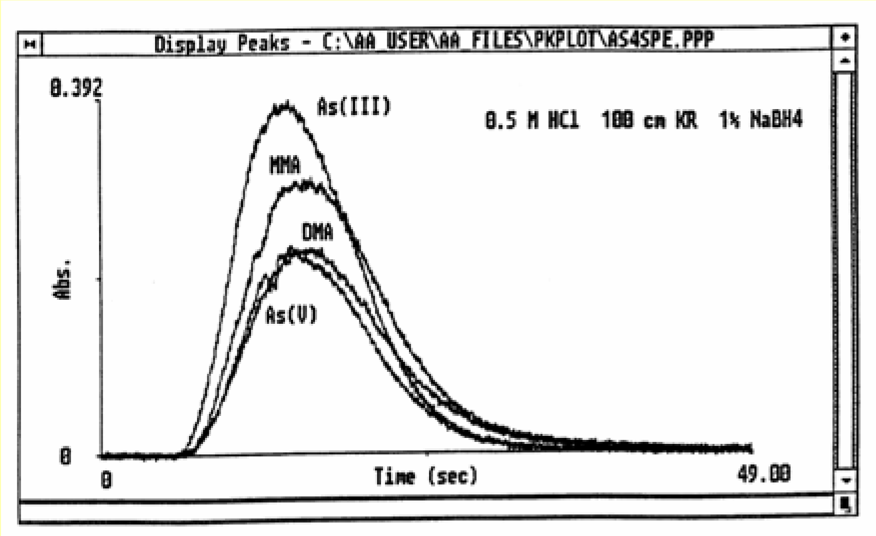






EFFECT of HCl CONCENTRATION on A_{int} SIGNAL for 4 ARSENIC SPECIES





- different HG pattern
- different optimal conditions (chemical, instrumental)
- different sensitivities

ON-LINE DECOMPOSITION and PRE-REDUCTION

	on-line dign.	VG	QTA (FIT)		As, Bi, Hg, Pb, Se, Sn
on-line dign.	on-line pre-redn.	VG	QTA (FIT)		As, Se, (Sb, Te)
	on-line pre-redn.	VG	QTA		As, Sb, Se
		VG	pyrolysis chamber	QTA	Hg
		‘thermochemical vapour generation’ (THG)		FIT	As, Cd, Hg, Pb, Se, Sn

SELECTED REAGENTS for ON-LINE DECOMPOSITION

Reagents	Room temp.	Thermal heating	MW heating	UV	UV + thermal heating	Analyte
$K_2S_2O_8$–NaOH	- - -	+	+ +	+ + +	?	As, Se
$K_2S_2O_8$–acid(s)	+ (Hg)	+	+ +	+ +	+ + +	As, Bi, Hg,Pb, Sn
$K_2S_2O_8$–$KMnO_4$–acid(s)	+ (Hg)	+ (Hg)	+ +	+	?	Hg
BrO_3^-–Br^- –acid(s)	+ (Hg)	+	+ + +	+ (Sn)	+ (Sn)	Bi, Hg, Se, Sn
BrO_3^-–Br^- –$K_2S_2O_8$–acid		+	+ + +			As, Hg
BrO_3^-–Br^- –$KMnO_4$–acid	+ (Hg)	+	+ + +			Hg
$K_2Cr_2O_7$–HNO_3 +/– Cd^{2+} cataly						
$KMnO_4$–HNO_3–H						

Fast and efficient oxidants

Compatible with subsequent analytical stage(s)

ON-LINE MICROWAVE DIGESTION

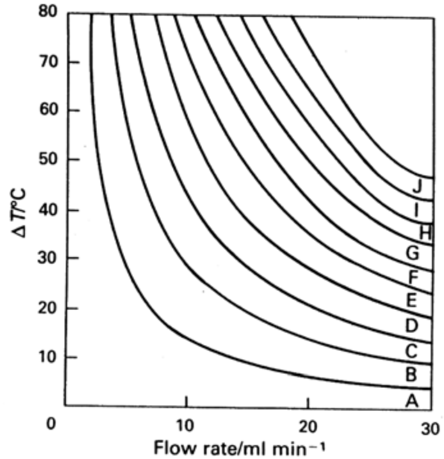


Fig. 3 Theoretical heating pattern of water: temperature increase (ΔT) *versus* the flow rate (F) at different MWD power settings (P), $\Delta T = (14.33 \times P)/F$. A, 10; B, 20; C, 30; D, 40; E, 50; F, 60; G, 70; H, 80; I, 90; and J, 100 W

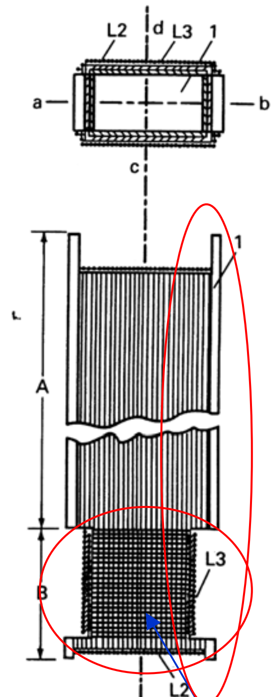
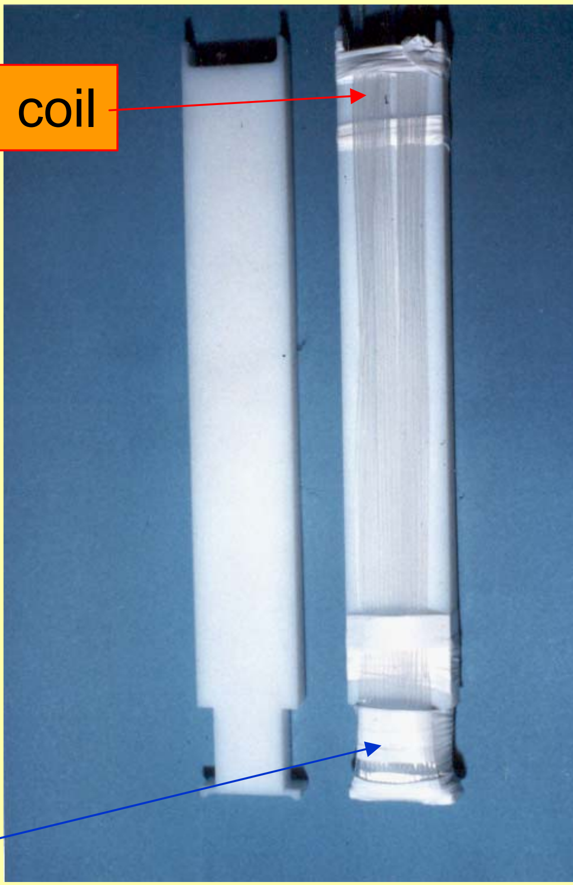


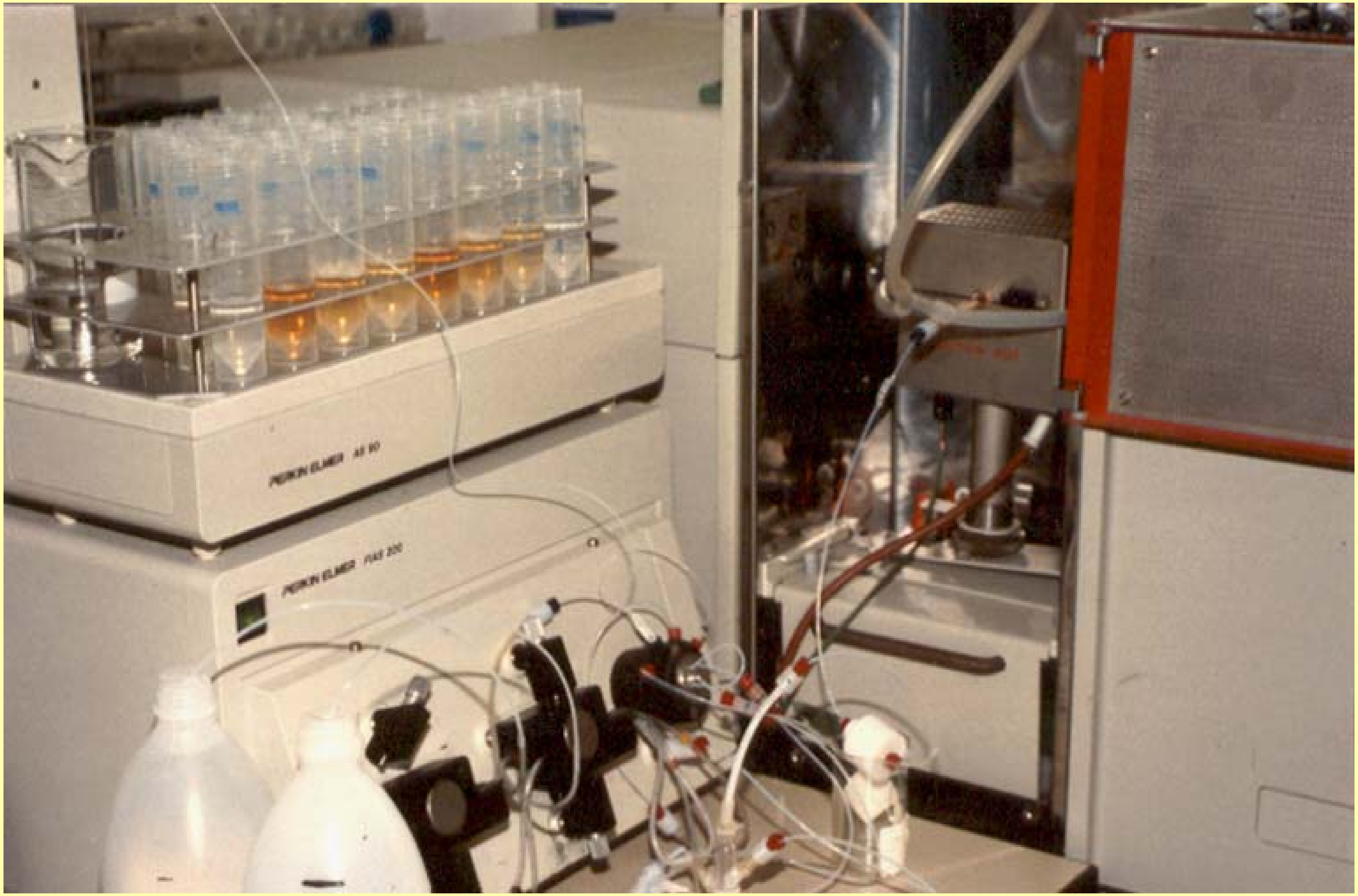
Fig. 2 PTFE shaft (1) with reaction coil (L2) and 'dummy load' coil (L3) wound in two perpendicular planes as detailed in the text. The upper part of the shaft (A) is situated in the chimney of the MWD while the lower part (B) resides within the irradiated zone of the MWD. Two orientations of the shaft within the MWD are possible: a–b ('parallel') and c–d ('perpendicular')



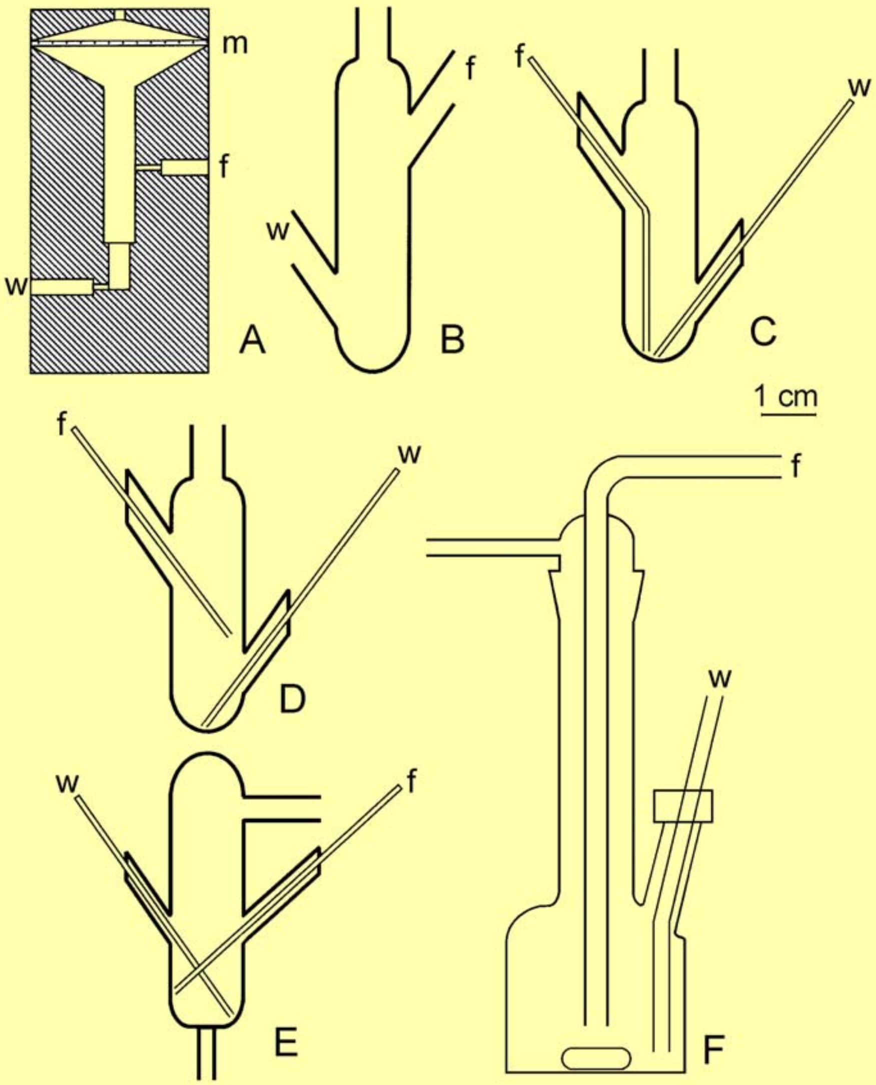
reaction coil

a ballast coil ("dummy coil")

FLOW INJECTION SAMPLE PRETREATMENT USING FOCUSING MICROWAVE (FI-MWD-VGAAS)



GAS-LIQUID SEPARATORS



Sn in urine by FI-MWD-HGAAS

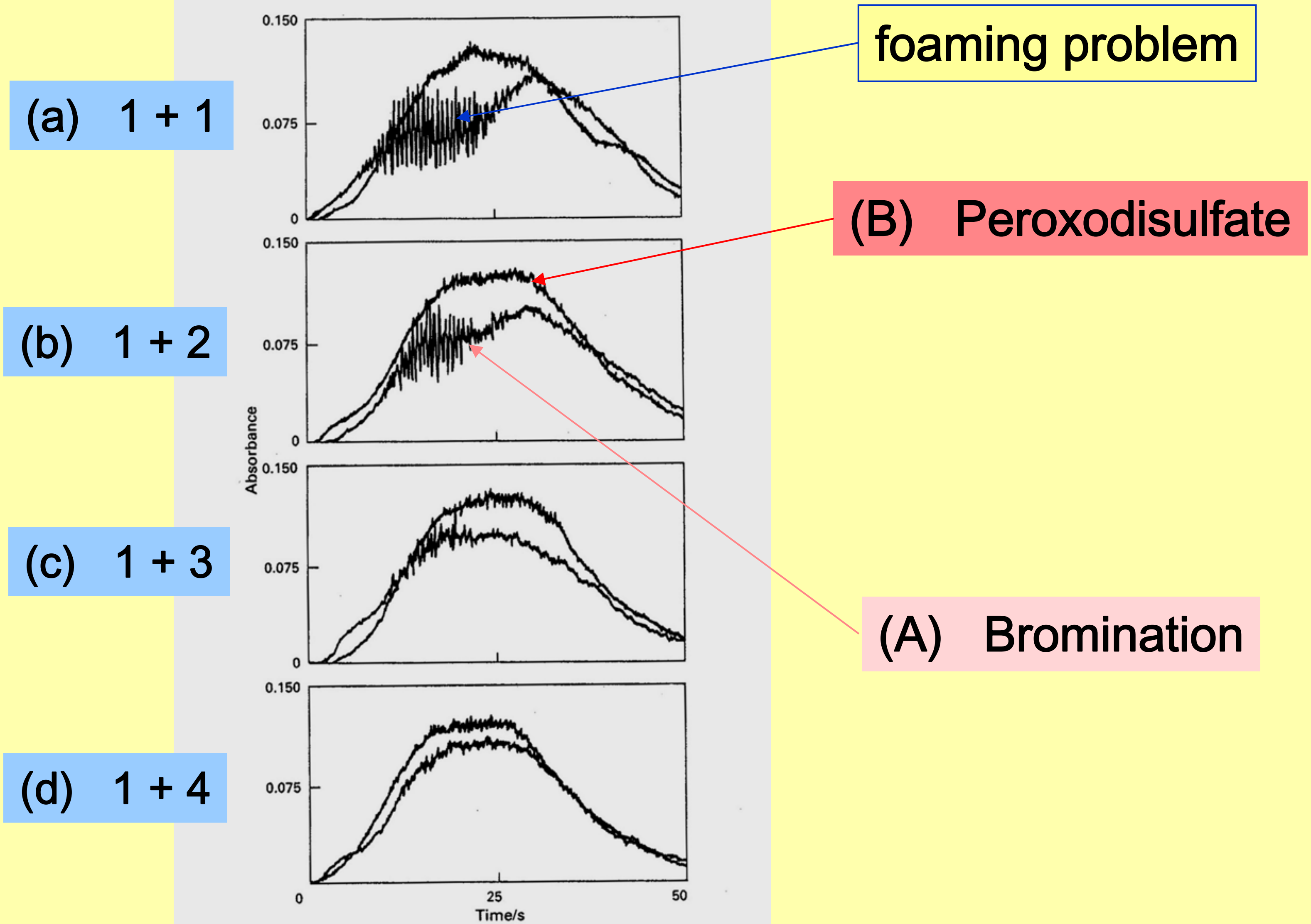


Fig. 3 Effect of foam formation on peak shape for 10 µg l^{-1} Sn added to urine at different dilutions: (*a*) 1 + 1; (*b*) 1 + 2; (*c*) 1 + 3; and (*d*) 1 + 4. Urine diluent: A, BDM + 2% tartaric acid; and B, 2% $K_2S_2O_8$ in 90 mmol l^{-1} H_2SO_4 + 2% tartaric acid. Microwave power, 60 W; pH, 1.7; and reductant, 0.1% $NaBH_4$ + 0.05% NaOH + 0.04% antifoam

PROBLEMS with ON-LINE MICROWAVE DIGESTION

- non-homogenous power distribution within the MW cavity
- high % of non-absorbed power
- short residence times, hence short reaction times
- incomplete decomposition of the organic matter
- evolution of gases/vapours during digestion
- disturbances of liquid flow
- pressure build-up in closed systems
- effects of sample composition and mass on MW power absorption and on the efficiency of decomposition
- increased dispersion of sample zone
- foaming
- aerosol formation and condensation of water vapours

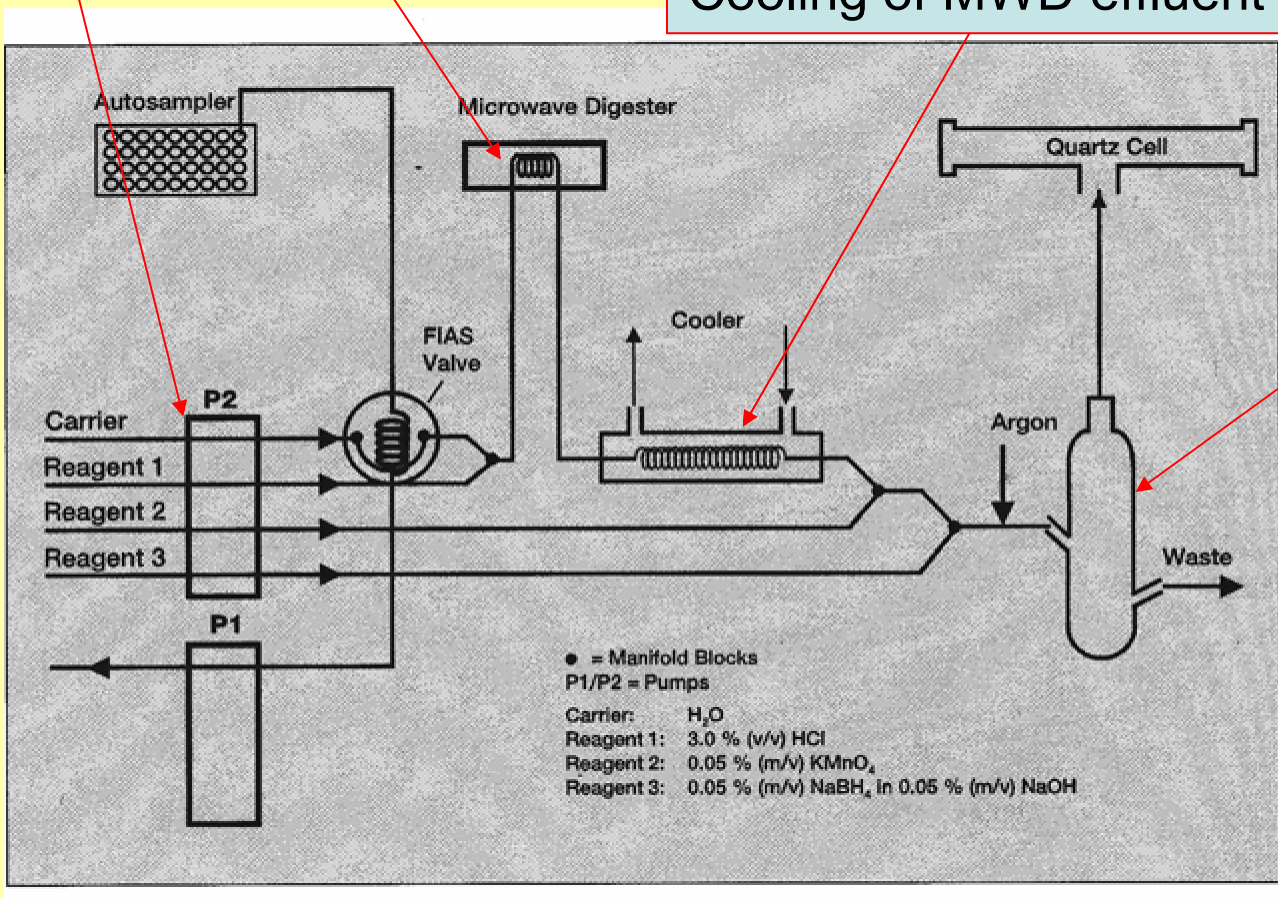
Perkin-Elmer adopted design

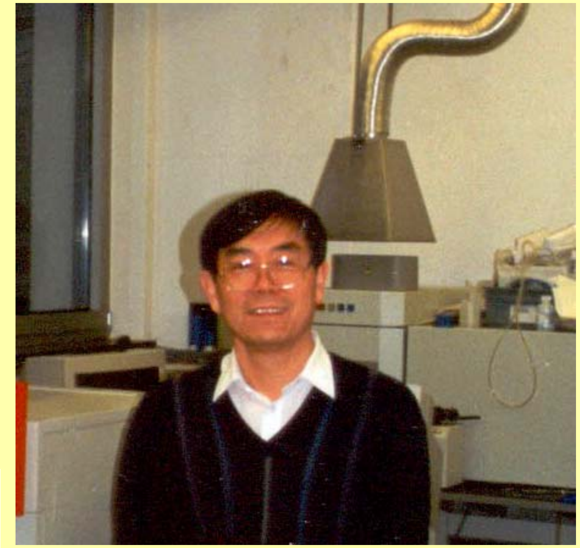
On-line merging with reagents ($KMnO_4$)

Knotted reactor

Cooling of MWD effluent

Glass GLS (4.5 mL)





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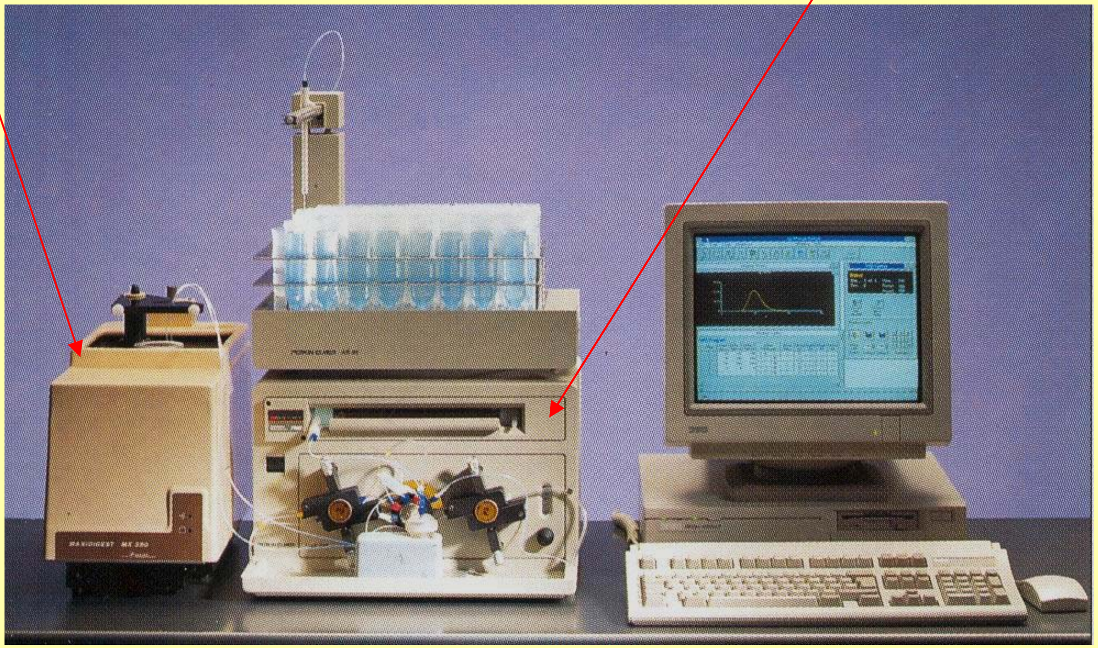
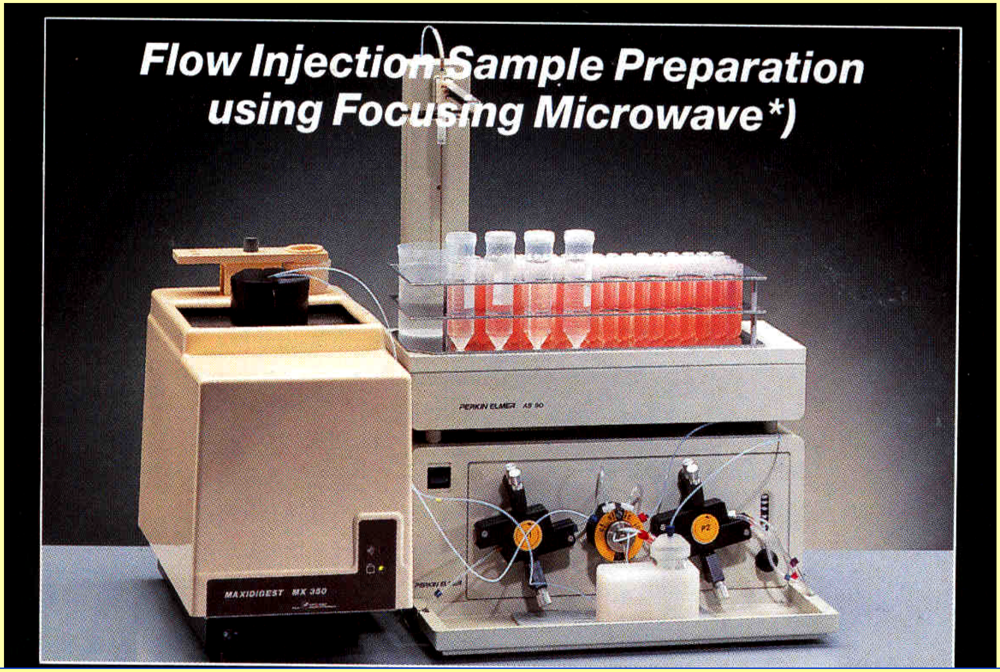
Commercialized MWD-VGAAS instrumentation

Prolabo MX 350
Maxidigest Microwave
Station

Perkin-Elmer FIAS-200 in MHS mode
or FIMS (Flow Injection Mercury System)



Commercialized MWD-VGAAS instrumentation

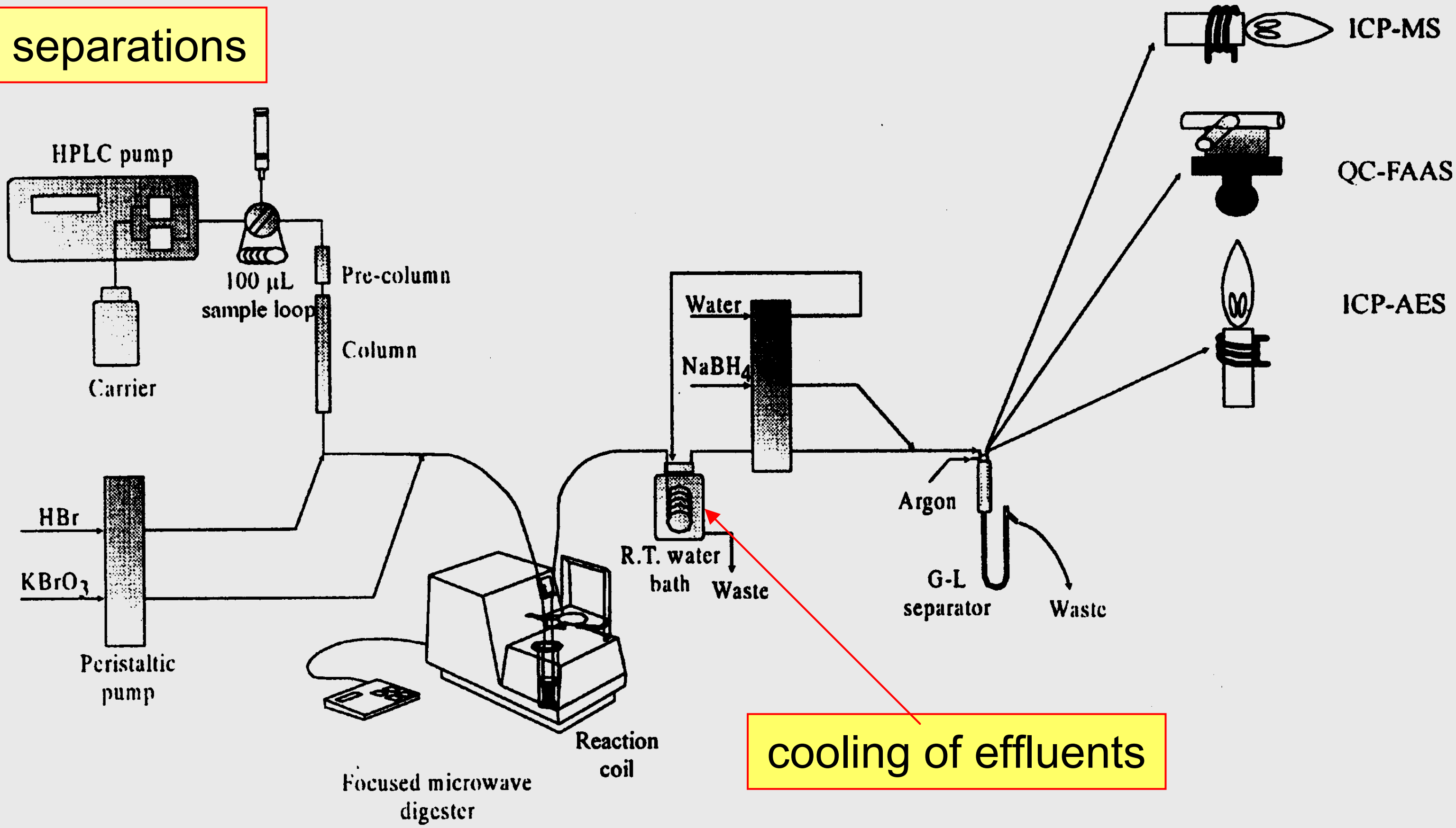


- applications to Hg, Bi, Sn, As, Pb, etc.
- automated treatment of water, urine, serum, saliva etc. in a closed system
- reduced risk of contamination and analyte loss
- sub-ppb LODs - down to 8 pg/mL for Hg
- 20–40 samples / hr in direct mode
- 7–20 samples/hr with amalgamation
- commercially available

Further applications and modifications in other labs

other at. spectrometric detectors

HPLC separations



cooling of effluents

Figure 13.5 Schematic diagram of the coupling of HPLC-focused MW assisted digestion-HG-(QC-FAAS/ICP-OES/ICP-MS) (reproduced from Reference 49, with permission).

UV *vs.* MW treatment

VGAAS COUPLED with CHROMATOGRAPHY for SPECIATION

		HPLC	*VG*	QTA		As, Hg, Sb, Sn
	HPLC	dign.	*VG*	QTA		As, Hg, Se
HPLC	dign.	predn.	*VG*	QTA		As, Se
derivatization	enrichment	HPLC	*VG*	dign.	QTA	Hg
	enrichment	HPLC	*VG*	QTA		Hg
derivatization	enrichment	HPLC	*VG*	dign.	QTA	Hg
			VG	CT / GC	QTA (FIT)	As, Ge, Hg, Sb, Se, Sn, Te
		derivatization	*VG*	CT / GC	QTA (FIT)	As, Sb, Se, Sn

ON-LINE UV PHOTOOXIDATION of ORGANOELEMENT SPECIES

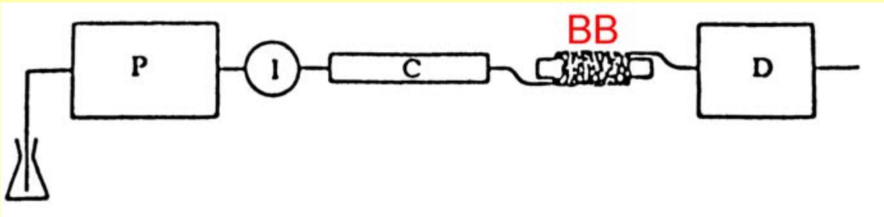
Species studied: org-As and org-Sn

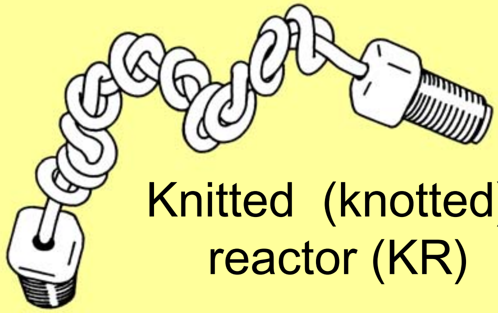
arsenite, arsenate, monomethylarsonate (MMA), dimethylarsinate (DMA), arsenobetaine (AB), arsenocholine (AC), i-Sn(IV), dimethyltin (Me_2Sn), trimethyltin (Me_3Sn), triethyltin (Et_3Sn), tripropyltin (Pr_3Sn), triphenyltin (Ph_3Sn), monobutyltin (BuSn), dibutyltin (Bu_2Sn), tributyltin (Bu_3Sn), tetrabutyltin (Bu_4Sn)

Interesting in view of several ***possible applications:***

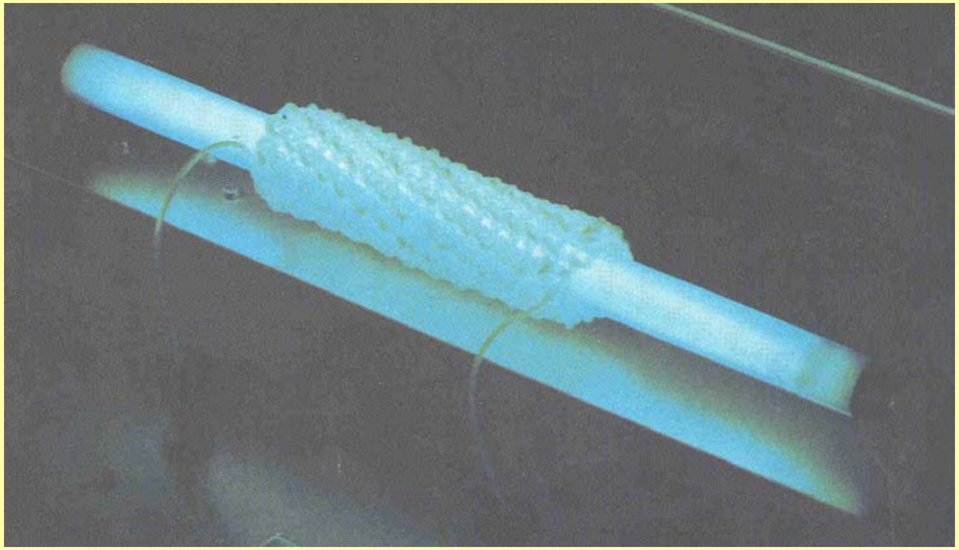
- direct determination of elements such as As, Sn, Hg and Se by VG techniques in samples such as environmental waters or biological fluids that may contain different organoelement species
  e.g. **FI-UV-HGAAS**
- coupling element-sensitive detectors to HPLC or GC
  e.g. **HPLC-UV-FI-HGAAS**
- determination of the sum of **toxicologically-relevant species**
  e.g. As(III) + As(V) + MMA + DMA *vs.* the total As (UV **off** ***/*** **on**)

Beam Boost™ Photochemical Reactor



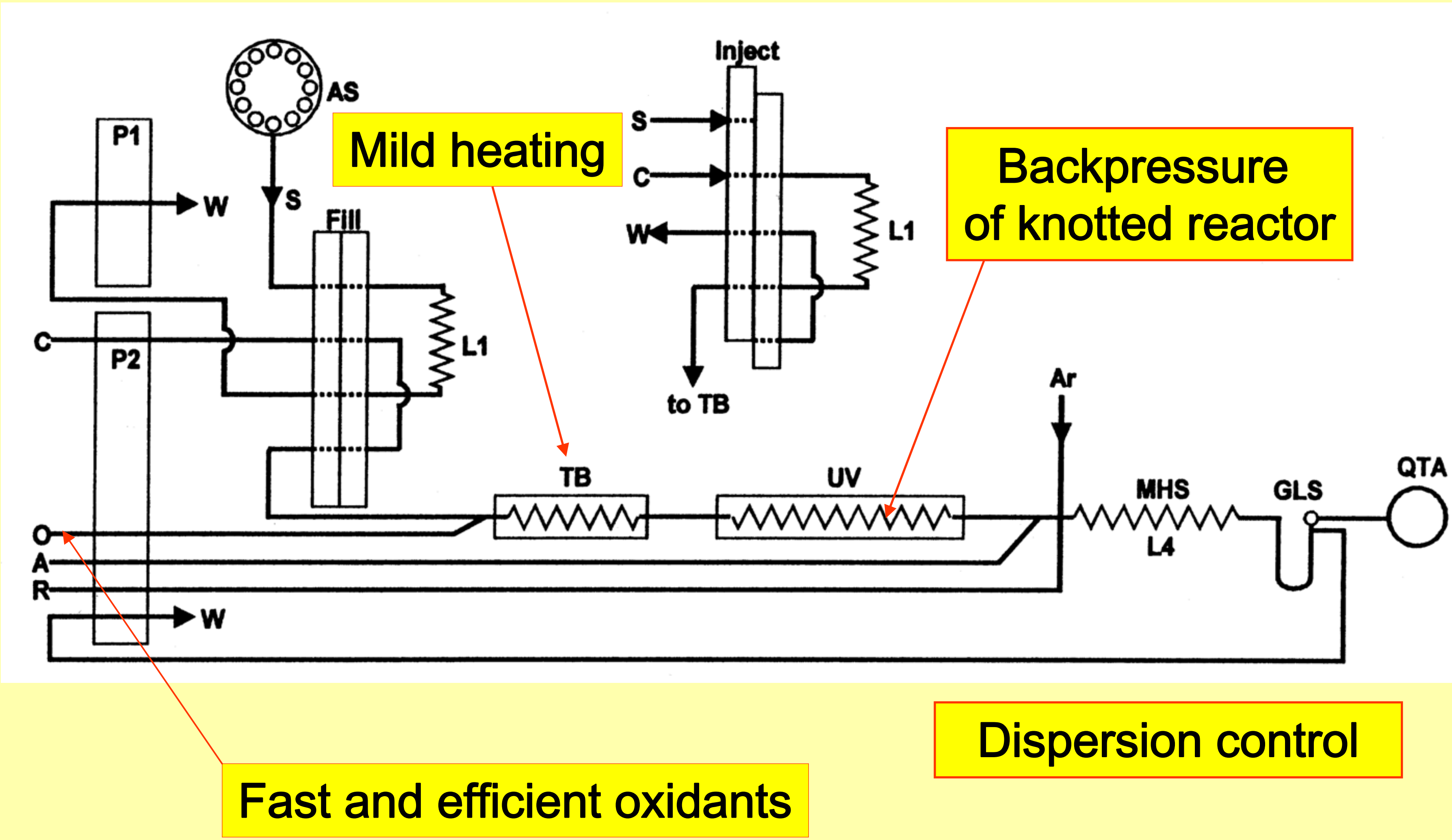


Knitted (knotted) reactor (KR)



10-m KR and a low pressure Hg lamp

ON-LINE UV PHOTOOXIDATION HGAAS MANIFOLD

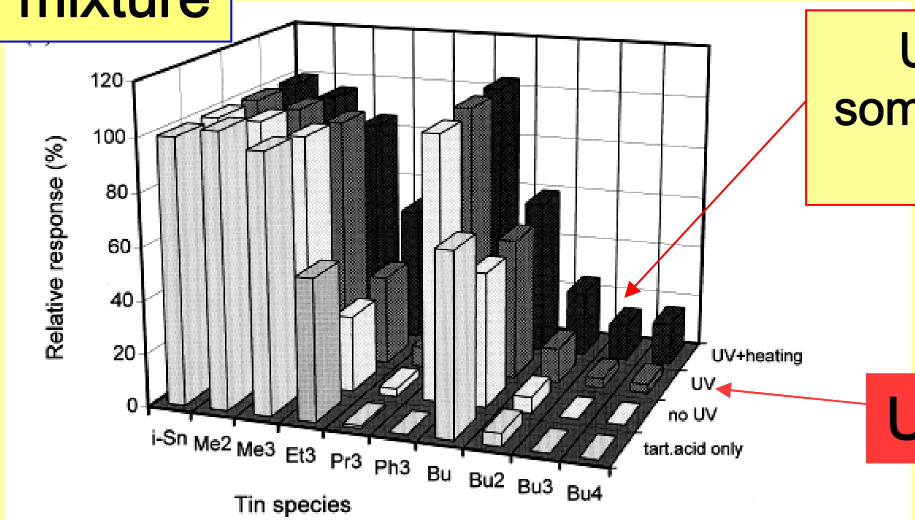


ON-LINE UV PHOTOOXIDATION of ORGANOELEMENT SPECIES (org-As, org-Sn)

Chemistry	Instrumentation
Oxidant for org-As: 1–4% m/v $K_2S_2O_8$—0.5–1 *M* NaOH	P-E 4100 AAS + FIAS 400 MHS + AS 91 ICT Beam Boost Photochemical Reaction Unit
Oxidant for org-Sn: 1–4% m/v $K_2S_2O_8$—1% tartaric acid—100 m*M* H_2SO_4	Flow-rates of carrier, oxidant and acid **1 mL/min** Flow rate of reductant 1 mL/min
Reductant: 0.4% m/v $NaBH_4$—0.067% m/v NaOH—0.08% v/v antifoam agent	5, 10 and 15 m knotted reactors, 0.5 mm i.d. Sample loop 100 µL
Neutralization channel for As digests: 4 *M* HCl	Purge gas 45 mL/min Ar (for As) 45 mL/min Ar + 0.1% v/v O_2 (for Sn)

Behaviour of 10 org-Sn species in FI-UV-HGAAS (QTA)

Acidic bromination mixture



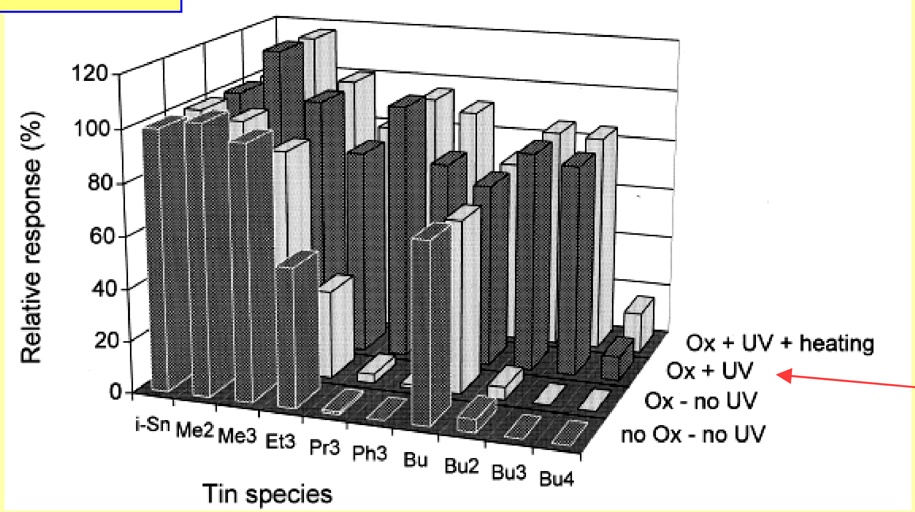
UV + heating
some improvement
for butyltins

UV

Poor efficiency for Ph- and Bu-tins

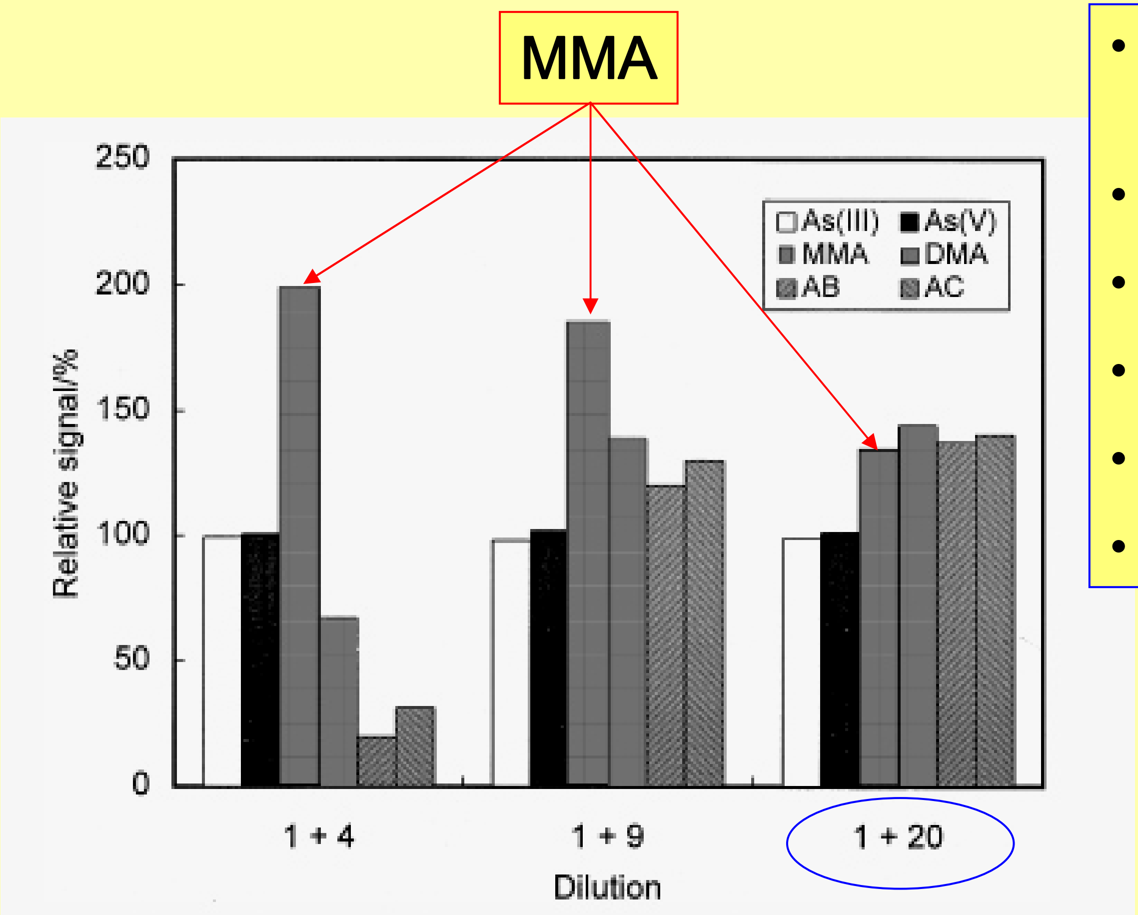
Acidic peroxodisulphate

slightly better



UV

Effect of urine dilution on relative A_{int} signal for As in FI-UV-HGAAS (QTA) for 6 org-As species



- Non-hydride As (AB, AC) → hydride active As
- Matrix effect on digestion
- Higher dilution beneficial
- org-As → $CH_3AsO(OH)_2$ (fast)
- MMA → i-As (slow)
- 100% recovery not reached

DIRECT AUTOMATED DETERMINATION of As in URINE CRMs by FI-UV-HGAAS (µg/mL)

Sample	Certified value mean and conf. interval	Found mean ± SD (n = 4-11)
Bio Rad Level 1 Lot no. 69021	0.052 (0.042-0.062)	0.058 ± 0.015
NIST SRM 2670 Normal Level	(0.06)*	0.069 ± 0.021
Nycomed Pharma Lot no. 403125	0.100	0.122 ± 0.04
Bio Rad Level 2 Lot no. 69022	0.152 (0.121-0.182)	0.153 ± 0.025
NIST SRM 2670 Elevated Level	0.48 ± 0.10	0.463 ± 0.026

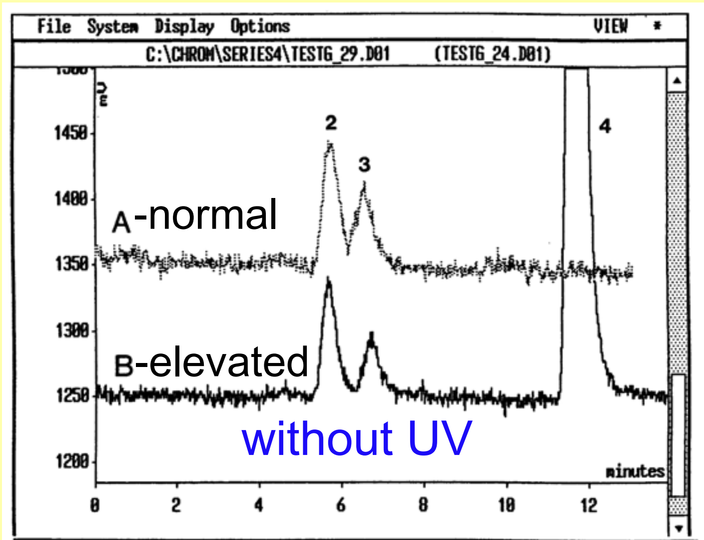
* Information value only

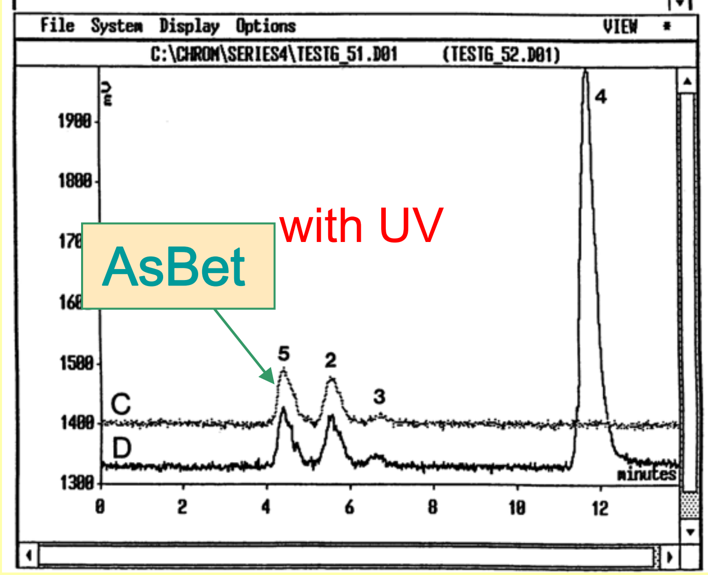
OPTIMISED PARAMETERS for As SPECIATION by MEANS of HPLC-UV-HGAAS-QTA

- **Analytical column:** PRP-X100 Strong anion exchange column (polystyrene divinylbenzene with trimethylammonium exchanger), 250 x 4 mm, 10 µm (CS Chromatographie Service GmbH, Langerwehe, Germany)
- **Pre-column:** PRP-X100, 20 x 4 mm
- **Mobile phase A:** 12 m*M* KH_2PO_4 - K_2HPO_4 buffer, pH 6.20 - 6.25 (0 - 6 min)
- **Mobile phase B:** 24 mM buffer (6-13 min) gradient elution
- **Oxidant:** 4% m/v $K_2S_2O_8$—1 *M* NaOH (0.5 mL/min)
- **Reductant:** 1% m/v $NaBH_4$—0.067% m/v NaOH—0.08% v/v antifoam agent (0.5 mL/min)
- **Purge gas flow:** 40 mL/min Ar
- **Neutralization channel:** 4 *M* HCl (0.5 mL/min)
- **Sample volume:** 50 µL

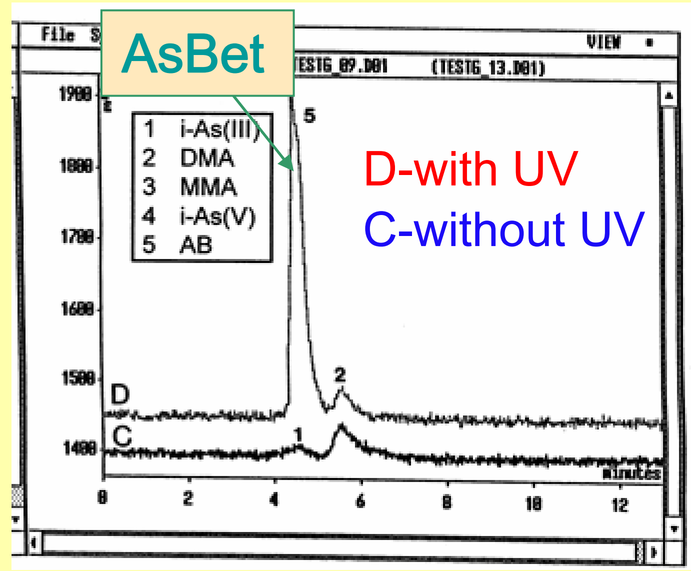
As SPECIATION in URINE by HPLC-UV-HGAAS-QTA

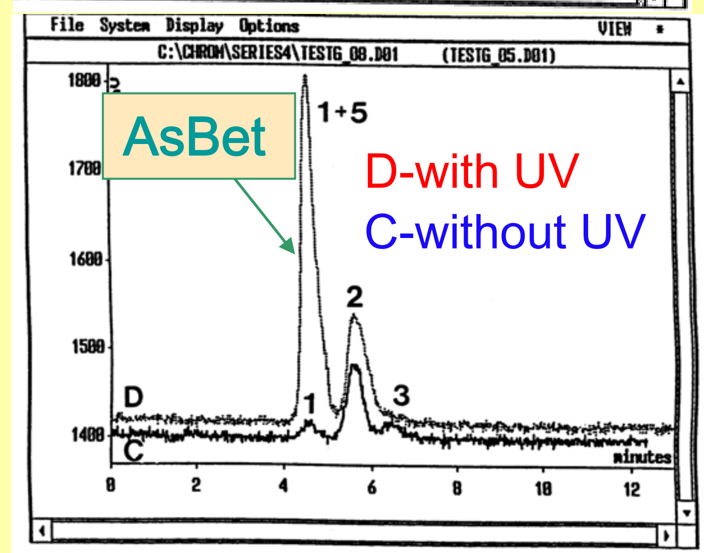
NIST SRM 2670



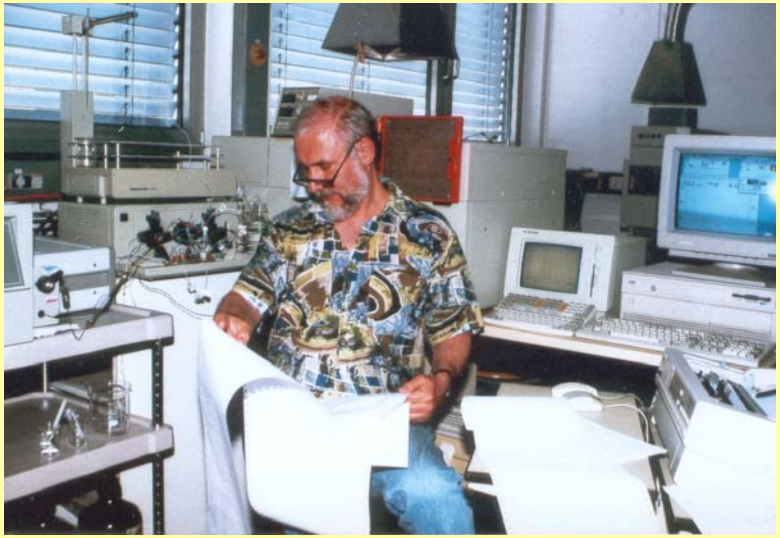


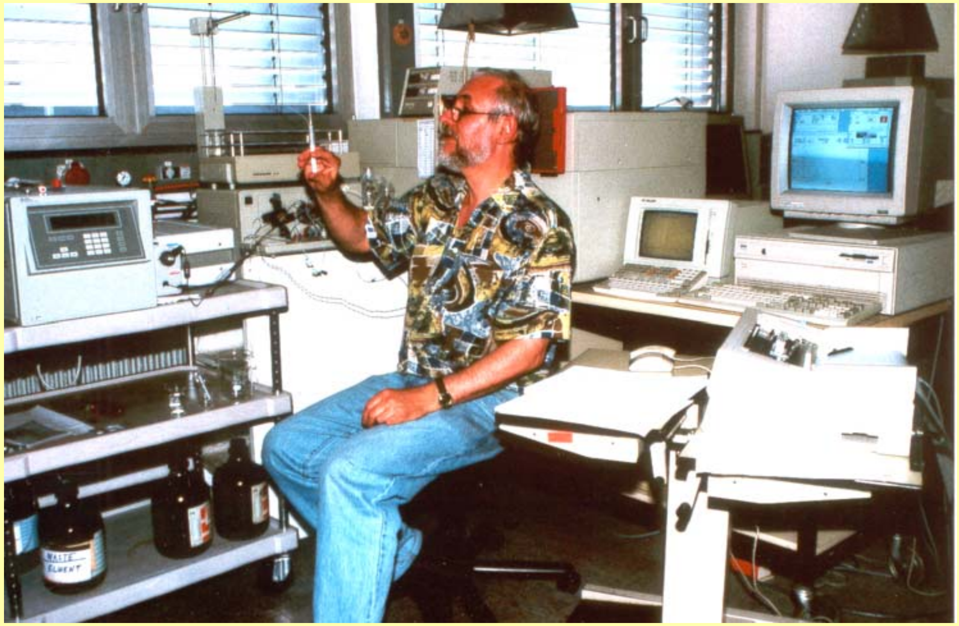
"Fish-eater's" urine





CLOSE-UP of the HPLC-UV-HGAAS-QTA SYSTEM





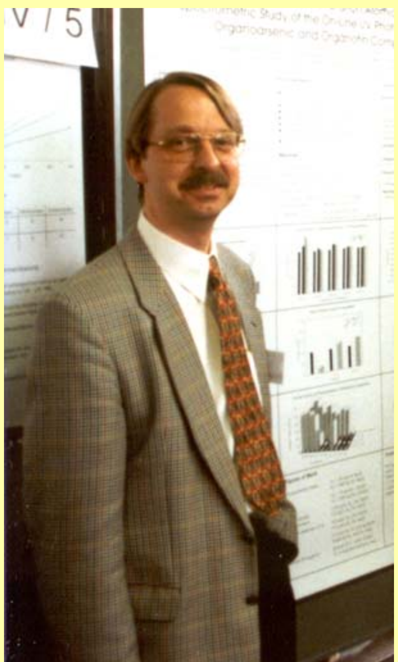
FRUITFUL COLLABORATION
A C K N O W L E D G E D

Germany

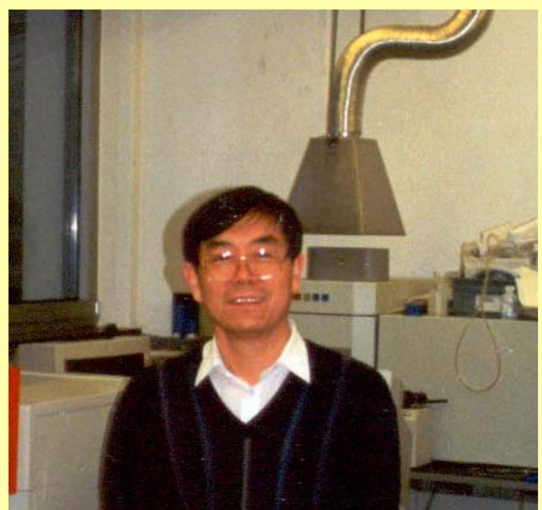
Bodenseewerk
Perkin-Elmer GmbH,
Ueberlingen

Bulgaria

University of Sofia,
Faculty of Chemistry



Michael Sperling



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Bernhard Welz