Pražské analytické centrum inovací
Projekt CZ.04.3.07/4.2.01.1/0002 spolufinancovaný ESF a Státním rozpočtem ČR

Efficient digestion and separation techniques in trace element analysis of difficult sample materials

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VŠCHT
PRAHA

Content

- **Sample decomposition**
  - **High pressure – high temperature wet digestion**
  - **Microwave assisted UV-digestion**
  - **Microwave assisted combustion**
- **Separation and preconcentration**
  - **Volatilization of the analyte**
  - **Liquid-liquid extraxtion**
- **Conclusion**

Analytical Steps

Drying

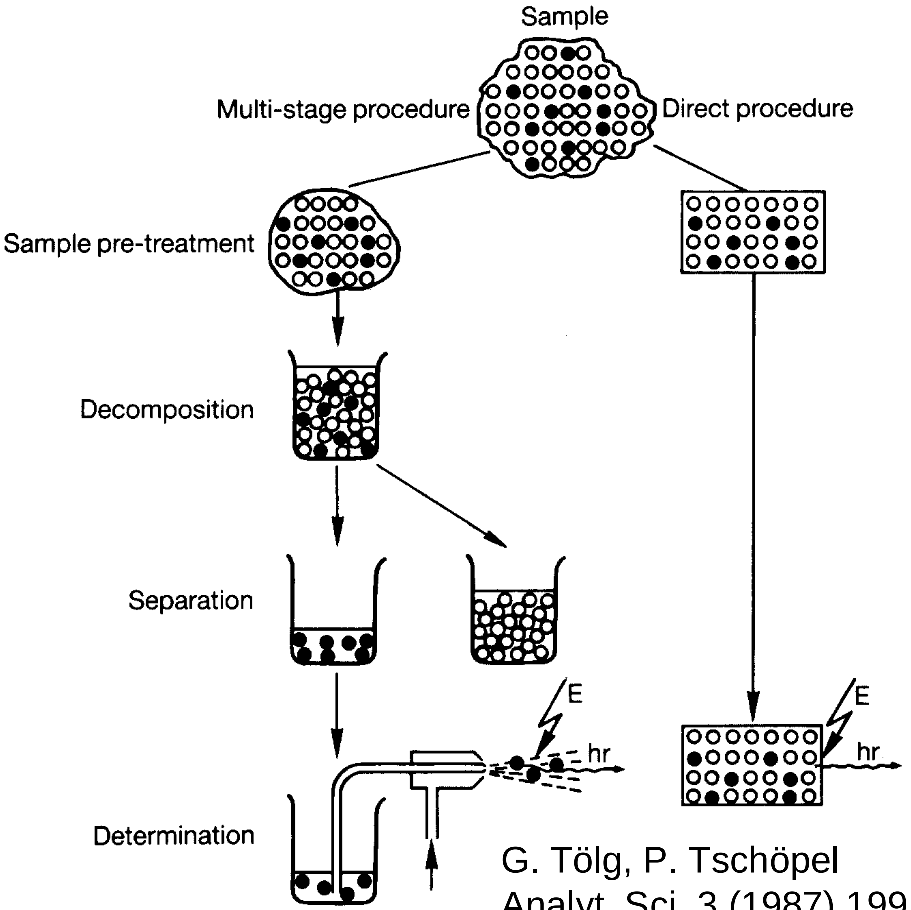
Homogenization

Decomposition

Separation

Preconcentration

Determination

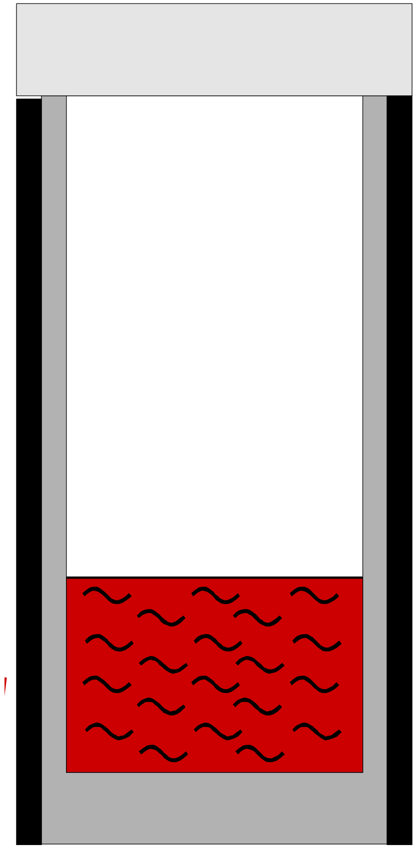


G. Tölg, P. Tschöpel
Analyt. Sci. 3 (1987) 199

Decomposition Methods for Element Analysis – an Overview

- **Fusion**
- **Wet digestion**
  - **In open vessels**
    - **Hot plate techniques with graphite blocks**
    - **Microwave assisted open vessel digestion**
  - **In closed vessels**
    - **Conductive heating → Teflon bombs, High temperature wet digestion**
    - **Microwave heating → Low-, medium- and high-pressure systems**
    - **Microwave assisted UV-digestion**
  - **In flow systems → in development**
- **Combustion**
  - **In open systems**
    - **Dry ashing**
    - **Low temperature ashing with oxygen plasma**
  - **In closed systems**
    - **Flask combustion with oxygen**
    - **Bomb combustion with oxygen**
    - **Microwave assisted combustion**

Advantages of Pressurized Wet Digestion



Advantages

+ **High temperatures beyond the boiling point**
+ **Improved dissolution of inorganic samples**
+ **Powerful oxidation of organic samples just with pure nitric acid**
+ **No element losses**
+ **Low reagent consumption**
+ **Reduced contamination**

Disadvantages

- **Limited sample weight**
- **Complicate vessel construction**
- **Higher equipment costs**

High Temperature Pressurized Wet Digestion

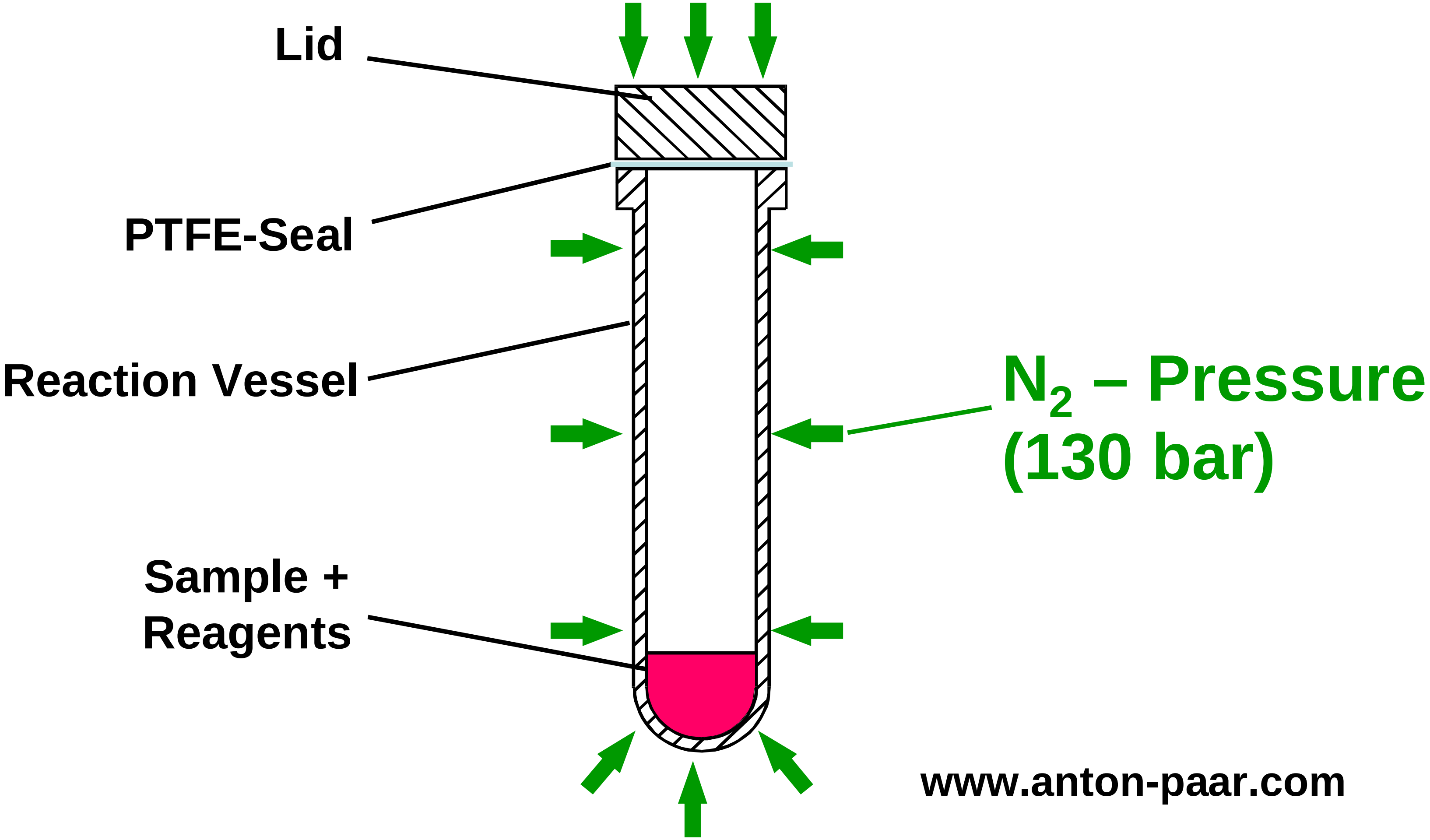
High pressure – high temperature wet digestion in quartz vessels up to 320°C

G. Knapp, A. Grillo, *Am. Lab.* March (1986) 76
G. Knapp, *ICP Inf. Newsl.* 12 (1986) 335
P. Schramel et al, *Fresenius Z. Anal. Chem.* 302 (1980) 6

Actual Version of the High Pressure Asher®

www.anton-paar.com

Principle of the High Pressure Asher®
Pressure Compensation



Lid

PTFE-Seal

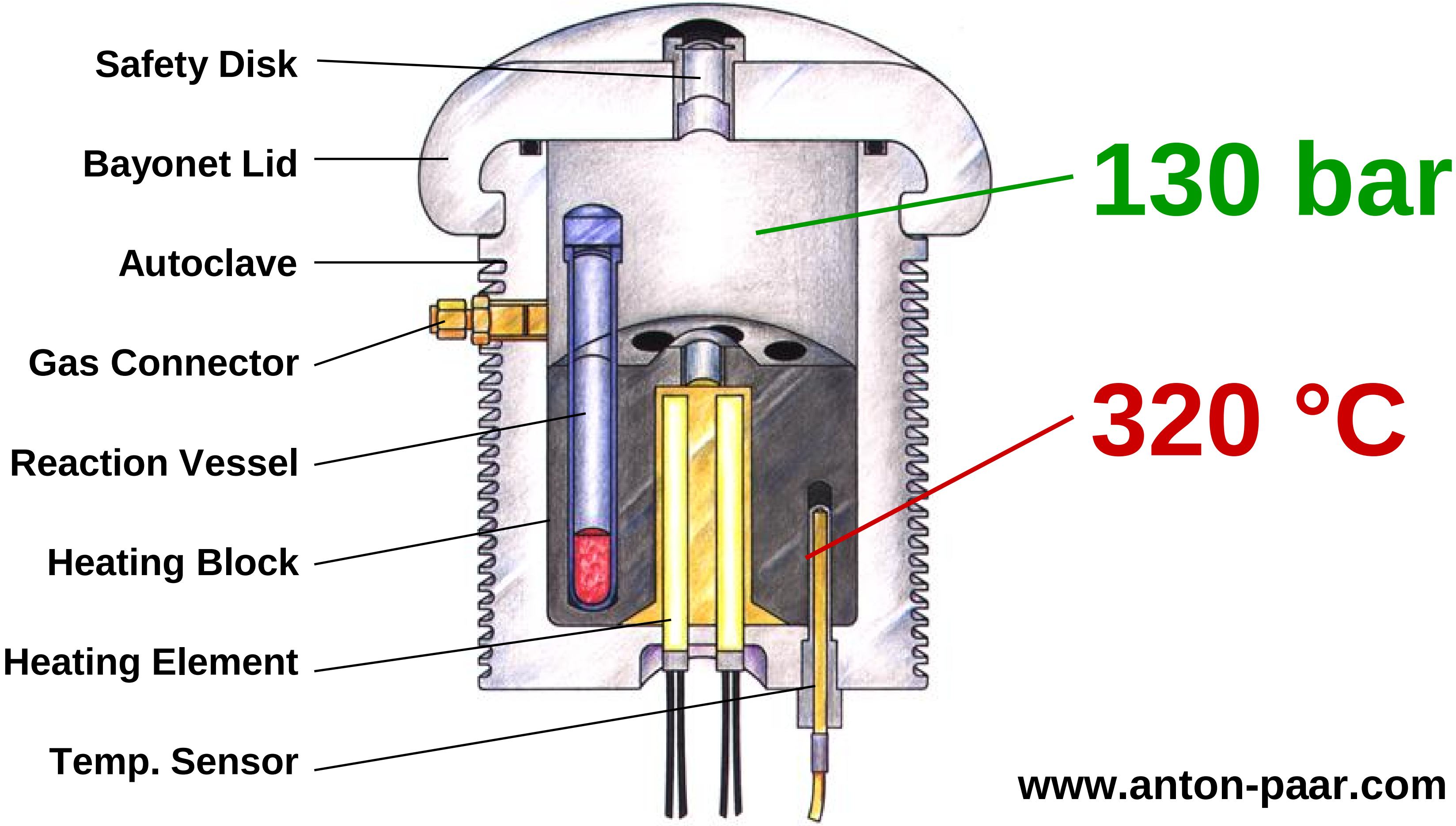
Reaction Vessel

Sample +
Reagents

N_2 – Pressure
(130 bar)

www.anton-paar.com

Scheme of the High Pressure Asher®



www.anton-paar.com

High Pressure Asher® HPA-S
Reaction Vessels

Number & Type of Vessel	max. sample
5 x Quartz 90 mL	1.5 g
7 x Quartz 50 mL	0.8 g
21 x Quartz 15 mL	0.2 g
6 x Glassy Carbon 20 mL	0.2 g

High Pressure Asher® HPA-S

Typical applications of high temperature wet digestion

Maximum Temperature of High Pressure Microwave Systems

~ 280°C

Maximum Temperature of the High Pressure Asher® HPA-S

320°C

High Temperature Wet Digestion ≥ 300°C
Typical Application – As and Se in Foodstuffs

Interlaboratory Comparison

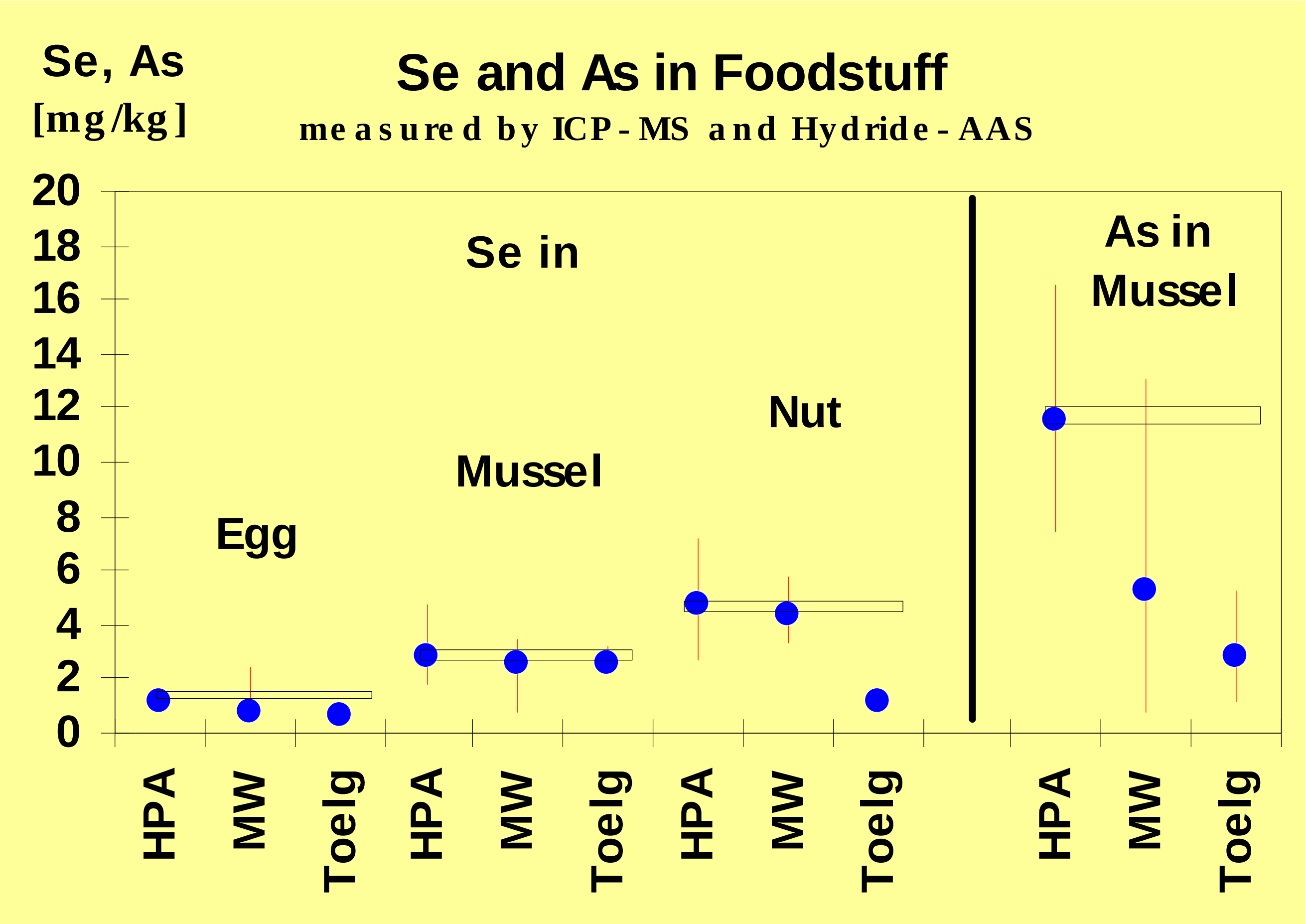
- **Samples: Egg powder, mussel tissue, brazil nut homogenate**
- **25 laboratories in Germany and Switzerland**
- **Microwave, HPA-S and conventional sample preparation**
- **Determination by HG-AAS, GF-AAS and ICP-MS**

Maximum reaction conditions

HPA-S	**320°C / 120bar**
Different microwave systems:	**200°C up to 280°C**
PTFE – bomb (Tölg):	**up to 200°C**

Ref.: P. Fecher, 1997, Interlaboratory comparison

High Temperature Wet Digestion ≥ 300°C
Typical Application – As and Se in Foodstuffs



High Temperature Wet Digestion ≥ 300°C
Typical Application – ICP-MS

Influence of residual carbon on ICP-MS – dilution effect

Sample: Caviar (high fat)

Microwave medium pressure: about 200°C

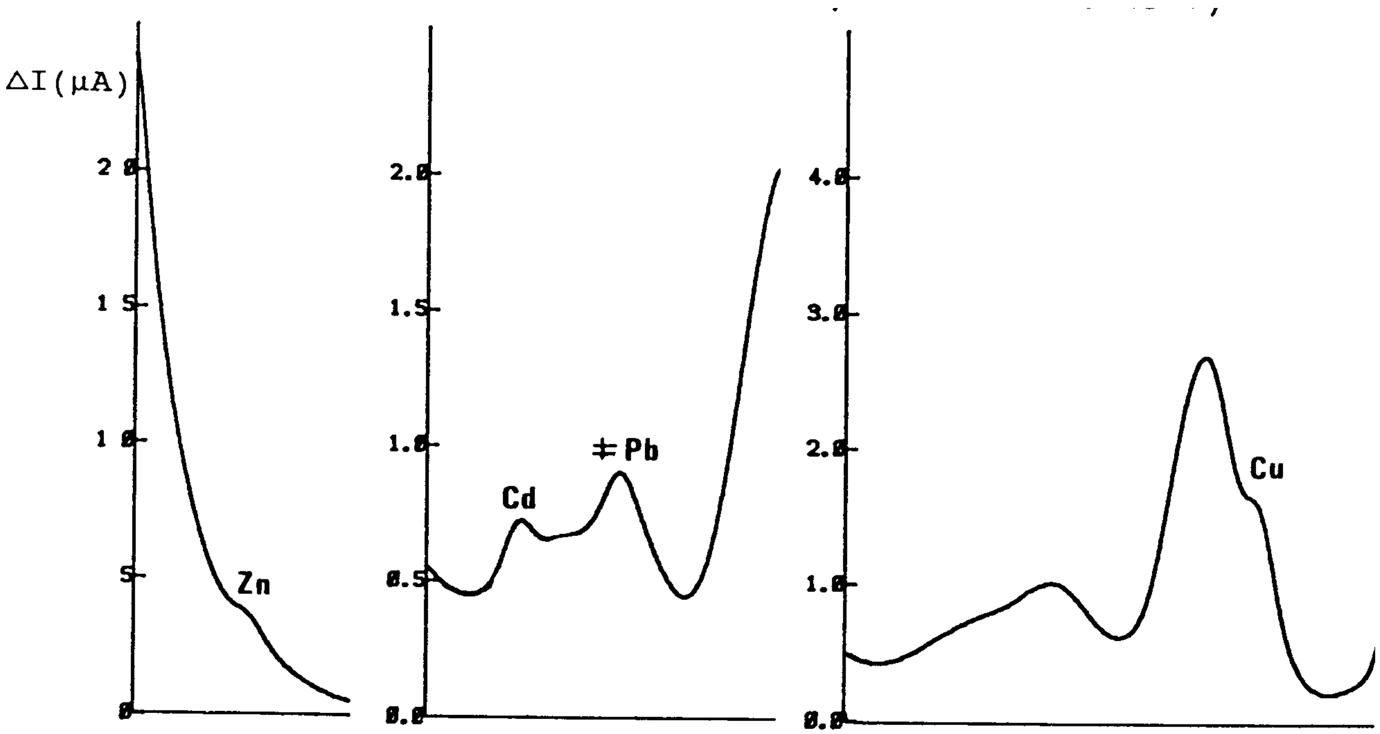
HPA-S method: T = 300°C, t = 120 min.

Element	Microwave		HPA-S	
mg/kg	Dil. 200x	40x	200x	40x
Cu	2.1	---	2.1	2.0
As	1.2	4.2	1.2	1.2
Se	2.7	2.3	2.8	2.7
Cd	0.001	0.006	0.001	0.001
Pb	0.1	0.03	0.1	0.1

Ref.: D. Imhof, Kantonales Labor Zürich

High Temperature Wet Digestion ≥ 300°C
Typical Application – Voltammetry

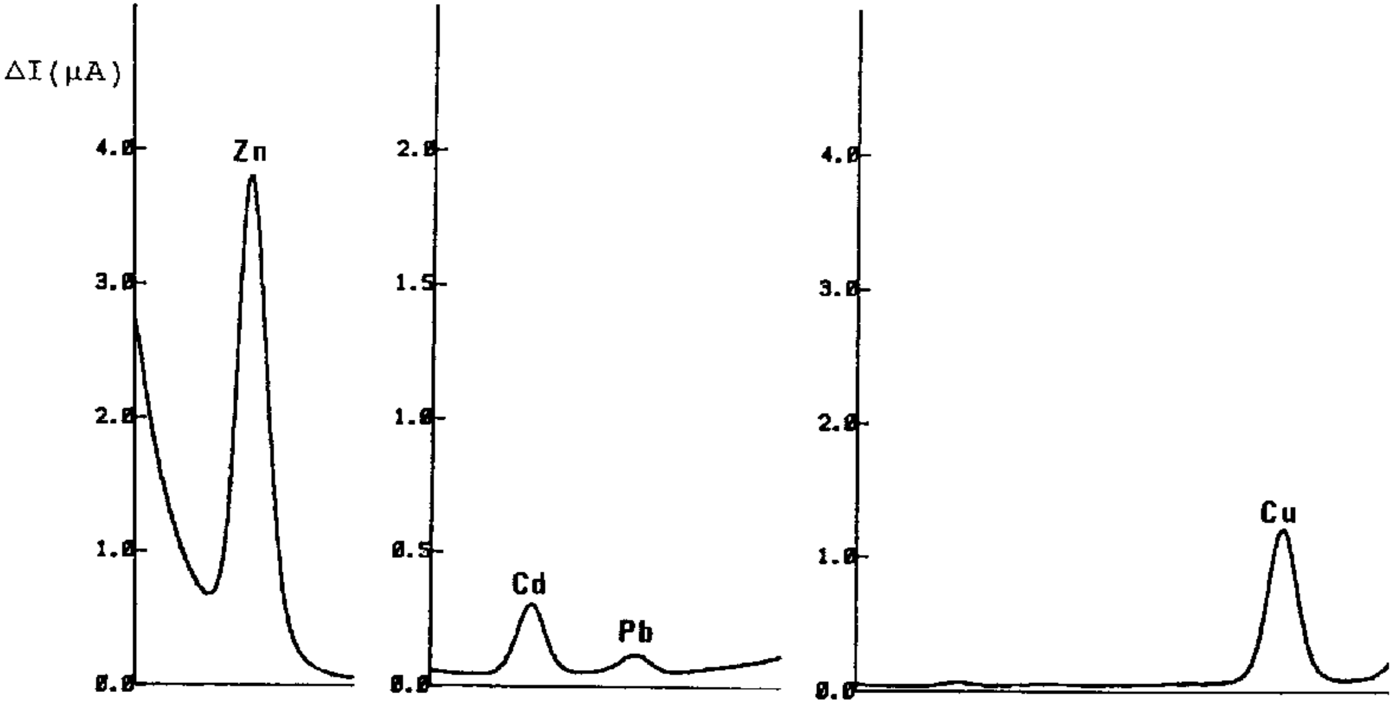
Influence of residual carbon on voltammetry



Sample: liver, decomposed with HNO_3 at 180°C
Ref.: M. Würfels, 1987

High Temperature Wet Digestion ≥ 300°C
Typical Application – Voltammetry

Influence of residual carbon on voltammetry



Sample: liver, decomposed with HNO_3 at 300°C
Ref.: M. Würfels, 1987

High Temperature Wet Digestion ≥ 300°C
Typical Application – Voltammetry

Influence of residual carbon on voltammetry and ICP-MS

Determination of zinc, copper, lead and cadmium in some medicinally important leaves by differential pulse anodic stripping analysis.
Jyothi, Nimmagadda Venkata Vijaya, …. ;
Journal of Trace Elements in Medicine and Biology (2003), 17(2), 79-83.

Trace analysis of platinum in biological samples: a comparison between sector field ICP-MS and adsorptive cathodic stripping voltammetry following different digestion procedures.
Zimmermann, S., ….. ;
Analytica Chimica Acta (2001), 439(2), 203-209.

High Temperature Wet Digestion ≥ 300°C
Typical Application – PGE's

High pressure asher digestion and an isotope dilution-ICP-MS method for the determination of platinum-group element concentrations in chromitite reference materials CHR-Bkg, GAN Pt-1 and HHH.
Paliulionyte, Vaida, ……. ;
Geostandards and Geoanalytical Research (2006), 30(2), 87-96.

Platinum-group element and rhenium concentrations in low abundance reference materials.
Meisel, Thomas, …….. ;
Geostandards and Geoanalytical Research (2004), 28(2), 233-249.

Reference materials for geochemical PGE analysis: new analytical data for Ru, Rh, Pd, Os, Ir, Pt and Re by isotope dilution ICP-MS in 11 geological reference materials.
Meisel, Thomas, …… ;
Chemical Geology (2004), 208(1-4), 319-338.

Concentration and Distribution of Platinum Group Elements (Pt, Pd, Rh) in Airborne Particulate Matter in Frankfurt am Main, Germany.
Zereini, Fathi, …… ;
Environmental Science and Technology (2004), 38(6), 1686-1692.

High Temperature Wet Digestion ≥ 300°C
Typical Application – PGE’s and Cr

A simple procedure for the determination of platinum group elements and rhenium (Ru, Rh, Pd, Re, Os, Ir and Pt) using ID-ICP-MS with an inexpensive on-line matrix separation in geological and environmental materials.
Meisel, Thomas, …. ;
Journal of Analytical Atomic Spectrometry (2003), 18(7), 720-726.

Precise determination of the platinum-group elements and Os isotopic ratios in low-level rock samples.
Brugmann, Gerhard, ….. ;
Yanshi Xuebao (2001), 17(2), 325-331.

Isotope dilution inductively coupled plasma quadrupole mass spectrometry in connection with a chromatographic separation for ultra trace determinations of platinum group elements (Pt, Pd, Ru, Ir) in environmental samples.
Muller, M., ….. ;
Fresenius' Journal of Analytical Chemistry (2000), 368(1), 109-115.

Improved chromium determination in various food matrices using dynamic reaction cell ICP-MS.
Hammer, Daniel, …… ;
Atomic Spectroscopy (2005), 26(6), 203-208.

High Temperature Wet Digestion ≥ 300°C
Typical Application – Tough Polymers

An evaluation of analytical techniques for determination of lead, cadmium, chromium, and mercury in food-packaging materials.
Perring, L., …… ;
Fresenius' Journal of Analytical Chemistry (2001), 370(1), 76-81.

Producing SI-traceable reference values for Cd, Cr and Pb amount contents in polyethylene samples from the polymer elemental reference material (PERM) project using isotope dilution mass spectrometry.
Vogl, J. ….. ;
Accreditation and Quality Assurance (2000), 5(8), 314-324.

Development of an ICP-IDMS method for accurate routine analysis of toxic heavy metals in polyolefins and comparison with results by TI-IDMS.
Diemer, Jurgen, …… ;
Fresenius' Journal of Analytical Chemistry (2000), 368(1), 103-108.

Microwave Assisted Sample Decomposition with Pressurized Oxygen

Requires a microwave system with

- **Quartz vessels for high pressure digestion**
- **Simultaneous pressure measurement in all vessels**
- **Vessel construction with a valve for loading with gas and pressure release after digestion**
- **High sophisticated safety facilities**

▶ **all this features are fulfilled by the Multiwave 3000® developed in cooperation with Anton Paar (www.anton-paar.com)**

MULTIWAVE 3000®

Anton Paar, Graz, Austria; www.anton-paar.com

MULTIWAVE 3000®

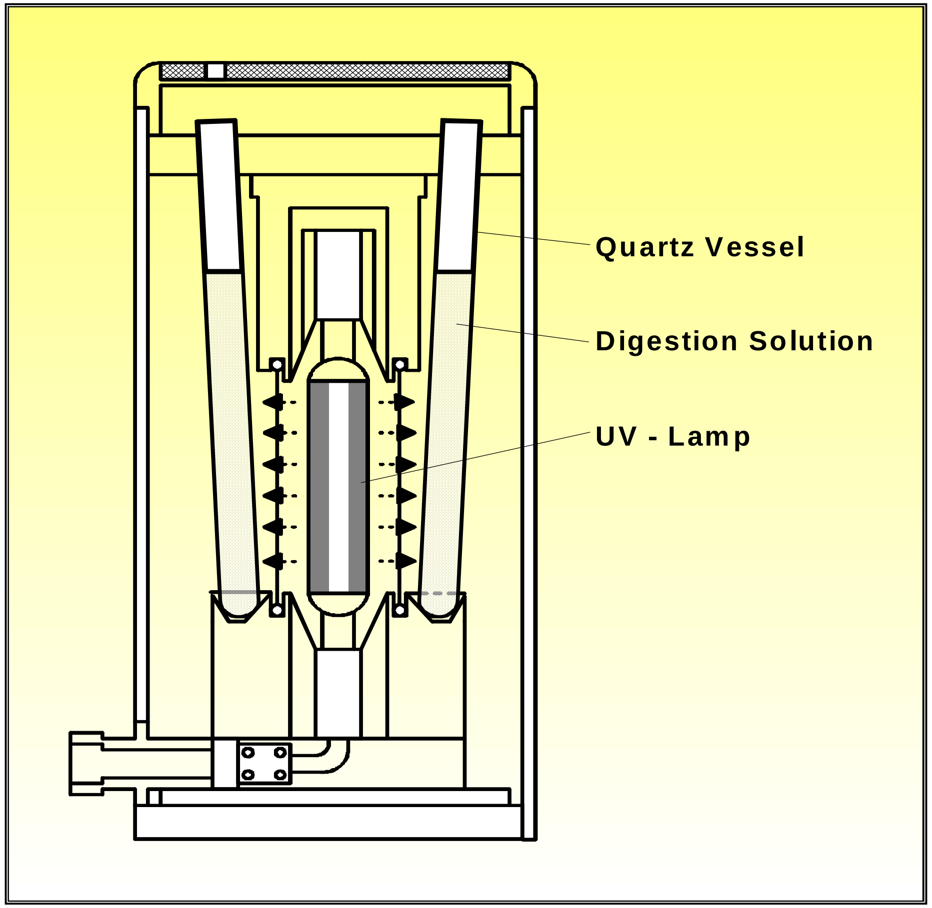
Rotor for Simultaneous Pressure Measurement and Vessels with Connection Valves for Oxygen Loading

Anton Paar, Graz, Austria; www.anton-paar.com/ap/

Special Sample Decomposition Techniques by means of the Multiwave 3000 System

- Microwave assisted UV-digestion
  for ultratrace analysis
- Microwave assisted sample combustion
  for volatile analytes
  and tough sample materials

Conventional UV-Digestion at Low Temperatures <100°C



Electrically driven UV source symmetrically surrounded by by open quartz vessels;

Advantage:
- **Low concentration of HNO_3 and H_2O_2**
- **Low blank levels**

Disadvantage:
- **Long digestion time**
- **Only for samples with low DOC**

M. Kolb, P. Rach, J. Schäfer, A. Wild;
***Fresenius J. Anal. Chem.* 342 (1992) 341**

G. Schwedt, J. Petri;
***Labor Praxis* (1992) 1223**

Microwave-Assisted UV-Digestion at High Temperatures >250°C

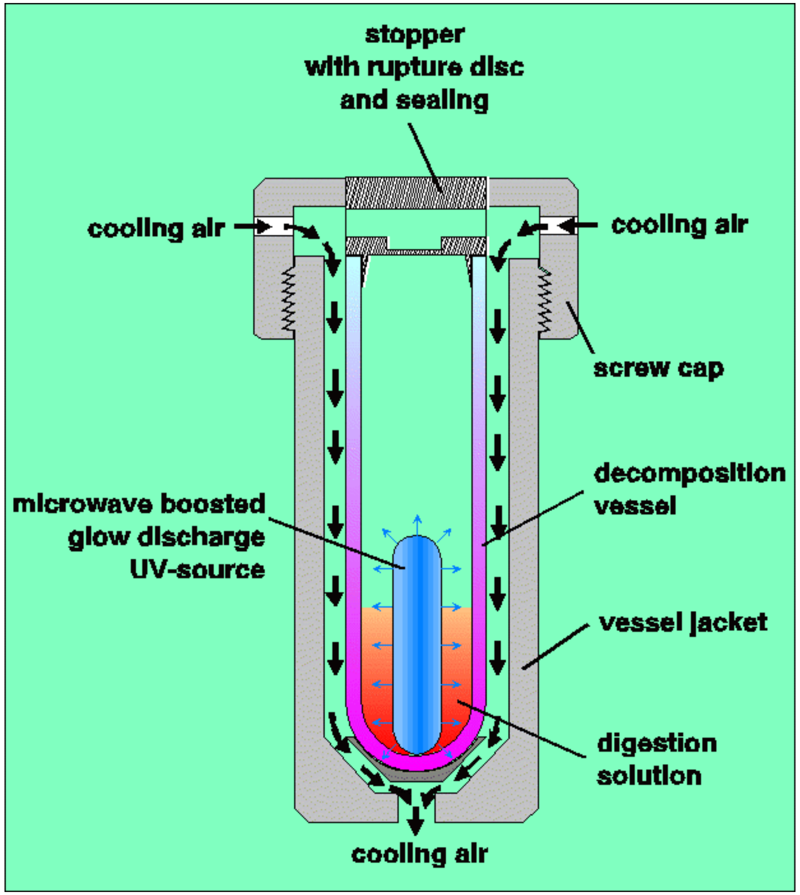
Microwaves as energy source

- **for simultaneous heating of the reaction mixture**
- **for generation of UV radiation**

Dieter Florian, Günter Knapp; Anal. Chem. 2001, *73,* 1515-1520

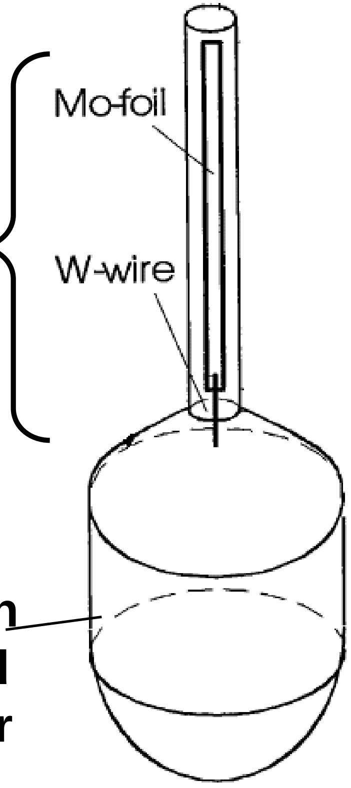
G. Knapp, US Pat. 6,210,538 B1; Apr. 2001

Microwave-Assisted UV-Digestion with H2O2 and Ozone



- UV source directly immersed in digestion solution in closed vessel
- Lamp operation initiated and maintained by the oscillating microwave field
- Immersed UV lamp continuously emits UV irradiation

Microwave-Boosted UV Lamp



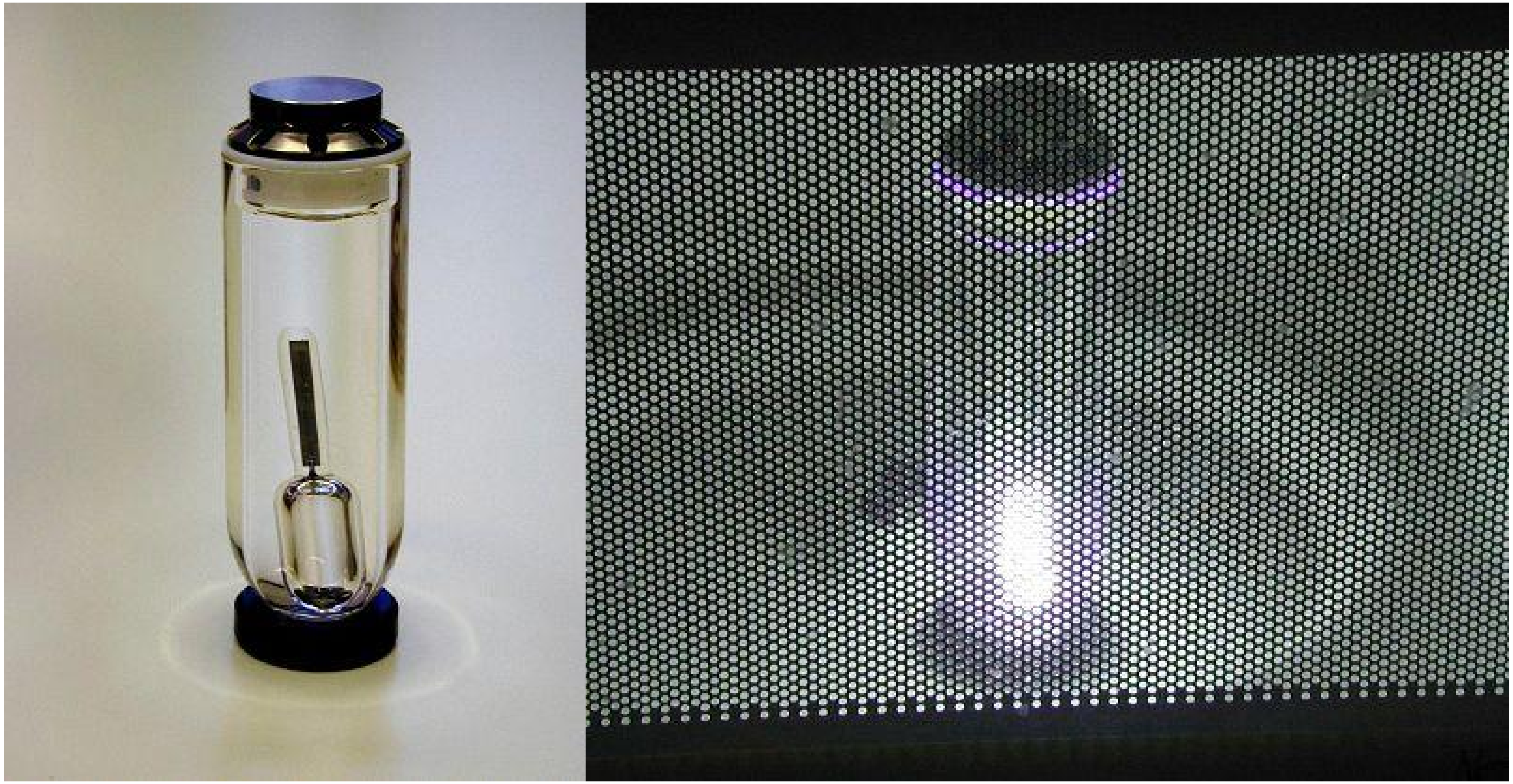
Antenna

Filled with
0.5mg Cd
5 mbar Ar

Schematic of a MWL.

Low pressure
Cd discharge lamp

Microwave-Assisted UV-Digestion



Microwave Assisted UV Digestion Procedure

- **Equipment for high pressure microwave digestion**
  - **Multiwave 3000 (Anton Paar Comp. / Perkin Elmer)**
  - **80 mL quartz vessel**

- **MWL**
  - **Low pressure Cd-discharge lamp (Anton Paar Comp.)**

- **Sample materials**
  - **Phenylalanine, glycine, wheat flour, bovine liver**

- **Procedure**
  - **50 – 100 mg sample + 7 mL H2O + 1 mL H_2O_2 + 0.05 mL HNO3**
  - **vessel pressurized with 20 bar oxygen**
  - **digestion 30 Min. at 80 bar (about 250°C)**

Microwave Assisted UV Digestion Results

Comparison of sample digestion with and without MWL

Sample material	Sample weight [mg]	Residual carbon [%]	
		with lamp	without lamp
Phenylalanine	50	1,9	12,3
Glycine	50	0,9	19,5
Bovine liver	100	8,2	24,6
Wheat flour	100	0,9	5,3

Microwave Assisted UV Digestion Advantages

- **Acceleration of the degradation process owing to high reaction temperature (250 – 280 °C)**
- **Best efficiency of generated UV-radiation (immersion system)**
- **Enhancement of reactivity due to simultaneous microwave and UV-irradiation**
- **Oxidation with H_2O_2 and Ozone**
- **Suitable for samples with high DOC (5000-7500 mg/l carbon)**
- **Digestion technique for ultra trace analysis**

Special Sample Decomposition Techniques by means of the Multiwave 3000 System

- Microwave assisted UV-digestion
  for ultratrace analysis

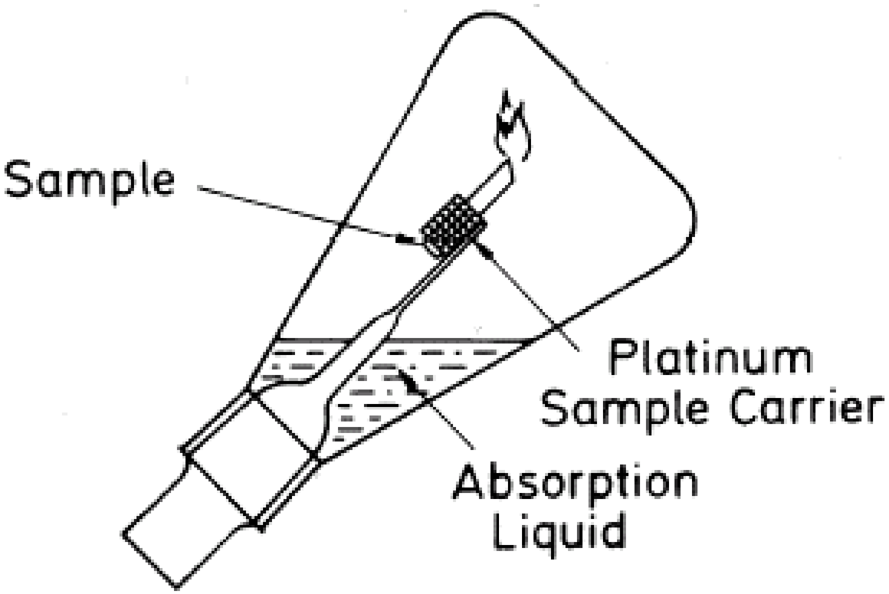
- Microwave assisted sample combustion
  for volatile analytes
  and tough sample materials

Combustion Systems

Combustion of organic samples in closed systems is state of the art

- **for the determination of volatile nonmetals**
- **for decomposition of tough organic materials like cole, coke, some polymers, etc.**

Schöniger Flask Combustion

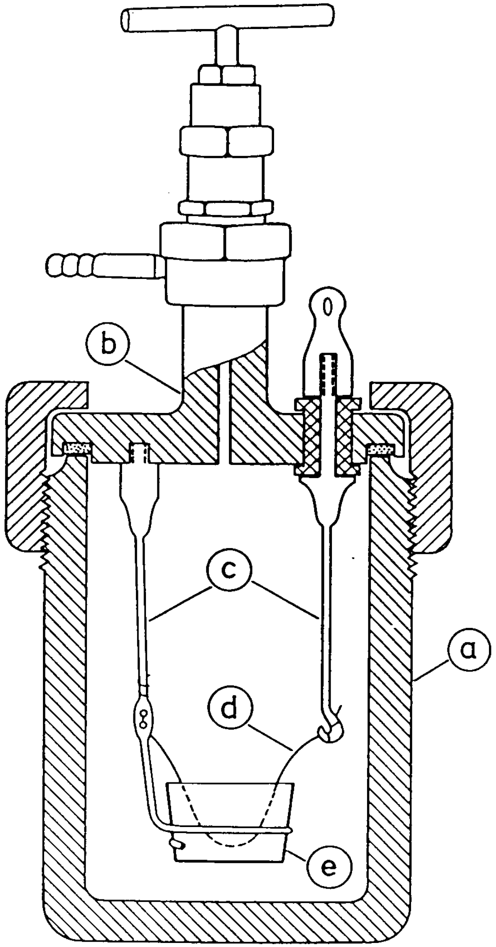


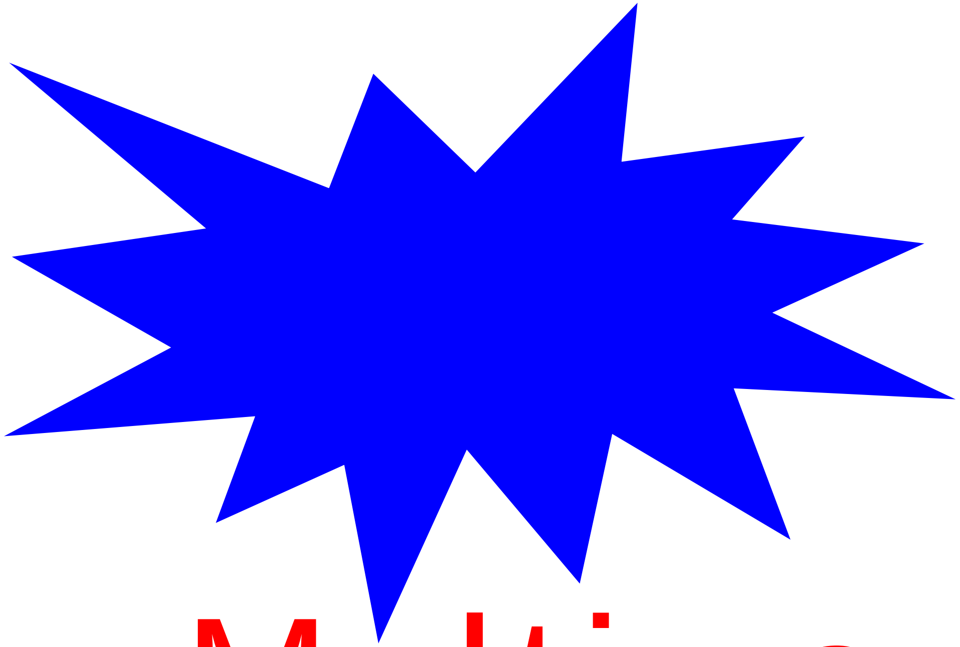
Oxygen Bomb Combustion

- **a) Steel bomb**
- **b) Lid with valve**
- **c) Electrodes**
- **d) Ignition wire**
- **e) Sample holder**

e.g. 500 mL O_2-Bomb

Parr Instrument, USA





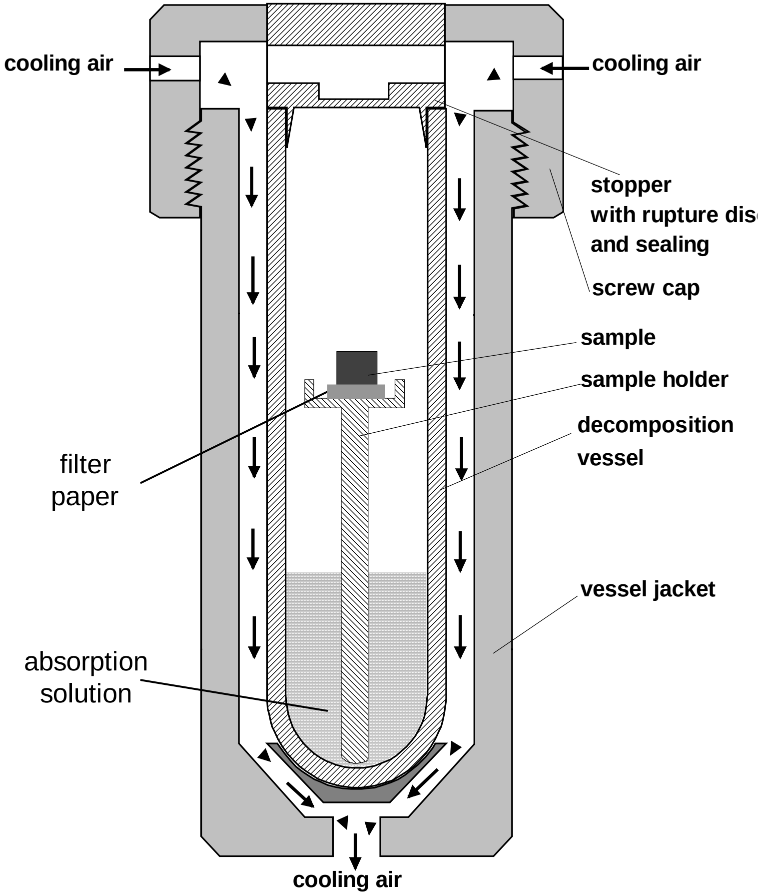
Multiwave 3000

Microwave assisted oxygen combustion

E.M. Flores, J.S. Barin, J.N. Paniz, J.A.Medeiros, G. Knapp; Anal. Chem. **2004**, *76*, 3525

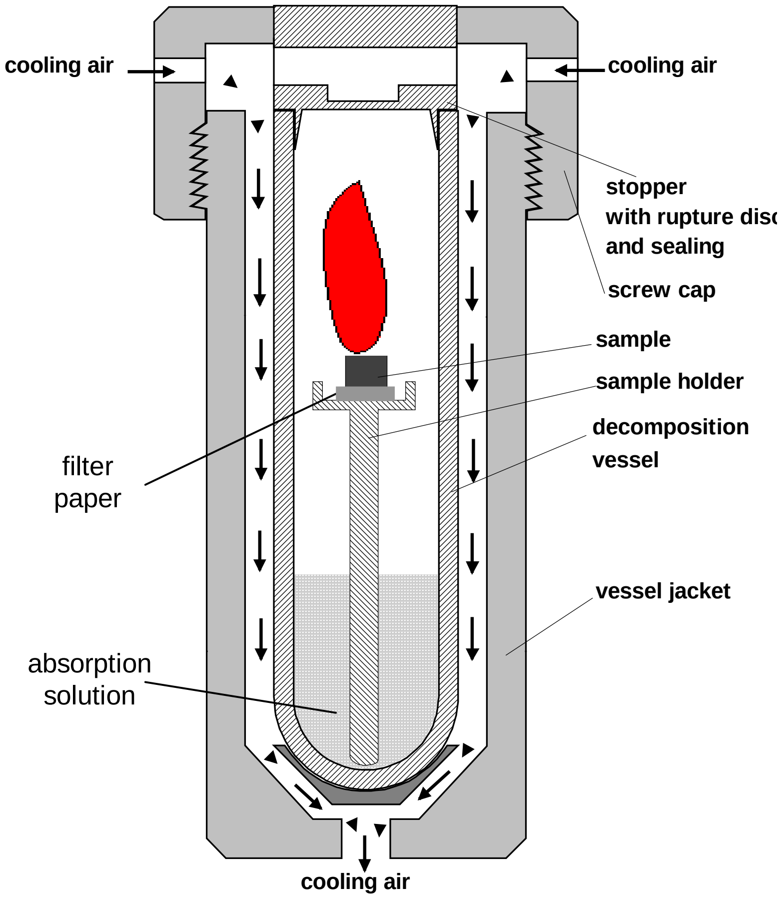
E.M. Flores, M.F. Mesko, D.P. Moraes, J.F. Pereira, P.A. Mello, J.S. Barin, G. Knapp; Anal. Chem. **2008**, *80*, 1865

Microwave Assisted Oxygen Combustion



- **Multiwave 3000**
- **80 mL quartz vessels XQ80**
- **0.3 - 0.4 g organic organic sample pressed to a tablet**
- **10 ml absorption solution (mobile phase of ion chromatography)**
- **Put sample on impregnated filter paper (1 drop of 50% NH_4NO_3)**
- **Load with 20 bar oxygen**

Microwave Assisted Oxygen Combustion



- **Ignite impregnated filter by means of microwave power**
- **Program:**
    - **1400W / 1 min**
    - **Cool 15 min at level 2**
- **Up to 8 combustions simultaneously**
- **Absorption time 1 hour**
- **Analysis of absorbed ions**
    - **IC for Cl^-, Br^-, I^- and S (sulfate)**
    - **Ion selective electrode for F^-**

Microwave Assisted Oxygen Combustion Results

	Cl (µg/g)		S (µg/g)	
	Certified	measured	certified	measured
BCR 60 Aquatic plant	10	9.3 ± 0.8	5.2	5.0 ± 0.4
BCR 61 Aquatic plant	2.3	2.3 ± 0.3	2.3	2.1 ± 0.3
BCR 63 Milk powder	9.94 ± 0,3	10.1 ± 1.0		
BCR 100 Peach leaves	1.49 ± 0.06	1.55 ± 0.1	2.69 ± 0.04	2.7 ± 0.1
BCR 186 Pig kidney	9.4	9.5 ± 0.5		

MAC – Results

BCR 151 Milk powder	Element	Certified (µg/g)	Measured (µg/g)
(C~50%)	Ca	-	12890±191
	Cu	5,23±0,08	5,26±0,21
	Fe	50,1±1,3	48±0,3
	Hg (ng/g)	101±10	104±7
	Mg	-	1272±22
	Mn	(0,223)	0,264±0,01
	Na	-	5467±195
	Pb	2,002±0,026	1,97±0,22
	Zn	(50)	48,5±4
	DOC	-	< 0,2%

MAC – Results

BCR 185 Bovine liver	Element	Certified (µg/g)	Measured (µg/g)
(C~50%)	Ca	(131)	151±5
	Cd (ng/g)	298±25	325±22
	Cu	189±4	165±2,6
	Fe	214±5	195±2,5
	Hg (ng/g)	44±3	45±2
	Mg	(634)	622±12
	Mn	9,3±0,3	9,2±0,14
	Pb	11700	12170±223
	Zn	142±3	146±3,5
	DOC	-	< 0,2%

Microwave Assisted Oxygen Combustion Demonstration

- Combustion of 0.3 g Coal
- MULTIWAVE 3000®
- 80 mL Quartz vessel
- Loaded with 20 bar oxygen

[redacted]

Separation and Preconcentration

Volatilization

- **hydride generation**
- **halogen volatilization**

Liquid-liquid extraction

Coprecipitation

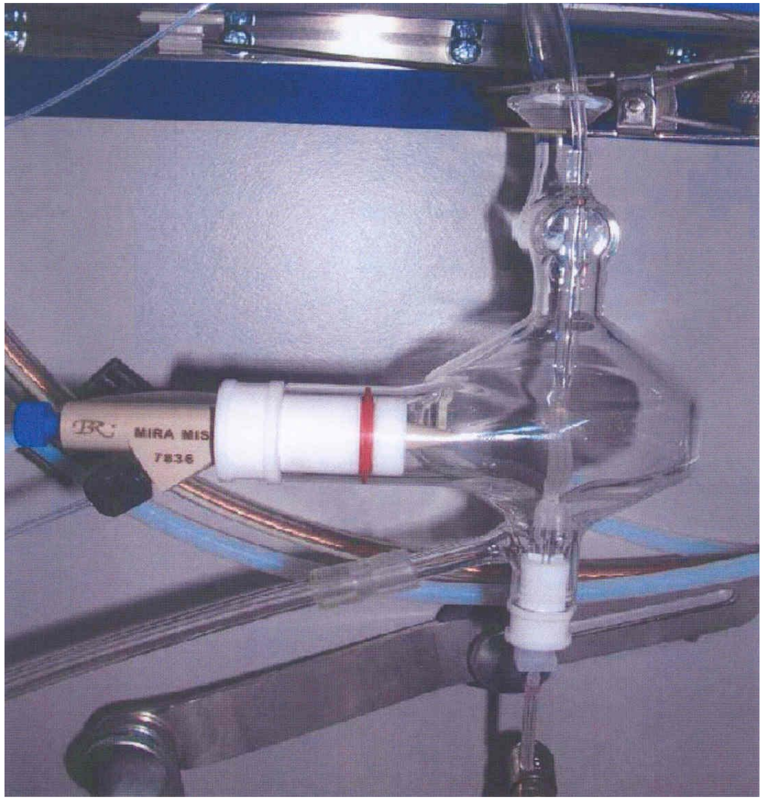
Sorption

- **of ions**
- **of metal-chelates**
- **of organic compounds**

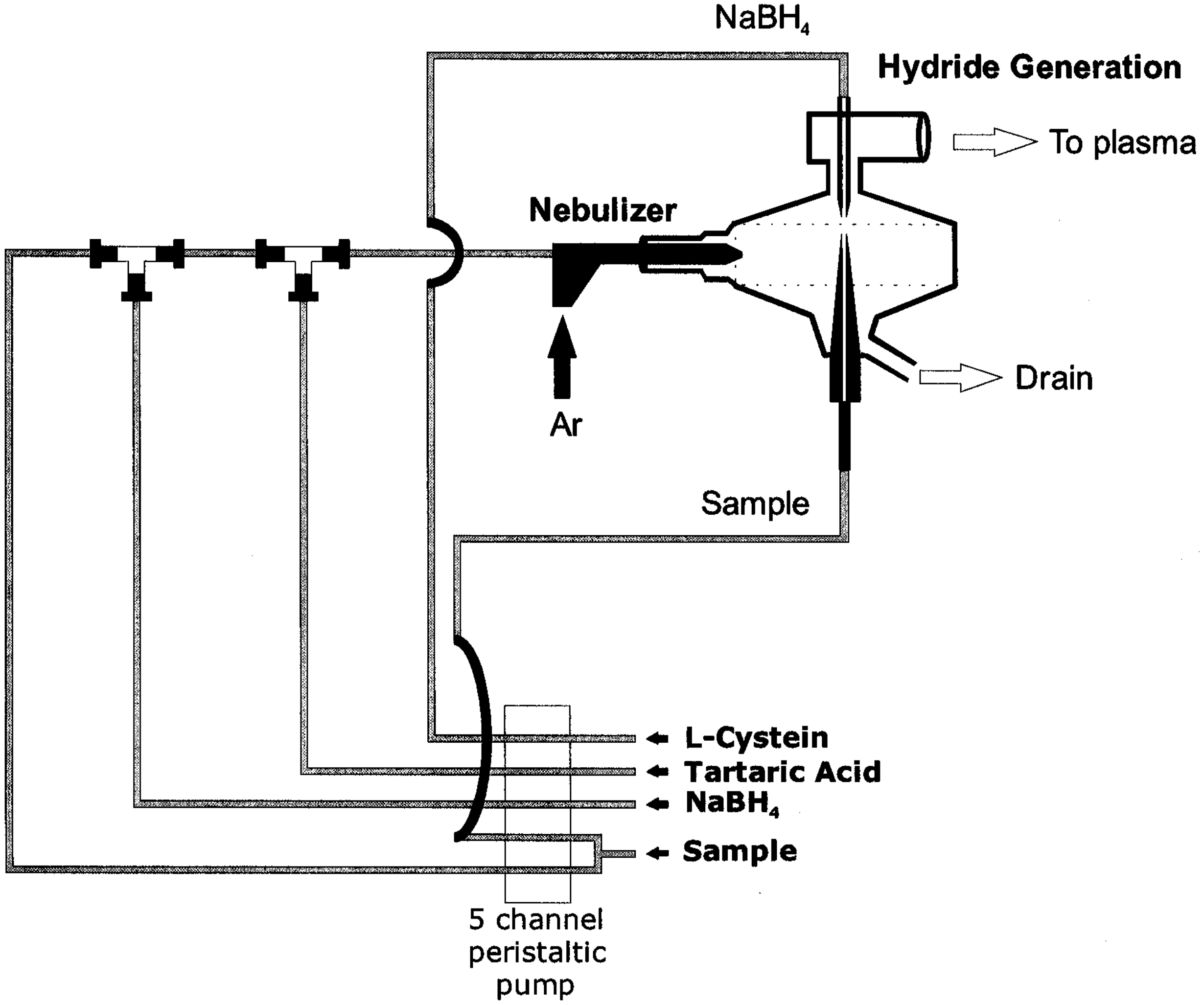
Separation and Preconcentration

Multimode sample introduction system − MSIS for hydride generation and nebulization

R.L.J. McLaughlin, I.D. Brindle U.S. Pattent no. 6.891.605



Separation and Preconcentration – MSIS



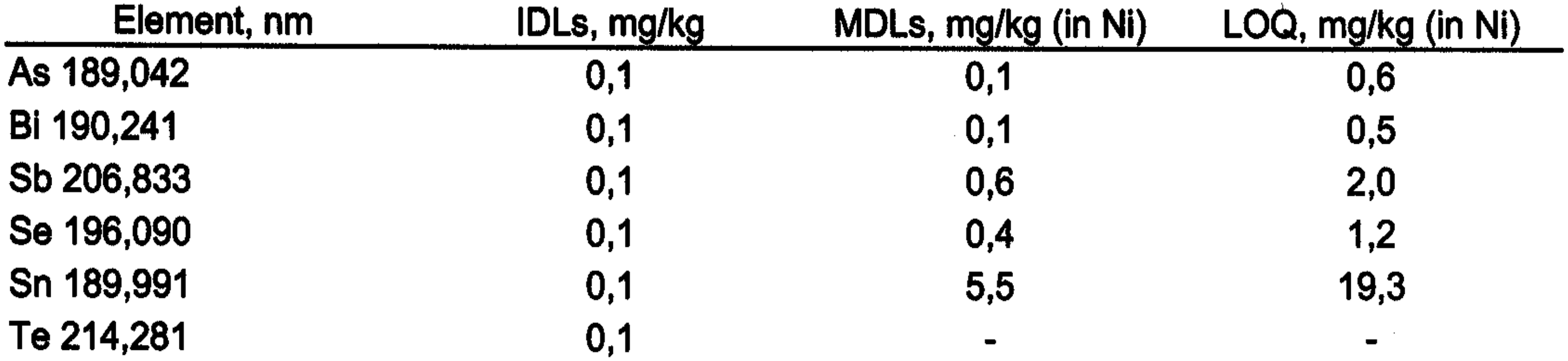
Separation and Preconcentration – MSIS

Determination of hydride elements in high alloy steels and nickel alloys

Plasma power	**1300 W**
Cooling gas	**15,0 L min^{-1}**
Nebulizer gas	**0,75 L min^{-1}**
Nebulizer	**Mira Mist**
$NaBH_4$	**30 g L^{-1}**
Tartaric acid	**400 g L $^{-1}$**
L-Cystein	**400 g L^{-1}**

Separation and Preconcentration – MSIS

Determination of hydride elements in high alloy steels and nickel alloys

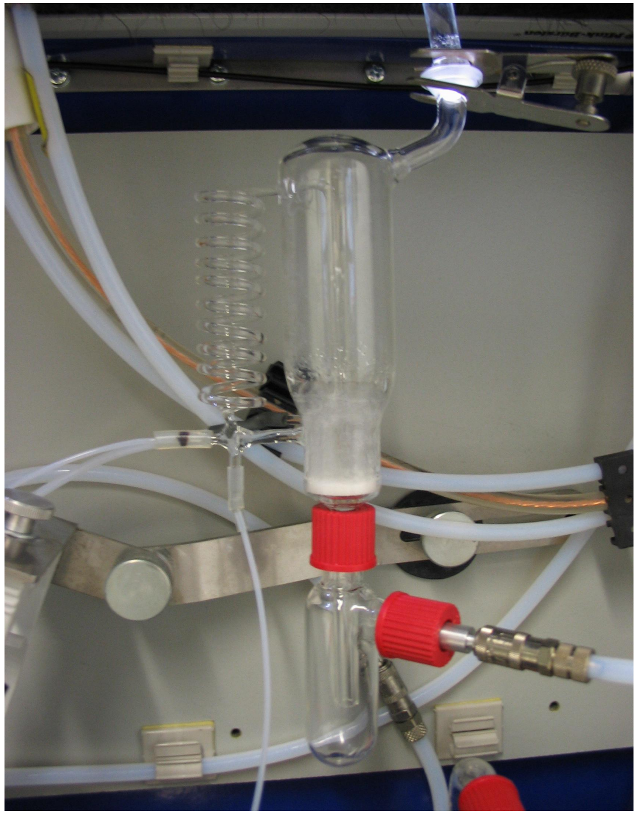


Element, nm	IDLs, mg/kg	MDLs, mg/kg (in Ni)	LOQ, mg/kg (in Ni)
As 189,042	0,1	0,1	0,6
Bi 190,241	0,1	0,1	0,5
Sb 206,833	0,1	0,6	2,0
Se 196,090	0,1	0,4	1,2
Sn 189,991	0,1	5,5	19,3
Te 214,281	0,1	-	-

Separation and Preconcentration

Volatilization of halogens

Determination of Cl, Br and I with ICP-OES



Oxidation of Chloride, Bromide and Iodide to the Elements

Reagent	E° (V)	Oxidation to the element
$K_2S_2O_8$	+2,12	$S_2O_8^{2-} + 2\ X^- + 2\ H^+ \Rightarrow X_2 + 2\ HSO_4^-$
H_2O_2	+1,77	$H_2O_2 + 2\ X^- + 2\ H^+ \Rightarrow X_2 + 2\ H_2O$
PbO_2	+1,69	$PbO_2 + SO_4^{2-} + 4\ H^+ + 2\ X^- \Rightarrow X_2 + PbSO_4 + 2\ H_2O$
$KMnO_4$	+1,51	$2\ MnO^{4-} + 10\ X^- + 16\ H^+ \Rightarrow 5\ X_2 + 2\ Mn^{2+} + 8\ H_2O$
$KBrO_3$	+1,42	$2\ BrO_3^- + 10\ X^- + 12\ H^+ \Rightarrow 5\ X_2 + Br_2 + 6\ H_2O$
$K_2Cr_2O_7$	+1,23	$Cr_2O_7^{2-} + 6\ X^- + 14\ H^+ \Rightarrow 3\ X_2 + 2\ Cr^{3+} + 7\ H_2O$
$NaNO_2$	+0,96	$2\ NO_2^- + 2\ I^- + 4H^+ \Rightarrow I_2 + 2\ NO + 2\ H_2O$
	+0,54	$I_2 + 2\ e^- \Rightarrow 2\ I^-$
	+1,07	$Br_2 + 2\ e^- \Rightarrow 2\ Br^-$
	+1,36	$Cl_2 + 2\ e^- \Rightarrow 2\ Cl^-$
	(+2,87	$F_2 + 2\ e^- \Rightarrow 2\ F^-$)

References:
1. T. Nakahara, T. Nishida, Spectrochim.Acta B, **53**, 1998, 1209-1220;
2. D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, CRC Press Inc., Boca Raton, Florida (1993);

Reduction of Iodate (IO_3^-) to the Element with H_2O_2

$H_2O_2 \Rightarrow 2\ H^+ + O_2 + 2\ e^-$ **E° = +0,68 V**

$2\ IO_3^- + 10\ e^- + 12\ H^+ \Rightarrow I_2 + 6\ H_2O$ **E° = +1,19 V**

Reference:
D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics CRC Press Inc.,
Boca Raton, Florida (1993)

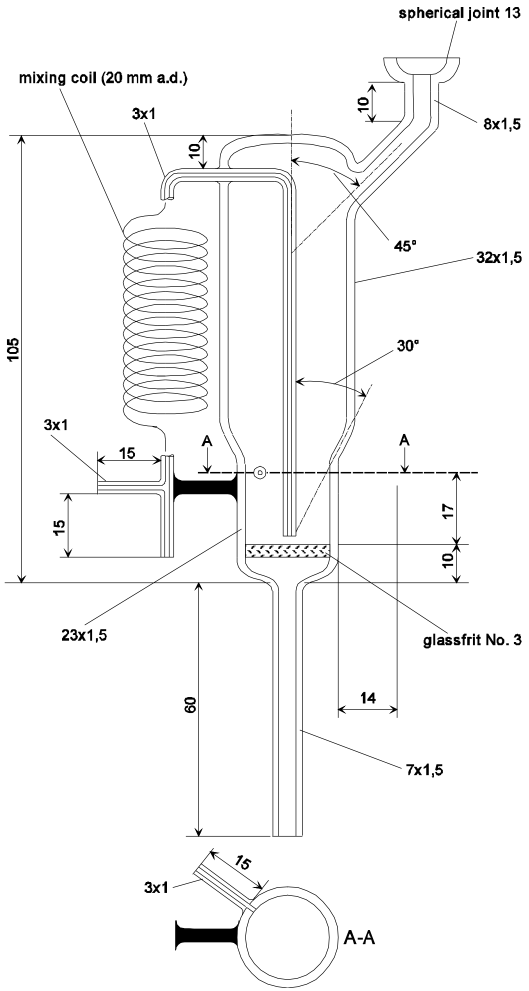
Separation of the Volatile Halogens by means of a Gas-Liquid-Separator

- **Advantage**
  - 10 to 50 times higher transport efficiency than a pneumatic nebulizer
  - no matrix constituents interfere with the measurement
- **Disadvantage**
  - memory effects
  - extended rinse time

Optimum Gas-Liquid-Separator

Optimized gas-liquid-separator for our purposes:

- **Optimized size and diameters to prevent foaming**
- **Optimized frit ⇒ pore width, hydrophobic surface; the glass frit is silanated to prevent penetration of the reaction solution, which leads to memory effects and increased rinse time.**
- **Attached reaction coil for oxidation or reduction**



Optimum Gas-Liquid-Separator

Influence of the pore size of the frit:

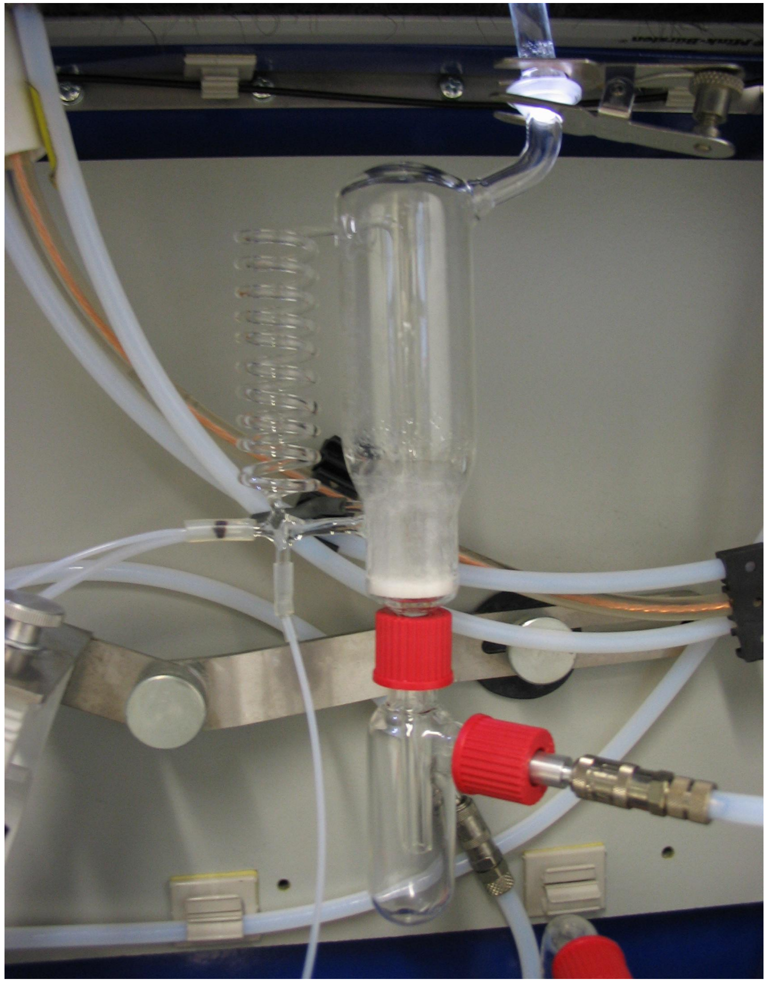
Porosity	Pore width	Max. gas flow without interfering aerosol formation
G2	40-90 µm	
G3	15-40 µm	0.9 L/min.
G4	9-15 µm	0.5 L/min.

- **the lower the pore width the higher the transport efficiency of the halogens;**

- **the lower the pore width the higher the formation of aerosols with transportation of matrix constituents into the plasma;**

An Optimum Gas-Liquid-Separator

Gas-liquid-separator connected to a SPECTRO CIROS VISION ICP-emission spectrometer;



Measurement of Cl^- and Br^- with ICP-OES Spectro Ciros Vision

Chloride and bromide are measured with the same instrument parameters and the same oxidation reaction

Instrument parameters:		**Wavelength: Cl 134.724, Br 154.065**
		Plasma power 1450W
		Pump speed 3
		Cooling gas 12L/min
		Plasma gas 0.9L/min
		Nebulizer gas 0.4L/min
Peristaltic pump:		**Sample tube orange/orange (3.3mL/min)**
		Reagent tube yellow/green (0.6mL/min)
Sample solution 6M H_2SO_4		
Reagent 0.1M $KMnO_4$		
LOD	**Cl 0.3µg/L**	**Br 0.5µg/L**
LOQ	**Cl 1.0µg/L**	**Br 2.0µg/L**

Measurement of I^- and IO_3^- with ICP-OES Spectro Ciros Vision

Iodide and iodate are measured with different reagents.

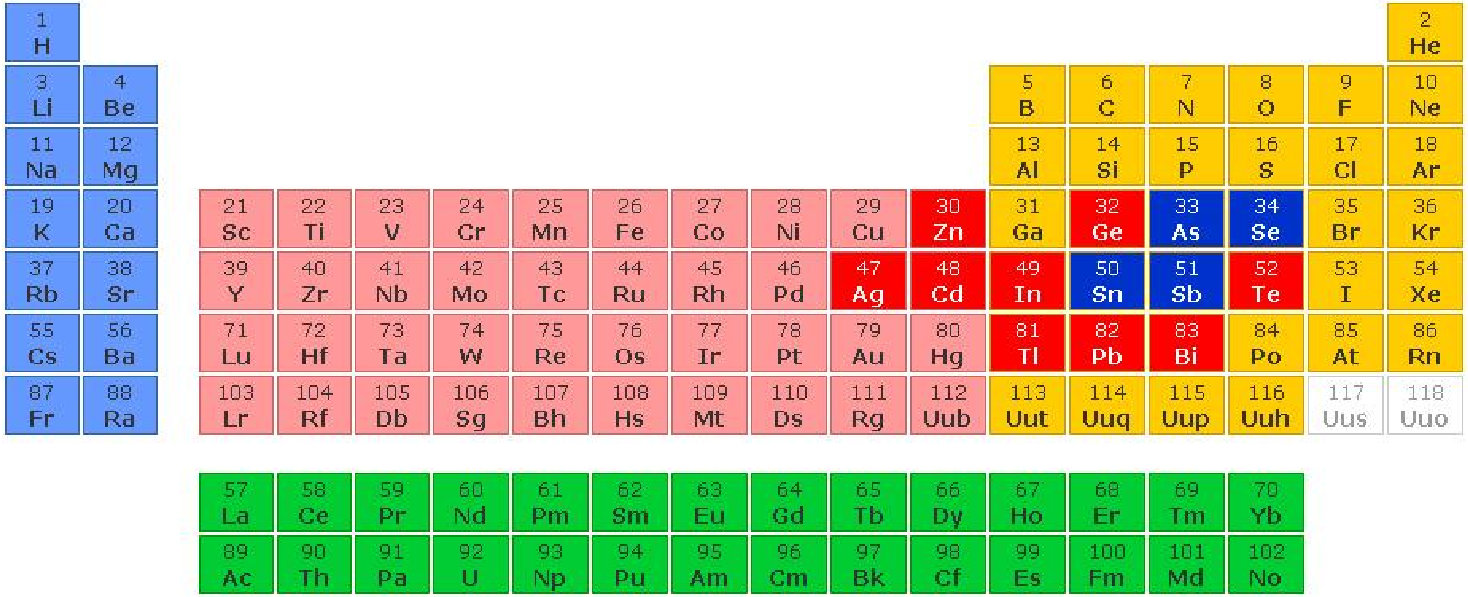
Instrument parameters:	**Wavelength: I 178.276** **Plasma power 1450 W** **Pump speed 4** **Cooling gas 12L/min** **Plasma gas 0.9L/min** **Nebulizer gas 0.6L/min**	
Peristaltic pump:	**Sample tube orange/orange (3.3mL/min)** **Reagent tube yellow/green (0.6mL/min)**	
	Iodide	**Iodate**
Sample solution	**0.1M HNO_3**	**2M HNO_3**
Reagent	**$NaNO_2$ 0.05M + HNO_3 0.5M**	**H_2O_2 30%**
LOD	**I 0.2 µg/L**	**I 0.5 µg/L**
LOQ	**I 0.7 µg/L**	**I 2.0 µg/L**

Separation and Preconcentration

Automated liquid-liquid extraction of heavy metals

Introduction

- **Determination of trace heavy metal impurities (< 10 mg/kg)**



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

- **Matrix: High alloy steel and Ni super alloy**
- **Matrix composition varies: eg. <1 - >50% Ni; <1 - >20% Cr**

Introduction: Analyte Extraction

- ***Ag, Bi, Cd, Pb, Sb, Se, Sn, Zn*** **form Iodide complexes → extraction with organic solvents**

- **Reagent: KI in large excess**

- **Organic extractions: Determination of the analyte concentration via ICP-OES* or F-AAS****

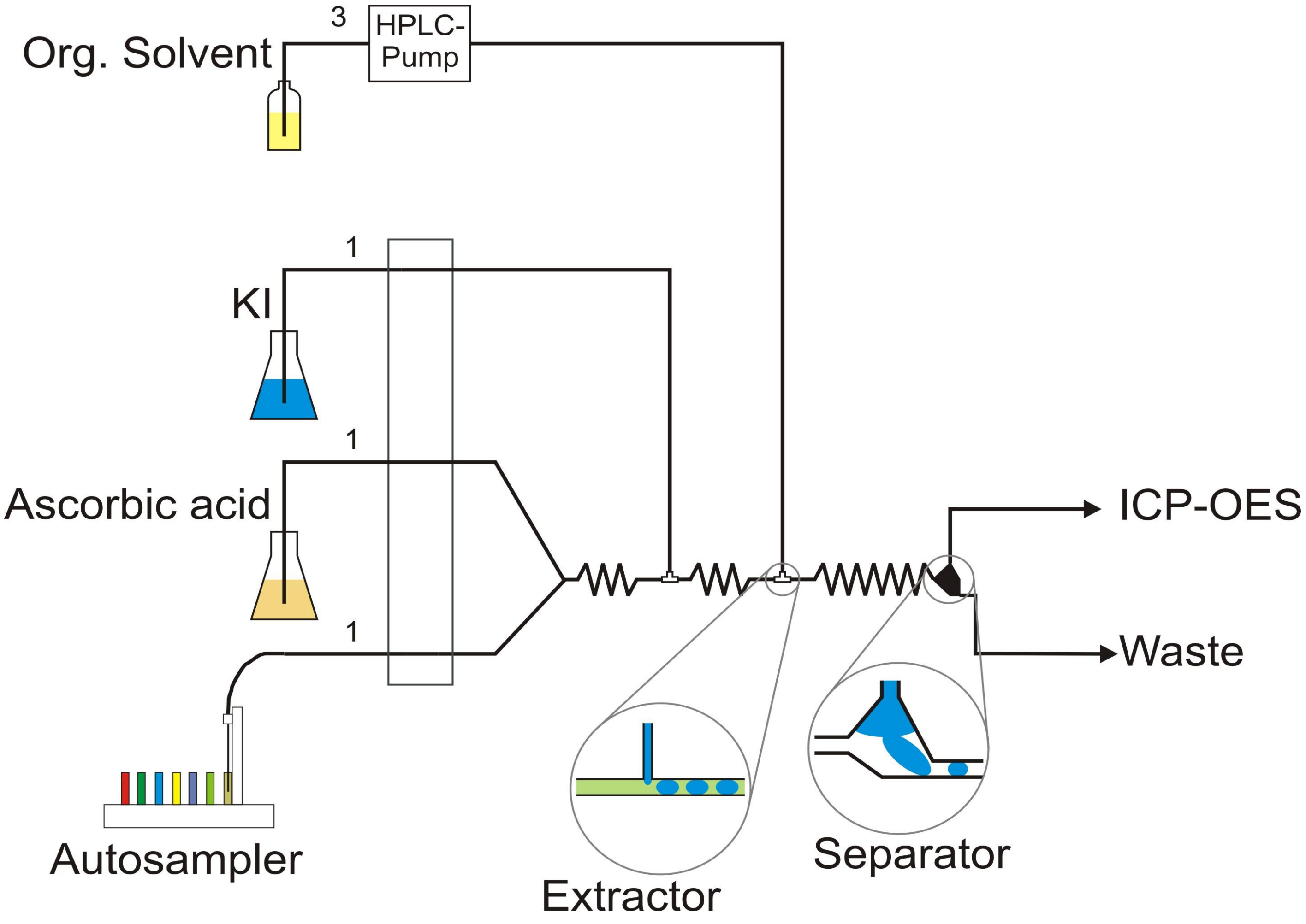
* Ciros Vision EOP, Spectro

** ContrAA, **Continuum source AAS, www.analytic-jena.com**

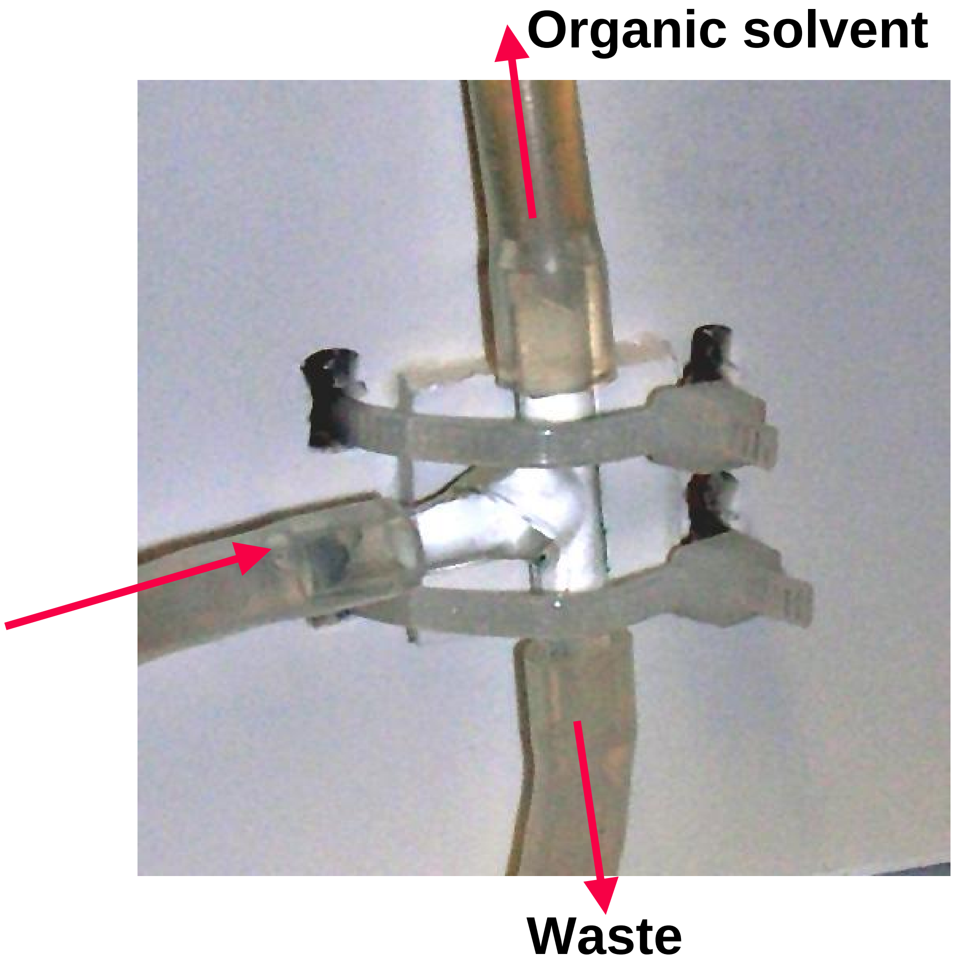
Automated liquid liquid extraction

- **Flow extraction:** Constant flow of samples and reagents
- **Batch extraction:** “Automated separating funnel”

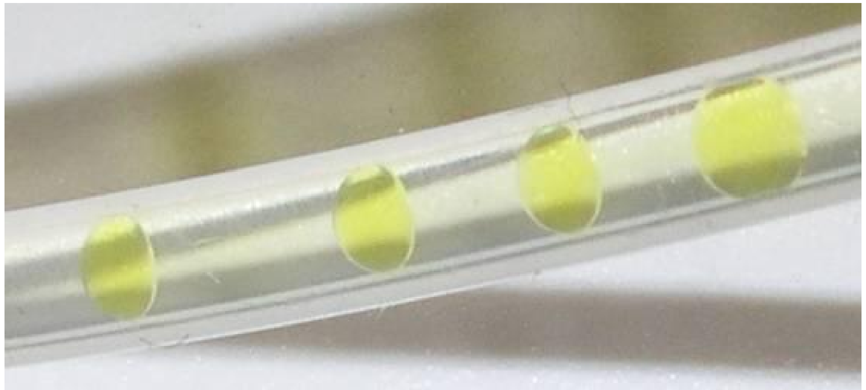
Flow Extraction Systems: Principle



Flow Extraction Systems: Phase separator



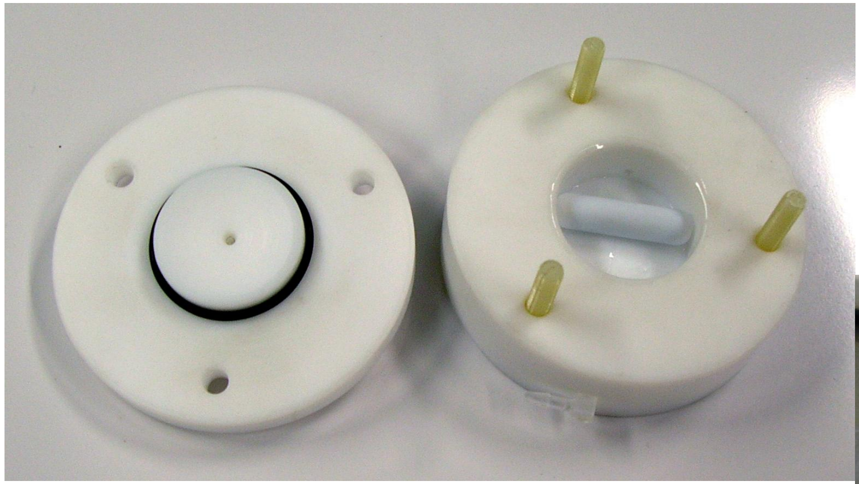
Flow Extraction Systems: Extraction Coil

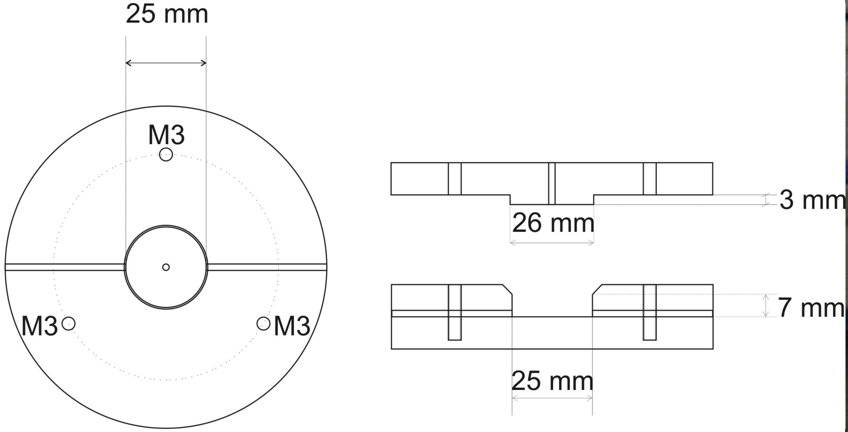


Disadvantage:

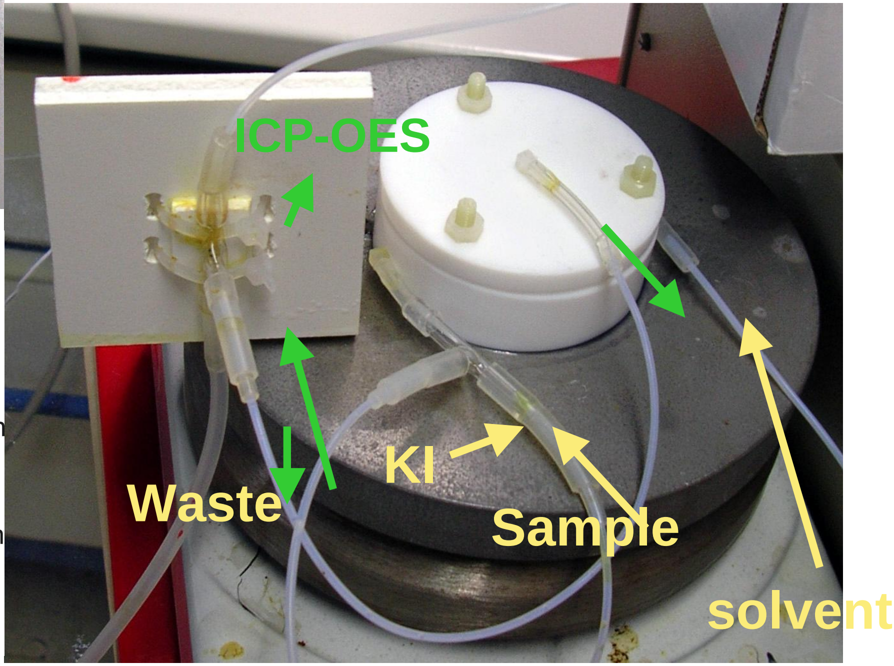
- Low contact between aqueous /organic phase
- Low extraction efficiency (< 20 %)

Flow Extraction Systems: Stirrer

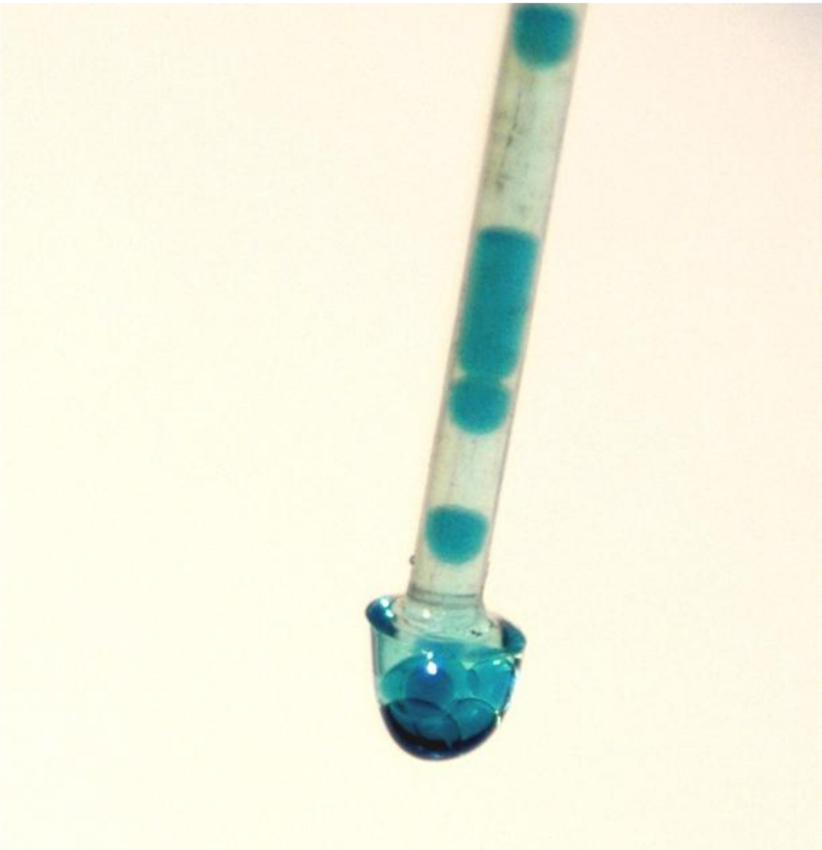




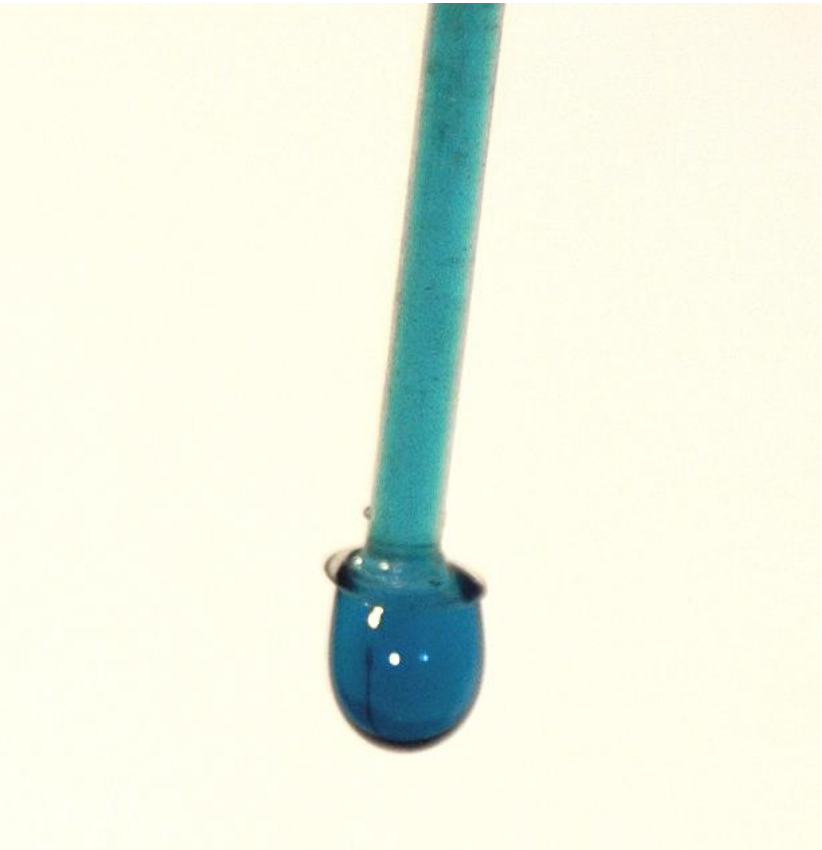
- Magnetically stirred
- Good contact between aqueous / organic phase



Flow Extraction Systems



Without stirring



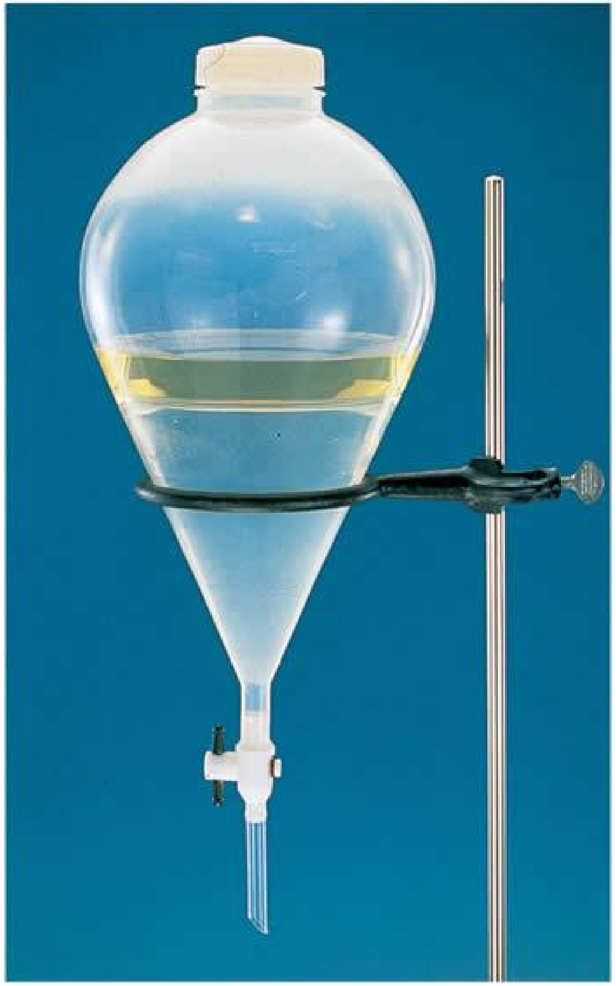
With stirring

Flow Extraction Systems: Extraction efficiency

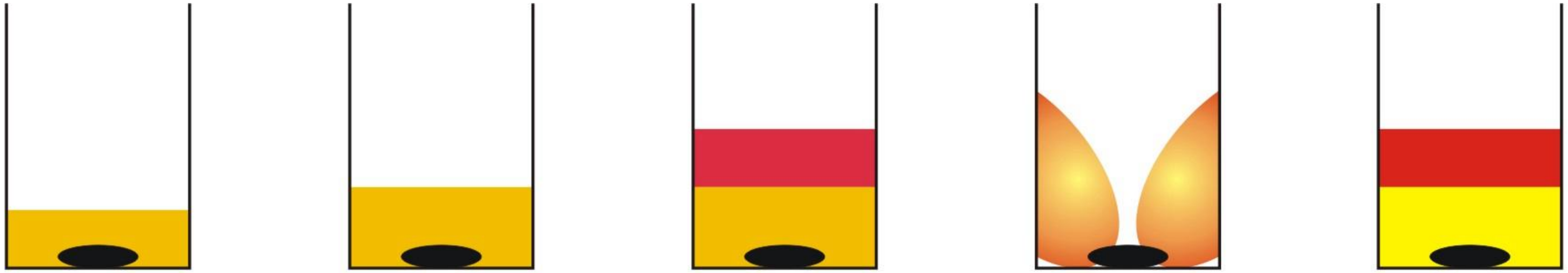
Element	Extraction efficiency*, %
Ag	97 ± 3
As	*14* ± *2*
Bi	101 ± 7
Cd	*55* ± *1*
Pb	70 ± 3
Sb	*39* ± *1*
Se	60 ± 7
Sn	*55* ± *3*
Tl	*22* ± *4*
Zn	*52* ± *1*

*For aqueous solutions without steel matrix

Batch Extractor: Principle



Batch Extractor: Automation



step 1:
add sample

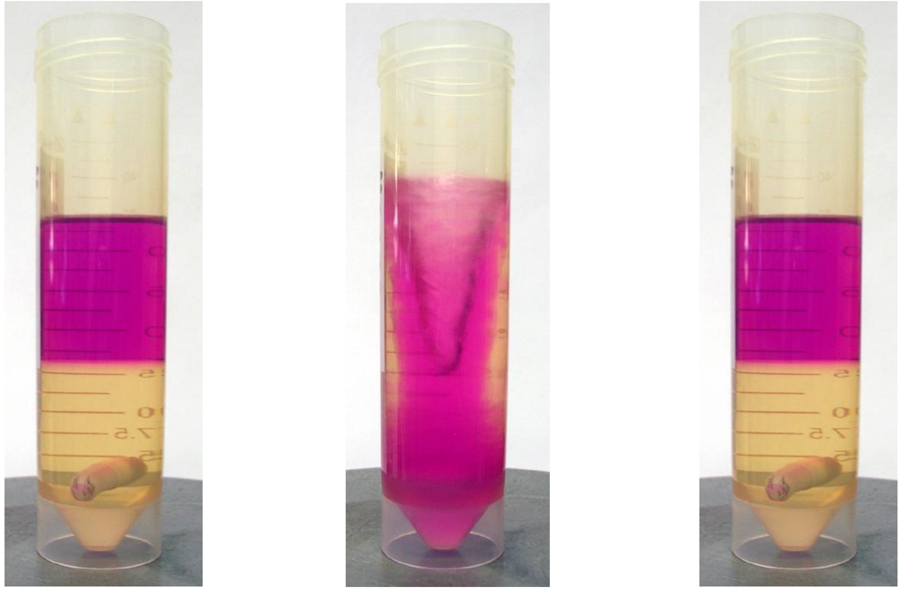
step 2:
add KI

step 3:
add org. Solvent

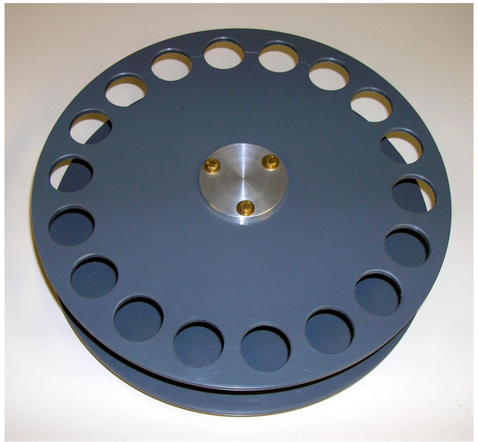
step 4:
extraction

step 5:
phase separation

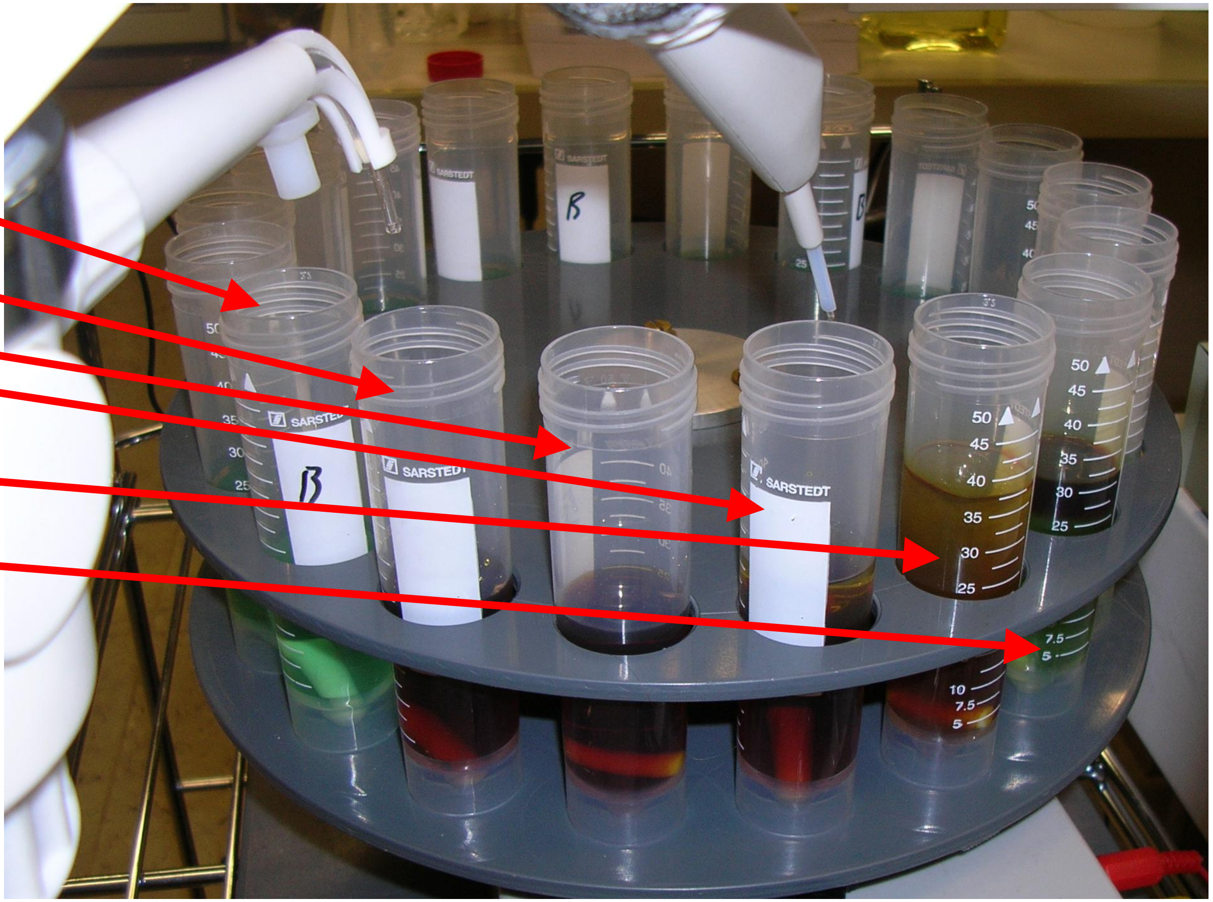
Characteristics:
- magnetically stirred
- no carry over between the samples



Batch Extractor: Automation



Batch Extractor: Automation



1) Sample
2) + KI
3) Mix
4) + Organic solvent
5) Extraction
6) Phase separation

Batch Extractor: Extraction efficiency

Element	Extraction efficiency*, %
Ag	95 ± 2
As	17 ± 4
Bi	99 ± 3
Cd	73 ± 2
Pb	91 ± 2
Sb	55 ± 6
Se	73 ± 4
Sn	87 ± 1
Tl	53 ± 6
Zn	81 ± 2

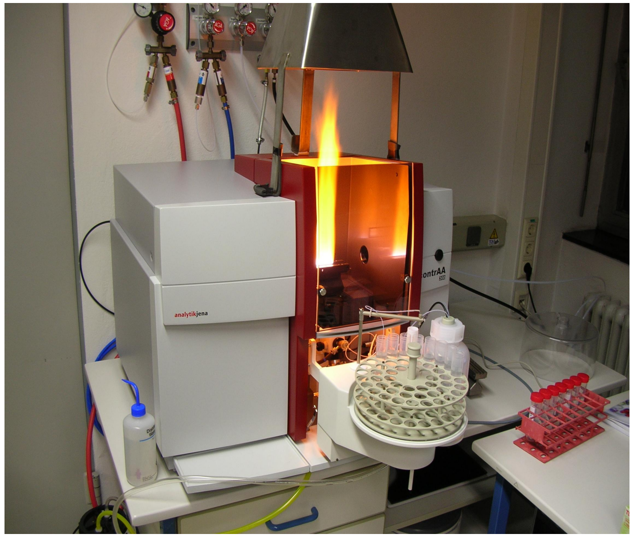
Comparison Flow Extractor – Batch Extractor

	Flow Extractor	Batch Extractor
+	• Simple • Low cost • Easy to integrate into ICP-OES: between autosampler and spray chamber	• Fast; limited only by data acquisition • No memory effect
-	• Memory effects • Slow	• Expensive • Integration into ICP-OES requires additional software

Comparison FAAS – ICP-OES

Advantage FAAS

- Higher nebulization efficiency of organic solvents improves DL's
- No solvent induced spectral interferences
- No structured background from organic solvent
- Low operation costs
- Fast sequential analysis of the extracted analytes is an alternative to ICP-OES → HR-CS-AAS



Conclusion

- **High temperature wet digestion at ≥300°C can solve some analytical problems, which cannot be solved with microwave assisted wet digestion**
- **Microwave assisted UV-digestion and microwave assisted combustion are powerful new methods in trace element analysis**
- **Separation and preconcentration techniques are still necessary in trace element analysis despite of powerful measurement techniques**

Acknowledgments

Dieter Florian

Erico Flores

Helmar Wiltsche

Ella R. Gladkikh

Peter Kettisch

Graz 2009

www.winterplasmagraz.at

European
Winter Conference
on Plasma Spectrochemistry

15.02. - 20.02.2009, Graz - Austria

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