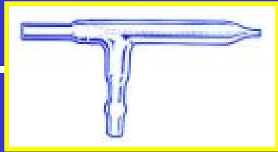

EVALUATION OF VARIOUS NEBULIZERS FOR USE IN MICROWAVE INDUCED PLASMA OPTICAL EMISSION SPECTROMETRY

Henryk Matusiewicz [a], Antonio Canals [b]

[a] Politechnika Poznańska, Department of Analytical Chemistry, 60-965 Poznań, Poland.
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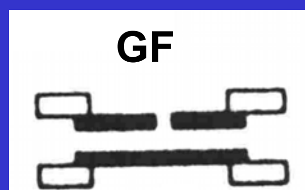
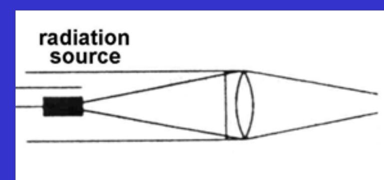
Is it still possible, necessary and beneficial to perform research in analytical atomic spectrometry?

AAS



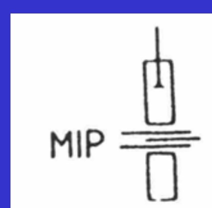
AFS



GDL DISCHARGE

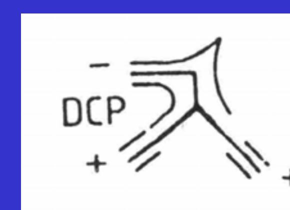
ICP DISCHARGE

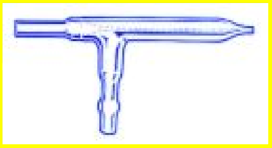
MIP DISCHARGE



CMP DISCHARGE

DCP DISCHARGE



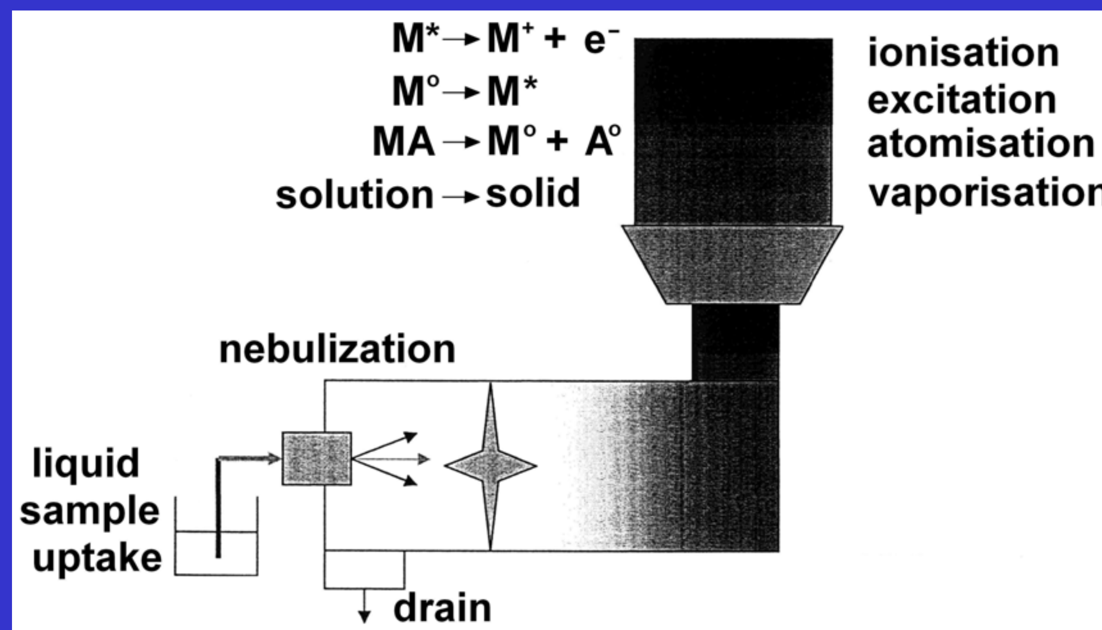


Analytical atomic spectrometric techniques are still a most appropriate techniques for elemental determinations

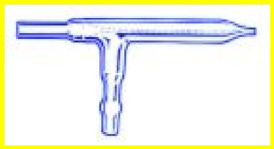
- Atomic Absorption Spectrometry (AAS)
- Plasma Optical Emission Spectrometry (OES)
- Atomic Fluorescence spectrometry (AFS)

mainly due to its simplicity and low cost.

Solution nebulization or liquid sample aliquoting are the most common methods for introducing sample into atomic spectrometers.

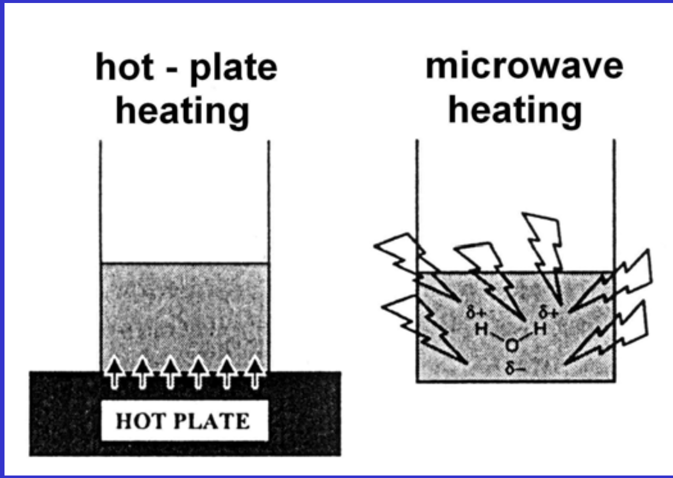


PROCESSES IN A FLAME / PLASMA



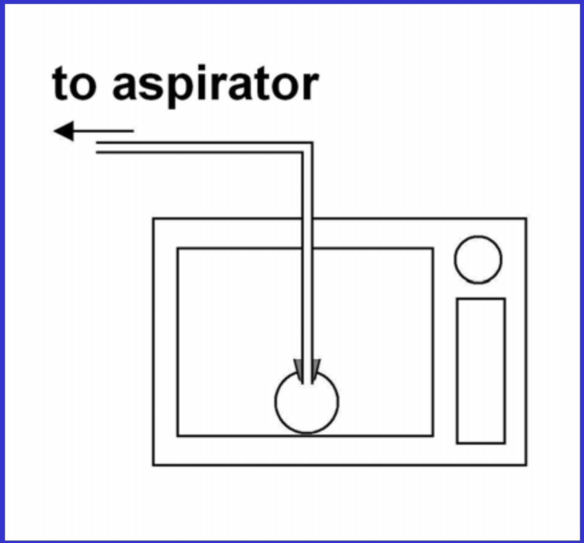
➢ MICROWAVE HEATING
(MICROWAVE - ASSISTED WET DIGESTION)

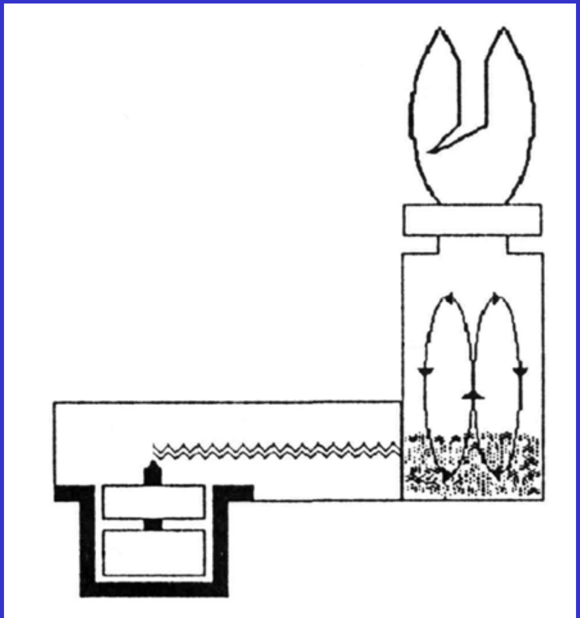
The most innovative source of energy for wet digestion procedure is MICROWAVES.



Analytical chemist first began using microwave techniques to wet digestion of biological samples in 1975 (the first paper published on microwave-assisted digestion).

A.Abu-Samra, J.S.Morris, S.R.Koirtyohann, *Anal.Chem.*, 47, 1475 (1975)

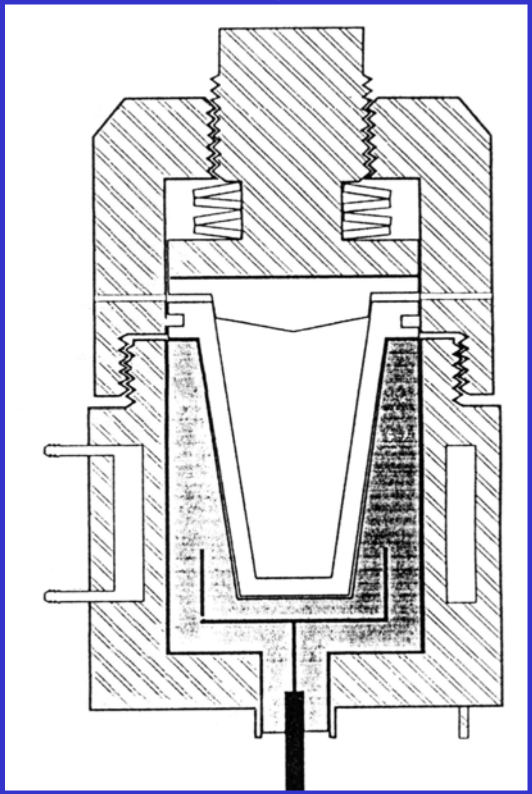




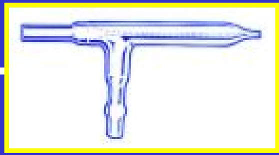
The focused-microwave-assisted system is primarily used for atmospheric pressure digestions.

It was developed a focused-microwave-heated bomb that would exceed the operational capabilities of existing microwave digestion systems and permit the construction of an integrated microwave source / bomb combination.

H.Matusiewicz, *Anal.Chem*., 66, 751 (1994)

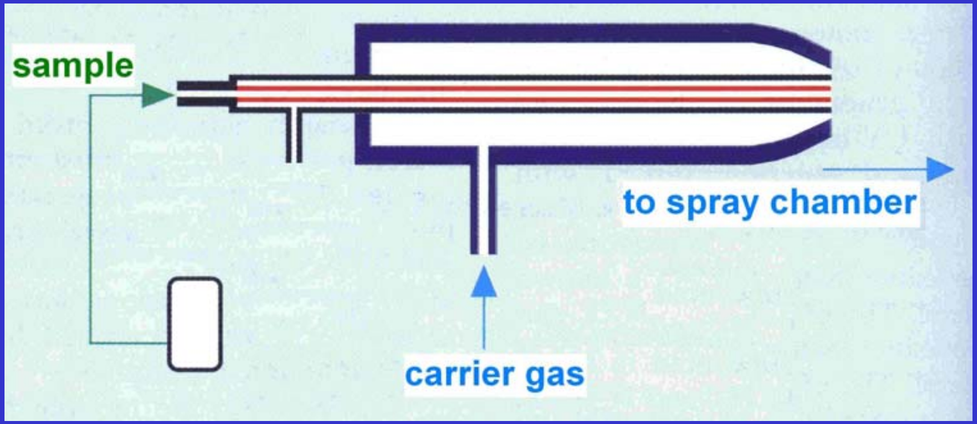


LIQUID-SAMPLE INTRODUCTION TECHNIQUES

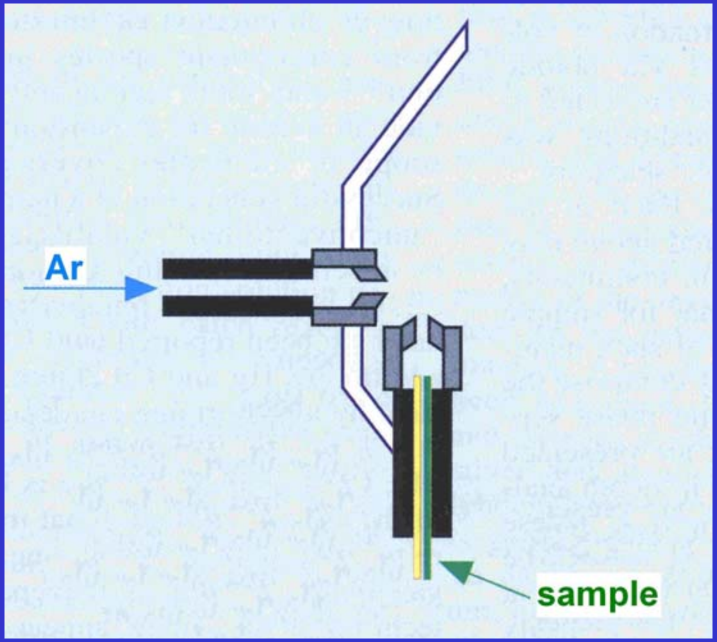


- PNEUMATIC NEBULIZATION

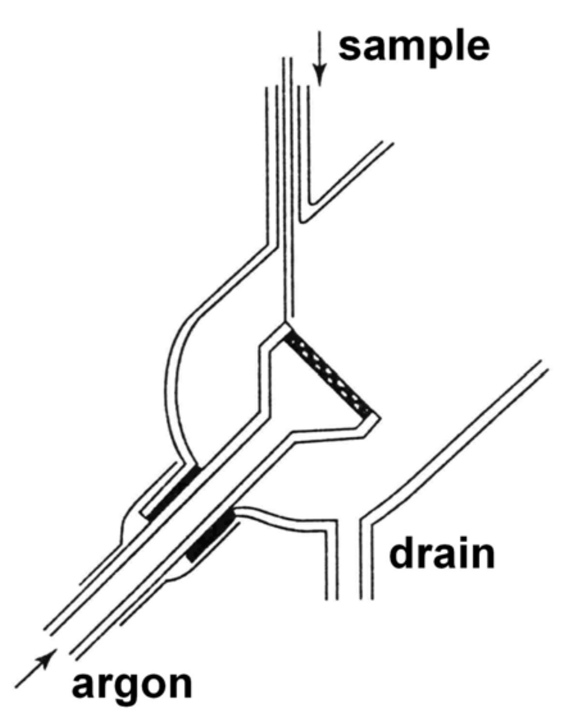
CONCENTRIC NEBULIZER



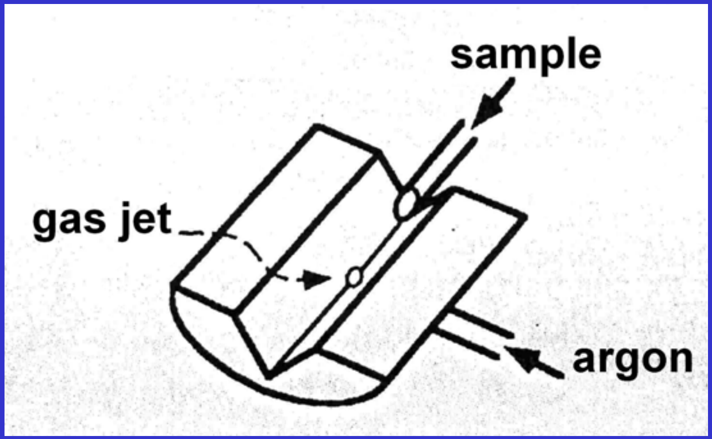
CROSS-FLOW NEBULIZER



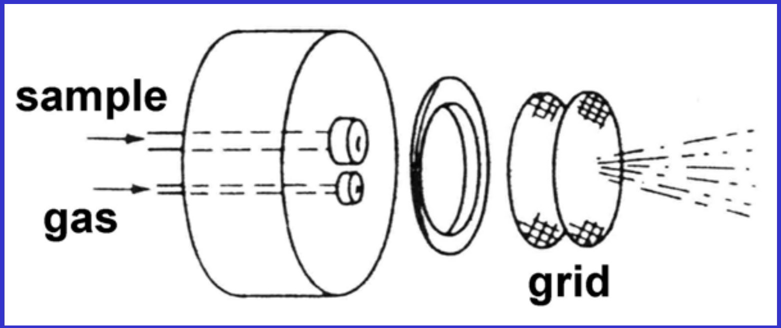
FRITTED-DISC NEBULIZER



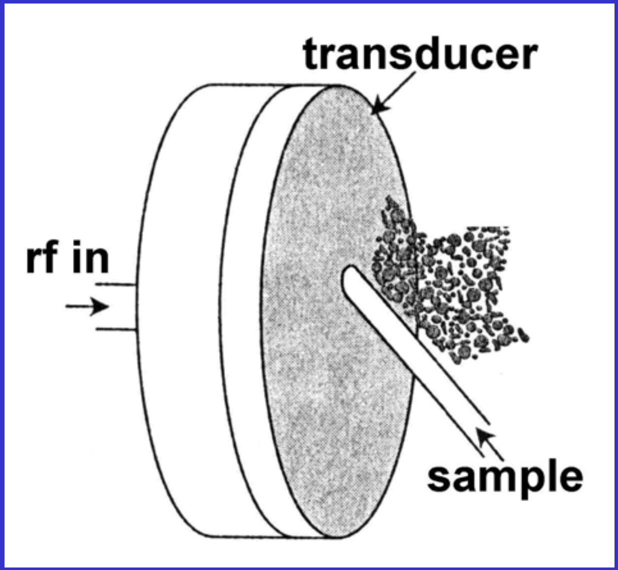
VEE-GROOVE NEBULIZER

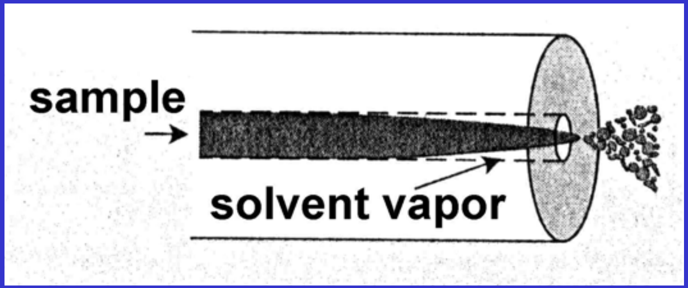


GRID-TYPE NEBULIZER

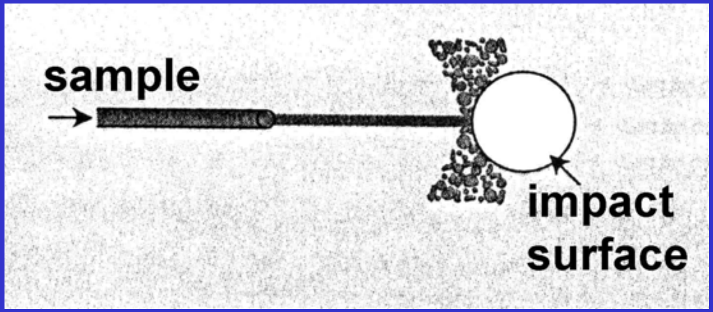


➢ ULTRASONIC NEBULIZATION

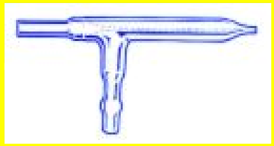




➢ THERMOSPRAY



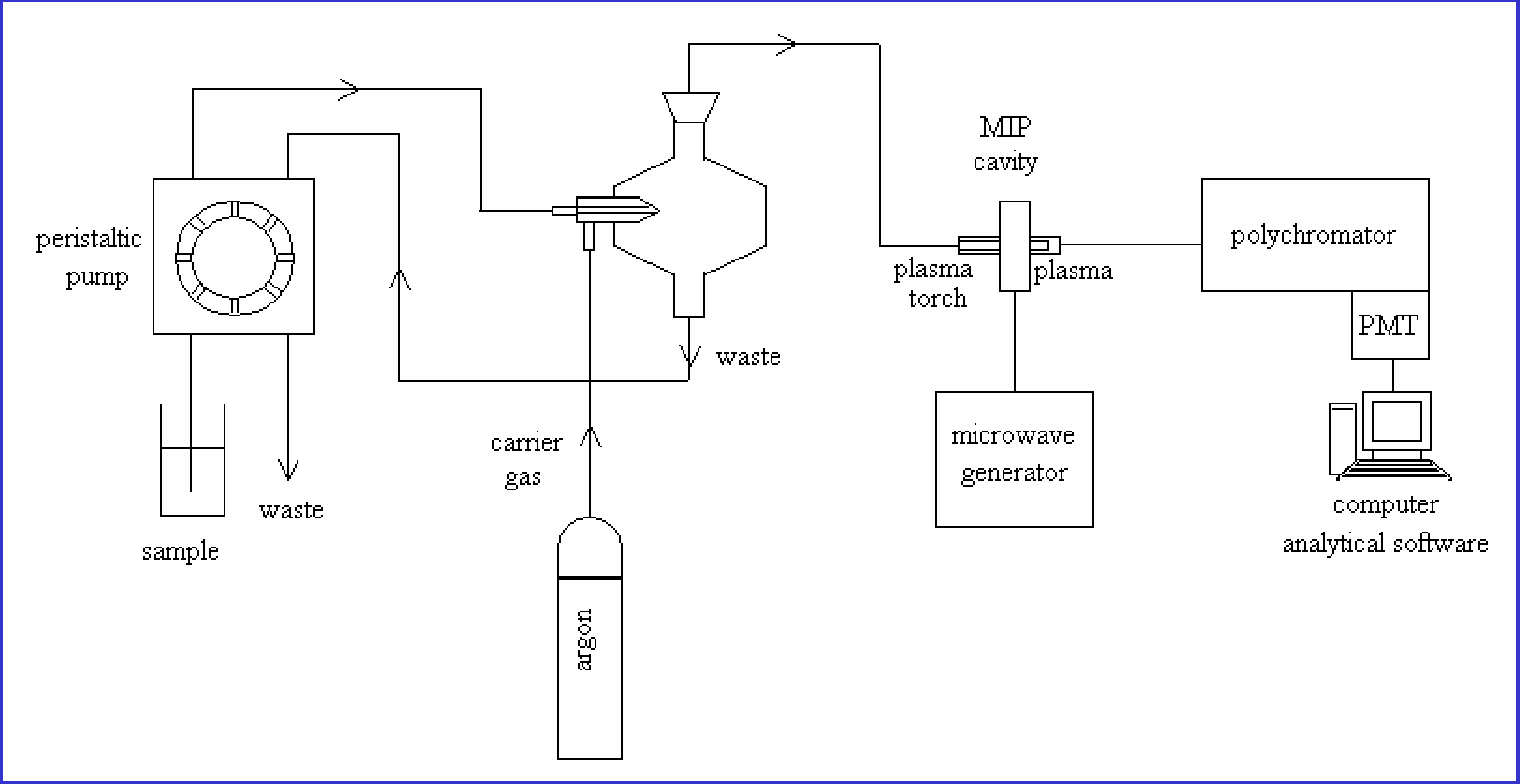
➢ JET IMPACTION

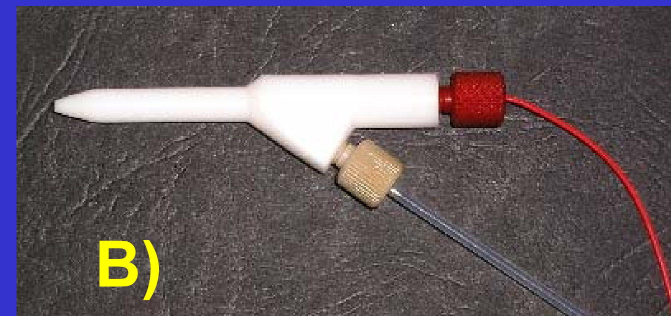


➢ MICROFLOW – SCALE NEBULIZERS

- microconcentric
- high efficiency
- direct injection
- micro – mist
- micro – ultrasonic

Component diagram of the elaborated nebulizer-MIP-OES system



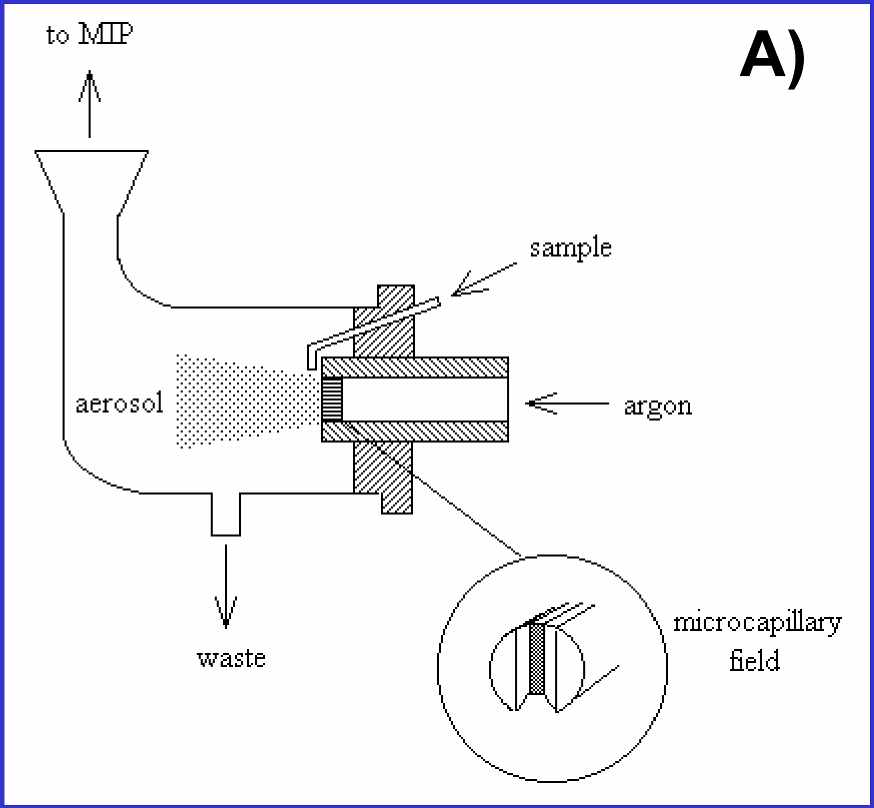


Pictures of the nebulizers:

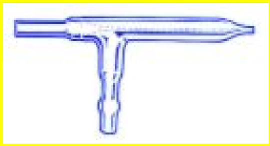
A) conventional pneumatic concentric nebulizer (PN, Meinhard);

B) micro 3 (M3);

C) flow focusing pneumatic nebulizer (FFPN)

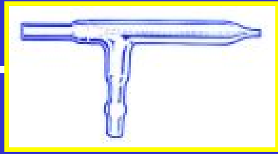


**NAR-1 microcapillary array nebulizer:
A) schematic diagram; B) picture of the NAR-1**



Instrumental parameters for Ar-MIP-OES system

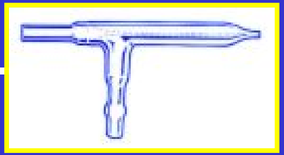
Microwave frequency	2450 MHz
Applied microwave plasma power	100-200 W, variable
Microwave cavity	TE101 rectangular, water cooled
Microwave generator	700 W, MPC-01 (Plazmatronika Ltd., Wrocław, Poland)
Plasma viewing mode	Axial
Plasma torch	Quartz tube, 2.5 mm i.d., air cooled
Plasma supporting argon flow rate	400 ml min^{-1}
Integration time	0.1 s
Determination	Simultaneous
Wavelength/nm (line type)	Ba 455.403 (II), Ca 317.933 (II), Ca 393.366 (II), Cd 226.502 (II), Cu 324.754 (I), Fe 238.204 (II), Mg 279.553 (II), Mg 285.213 (I), Mn 257.611 (II), Pb 405.783 (I), Sr 407.771 (II), Zn 213.857 (I), I 206.163 (I)

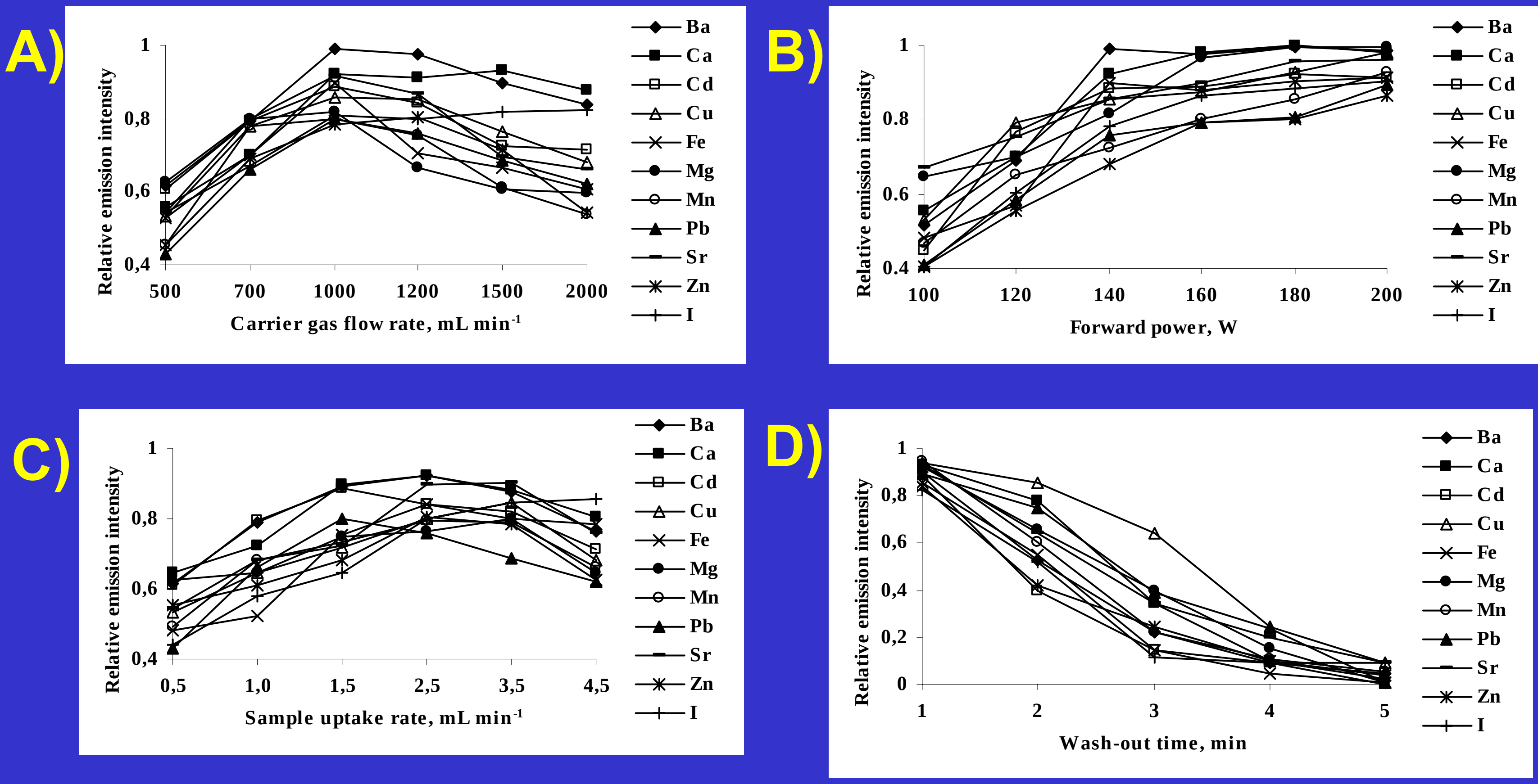


Optimum operating conditions for MIP-OES measurement [a] of elements obtained by simplex and univariate methods

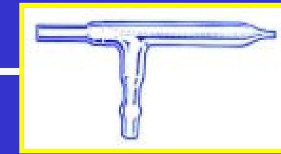
Parameter (variable)	Boundary limits of parameters, range				Univariate method				Simplex metod			
	PN	M3	FFPN	NAR-1	PN	M3	FFPN	NAR-1	PN	M3	FFPN	NAR-1
Forward power, W	100-200	100-200	100-180	100-180	160	160	160	160	155	160	160	150
Sample carrier argon flow rate, ml min^{-1}	400-2000	900-1500	600-1400	400-1000	1000	1200	1000	800	1050	1180	970	750
Sample liquid uptakerate (pumped), ml min^{-1}	0.5-4.0	0.2-1.0	0.4-1.0	0.05-0.35	2.5	0.6	0.8	0.15	2.7	0.5	0.8	0.17

[a] Response, peak height of the element emission intensity

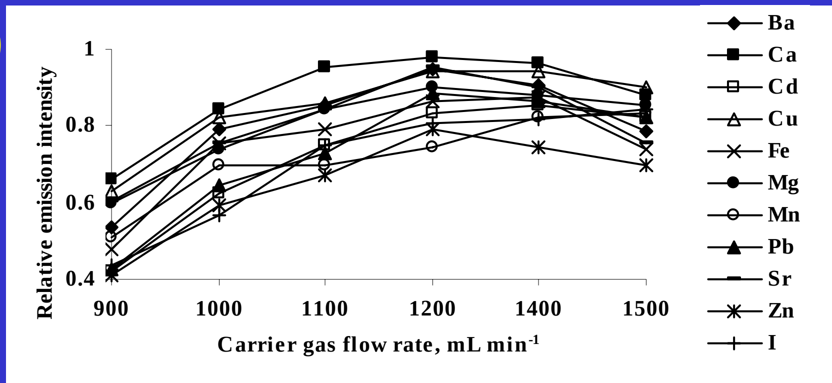




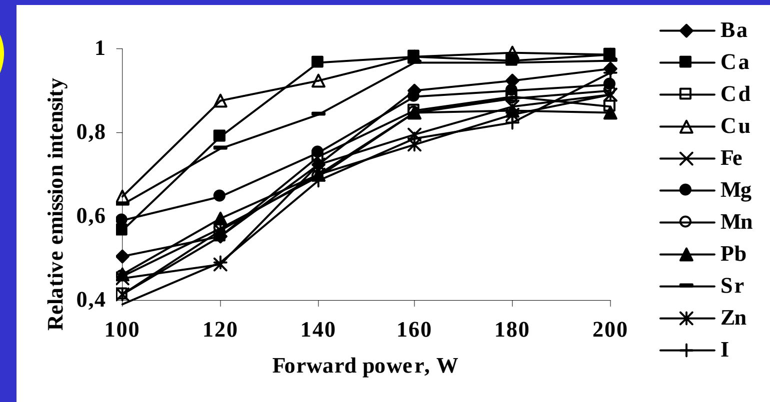
Effect of the variables on the element's normalized emission intensity for pneumatic nebulizer (PN)



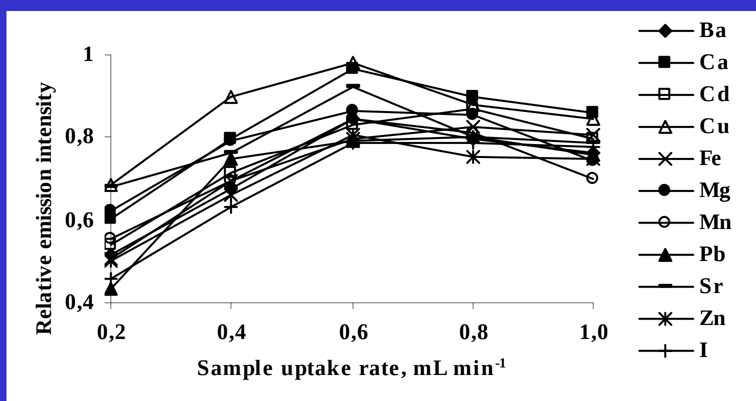
A)



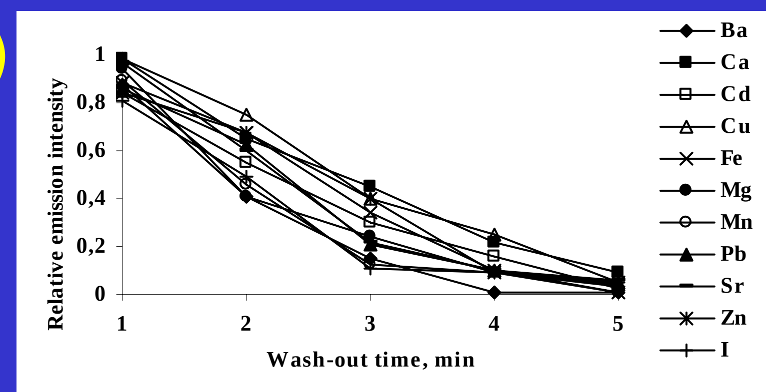
B)



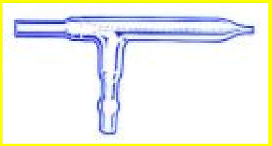
C)



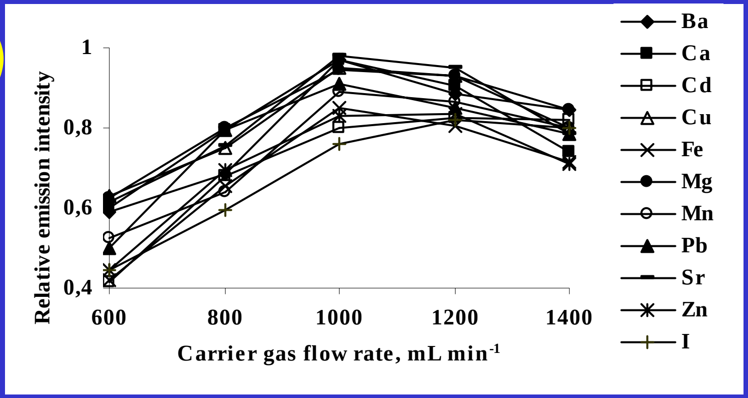
D)



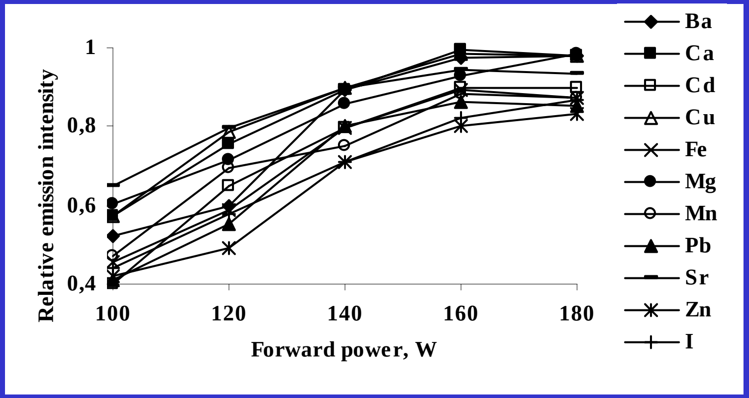
Effect of the variables on the element's normalized emission intensity for micro 3 nebulizer (M3)



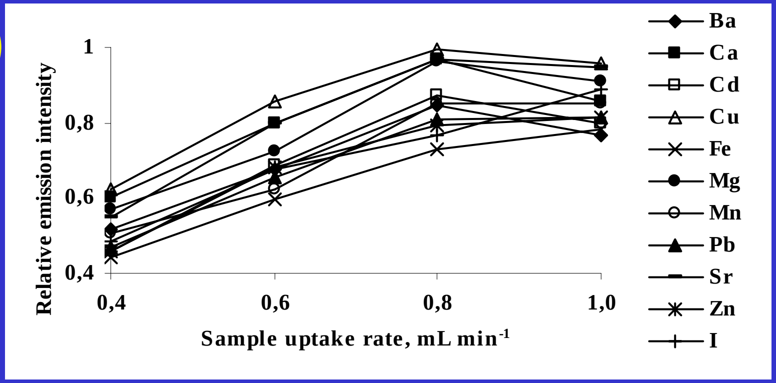
A)



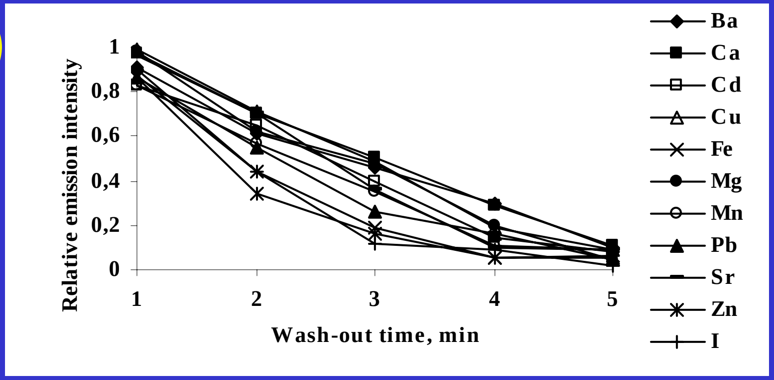
B)



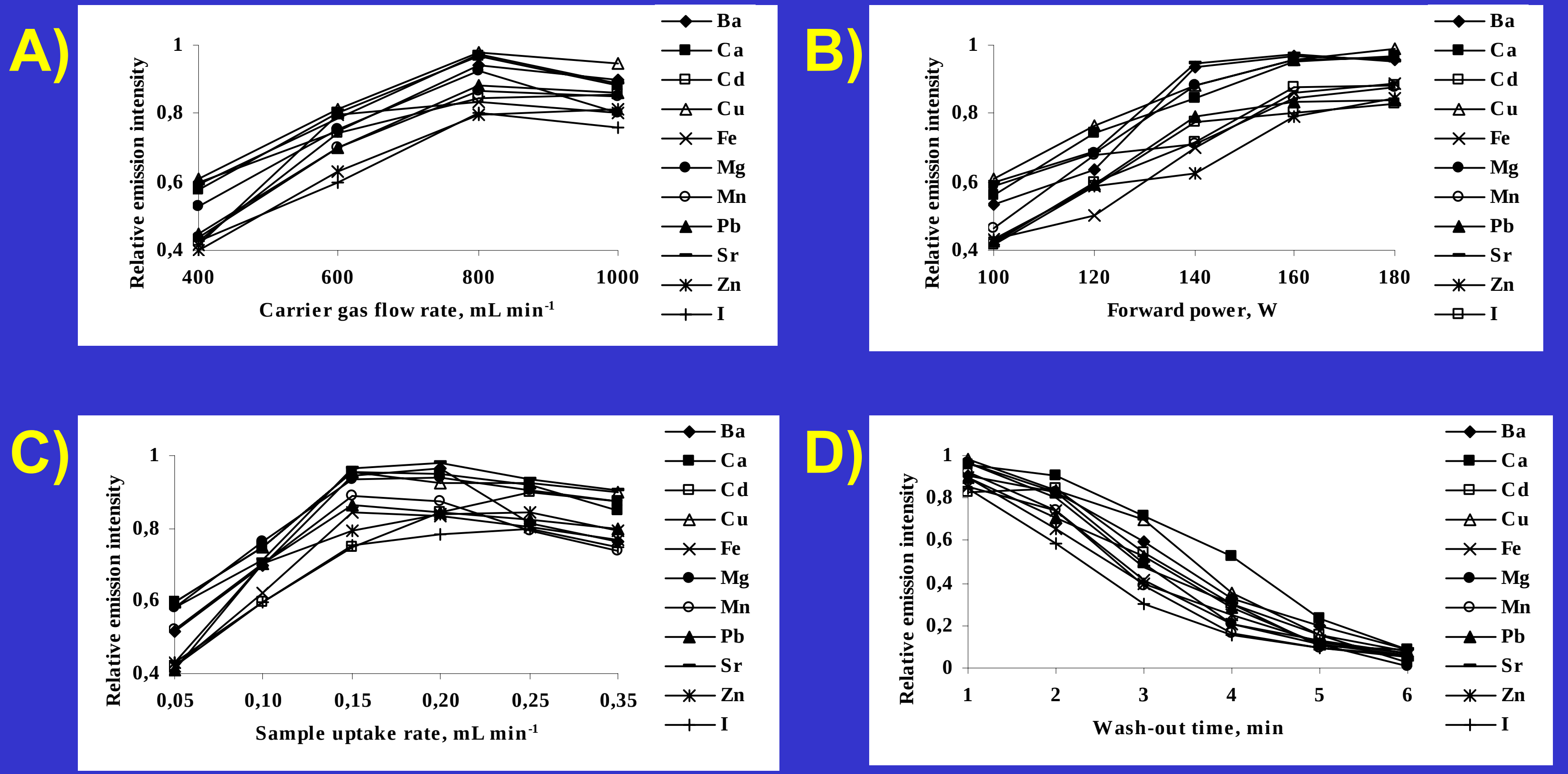
C)



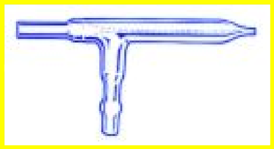
D)



Effect of the variables on the element's normalized emission intensity for flow focusing pneumatic nebulizer (FFPN)

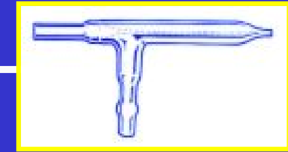


Effect of the variables on the element's normalized emission intensity for microcapillary nebulizer (NAR-1)



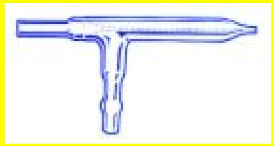
Optimum operating conditions for the determination of elements in soluble materials by Ar-MIP-OES *via* liquid nebulization systems

Parameter	Nebulizers			
	PN	M3	FFPN	NAR-1
Applied power, W	160	160	160	155
Nebulizer pressure, bar	3	3	4	5
Sample carrier gas flow rate, ml min^{-1}	1000	1200	1000	800
Sample liquid uptake rate (pumped), ml min^{-1}	2.5	0.6	0.8	0.15



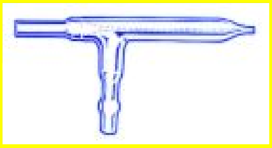
Limits of detection LOD ($\mu g\ ml^{-1}$) values for the elements and nebulizers tested

Element	Analysis wavelength (nm)	PN	M3	FFPN	NAR-1
Ba	455.403	0.099	0.046	0.020	0.044
Ca	393.366	0.049	0.020	0.007	0.030
Cd	226.502	0.055	0.030	0.010	0.028
Cu	324.745	0.010	0.010	0.007	0.008
Fe	238.204	0.078	0.079	0.020	0.062
Mg	285.213	0.068	0.009	0.004	0.006
Mn	257.611	0.011	0.008	0.004	0.006
Pb	405.783	0.069	0.059	0.008	0.022
Sr	407.713	0.025	0.007	0.004	0.007
Zn	213.857	0.080	0.067	0.010	0.008
I	206.163	12.3	11.4	11.0	10.0



Background equivalent concentration BEC (µg ml^{-1}) values for the elements and nebulizers tested

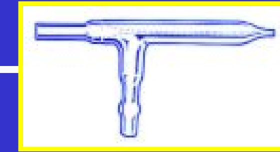
Element	Analysis wavelength (nm)	PN	M3	FFPN	NAR-1
Ba	455.403	0.221	0.108	0.052	0.100
Ca	393.366	0.120	0.052	0.020	0.009
Cd	226.502	0.104	0.055	0.024	0.084
Cu	324.745	0.028	0.041	0.018	0.036
Fe	238.204	0.184	0.175	0.047	0.137
Mg	285.213	0.140	0.020	0.012	0.014
Mn	257.611	0.028	0.017	0.014	0.013
Pb	405.783	0.144	0.125	0.019	0.039
Sr	407.713	0.059	0.017	0.011	0.019
Zn	213.857	0.172	0.148	0.028	0.015
I	206.163	26.8	23.6	20.9	20.7



Aerosol MIP-OES analysis (concentrations in μg g^{-1} ± SD of three parallel determinations) of certified (standard) reference materials using pneumatic nebulizer (PN)

Element	Lobster Hepatopancreas NRCC TORT-1		Human Hair NIES CRM-13	
	Found value	Certified value	Found value	Certified value
Ba	-	-	<DL[a]	2[b]
Ca	0.826 % ±0.075	0.895 % ± 0.058	835 ± 74	820[b]
Cd	30.1 ± 5.1	26.3 ± 2.1	<DL[a]	0.23 ± 0.03
Cu	441 ± 43	439 ± 22	16.7 ± 1.5	15.3 ± 1.2
Fe	200 ± 28	186 ± 11	153 ± 21	140[b]
Mg	0.239 % ± 0.021	0.255% ± 0.025	169 ± 14	160[b]
Mn	26.4 ± 3.1	23.4 ± 1.0	4.9 ± 0.6	3.9[b]
Pb	11.1 ± 1.3	10.4 ± 2.0	5.4 ± 0.7	4.6 ± 0.4
Sr	118 ± 11	113 ± 5	-	-
Zn	194 ± 25	177 ± 10	184 ± 24	172 ± 10

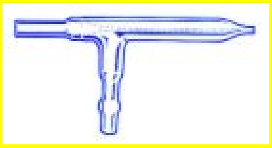
[a] Below detection limit [b] Non-certified value



Aerosol MIP-OES analysis (concentrations in μg g^{-1} ± SD of three parallel determinations) of certified (standard) reference materials using micro3 nebulizer (M3)

Element	Lobster Hepatopancreas NRCC TORT-1		Human Hair NIES CRM-13	
	Found value	Certified value	Found value	Certified value
Ba	-	-	3.1 ± 0.5	2[a]
Ca	0.843 % ± 0.094	0.895 % ± 0.058	829 ± 91	820[a]
Cd	28.6 ± 3.40	26.3 ± 2.1	<DL[b]	0.23 ± 0.03
Cu	445 ± 44	439 ± 22	16.2 ± 1.6	15.3 ± 1.2
Fe	193 ± 24.08	186 ± 11	149 ± 18	140[a]
Mg	0.241 % ± 0.023	0.255% ± 0.025	166 ± 17	160[a]
Mn	25.9 ± 2.51	23.4 ± 1.0	4.6 ± 0.5	3.9[a]
Pb	11.6 ± 0.93	10.4 ± 2.0	5.5 ± 0.6	4.6 ± 0.4
Sr	116 ± 10	113 ± 5	-	-
Zn	189 ± 24.5	177 ± 10	181 ± 24	172 ± 10

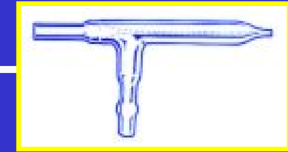
[a] Non-certified value [b] Below detection limit



Aerosol MIP-OES analysis (concentrations in µg g^{-1} ± SD of three parallel determinations) of certified (standard) reference materials using focusing pneumatic nebulizer (FFPN)

Element	Lobster Hepatopancreas NRCC TORT-1		Human Hair NIES CRM-13	
	Found value	Certified value	Found value	Certified value
Ba	-	-	2.4 ± 0.3	2[a]
Ca	0.885 % ± 0.081	0.895 % ± 0.058	826 ± 73	820[a]
Cd	27.1 ± 2.6	26.3 ± 2.1	<DL[b]	0.23 ± 0.03
Cu	442 ± 35	439 ± 22	15.9 ± 1.3	15.3 ± 1.2
Fe	189 ± 19	186 ± 11	147 ± 15	140[a]
Mg	0.252 % ± 0.026	0.255% ± 0.025	163 ± 16	160[a]
Mn	24.0 ± 2.2	23.4 ± 1.0	4.1 ± 0.4	3.9[a]
Pb	10.8 ± 1.0	10.4 ± 2.0	4.9 ± 0.4	4.6 ± 0.4
Sr	115 ± 9	113 ± 5	-	-
Zn	183 ± 20	177 ± 10	175 ± 19	172 ± 10

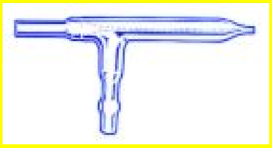
[a] Non-certified value [b] Below detection limit



Aerosol MIP-OES analysis (concentrations in $\mu g\ g^{-1} \pm$ SD of three parallel determinations) of certified (standard) reference materials using microcapillary array nebulizer (NAR-1)

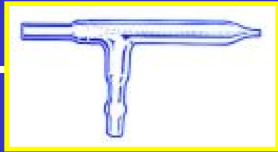
Element	Lobster Hepatopancreas NRCC TORT-1		Human Hair NIES CRM-13	
	Found value	Certified value	Found value	Certified value
Ba	-	-	3.0 ± 0.4	2[a]
Ca	0.856% ± 0.099	0.895 % ± 0.058	831 ± 84	820[a]
Cd	28.2 ± 3.7	26.3 ± 2.1	<DL[b]	0.23 ± 0.03
Cu	440 ± 52	439 ± 22	16.2 ± 1.9	15.3 ± 1.2
Fe	192 ± 23	186 ± 11	152 ± 18	140[a]
Mg	0.248 % ± 0.25	0.255% ± 0.025	165 ± 116	160[a]
Mn	24.5 ± 2.7	23.4 ± 1.0	4.3 ± 0.5	3.9[a]
Pb	11.2 ± 1.1	10.4 ± 2.0	5.1 ± 0.5	4.6 ± 0.4
Sr	115 ± 10	113 ± 5	-	-
Zn	179 ± 21	177 ± 10	177 ± 21	172 ± 10

[a] Non-certified value [b] Below detection limit



Determination of elements (concentrations in % ± SD of three parallel analyses) in feminatal tablets, Merck KGaA, Darmstadt, Germany using the MIP-OES method

Element	Nebulizers				
	PN	M3	FFPN	NAR-1	Information value (%)
	Found	Found	Found	Found	
Ca	0.151 ±0.014	0.160 ± 0.018	0.142 ±0.013	0.149 ±0.0138	0.120
Cu	0.173 ± 0.016	0.165 ± 0.016	0.160 ± 0.013	0.167 ± 0.017	0.143
Fe	4.51 ± 0.63	4.39 ± 0.56	4.17 ± 0.40	4.33 ± 0.42	3.99
Mg	10.6 ± 8.2	10.4 ± 9.4	10.2 ± 0.10	10.4 ± 1.13	9.98
Mn	0.161 ± 0.017	0.157 ± 0.016	0.150 ± 0.014	0.155 ± 0.016	0.143
Zn	1.84 ± 0.24	1.92 ± 0.21	1.65 ± 0.18	2.25 ± 0.23	2.14



Determination of iodine (three parallel analyses) in iodide tablets, Merck KGaA, Darmstadt, Germany using the MIP-OES method

Sample	NAR-1 nebulizer	
	Found value	Information value
Brine	211 ± 24 μg ml^{-1}	-
Tablet	916 ± 115 μg g^{-1}	799 μg g^{-1}