Solid Sample Analysis of non-metallic elements (I,P,S) via Electrothermal Vaporisation by Optical Emission Spectroscopy with Inductively Coupled Plasma

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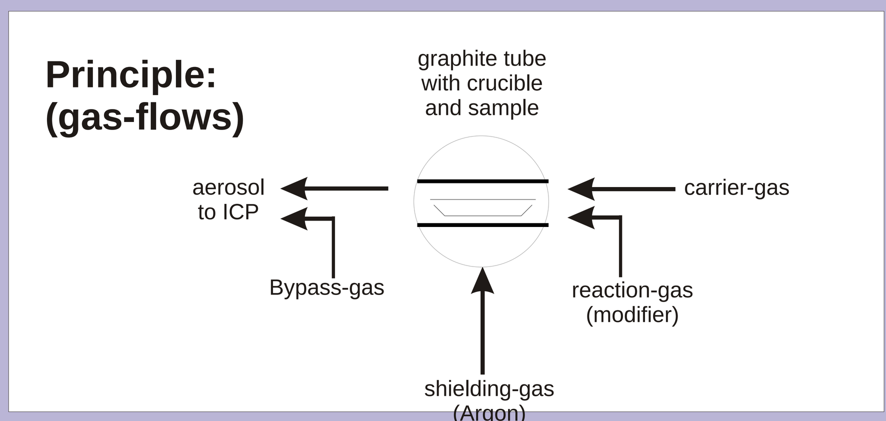
ETV: Principle of operation

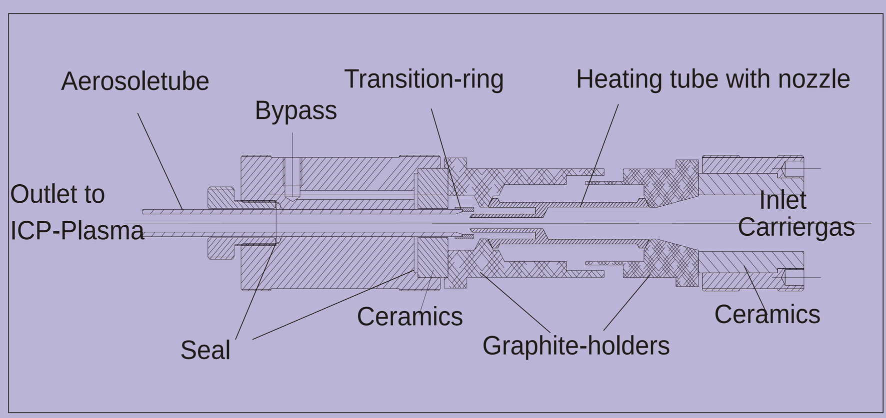
Temperature-controlled evaporation of sample in a graphite crucible positioned in a graphite-tube furnace with Argon atmosphere (up to 3000°C).
Electronic controlled addition of a small amount of reaction-gas (modifier).
Transport of the aerosol to the ICP-plasma by optimised gas guide with high transport-efficiency.
Integrated microprocessor-control with graphic LCD-display, electronic gas-flow-control and -mixing, synchronisation by electronic interface.
This allowes the application of individuel time-temperature-programs.
Automatic boat-temperature control by integrated online pyrometer from 10°C up to 3000°C.
Automated sample-handling by autosampler with up to 50 positions, microbalance.

Schematic of the gas-flow of ETV

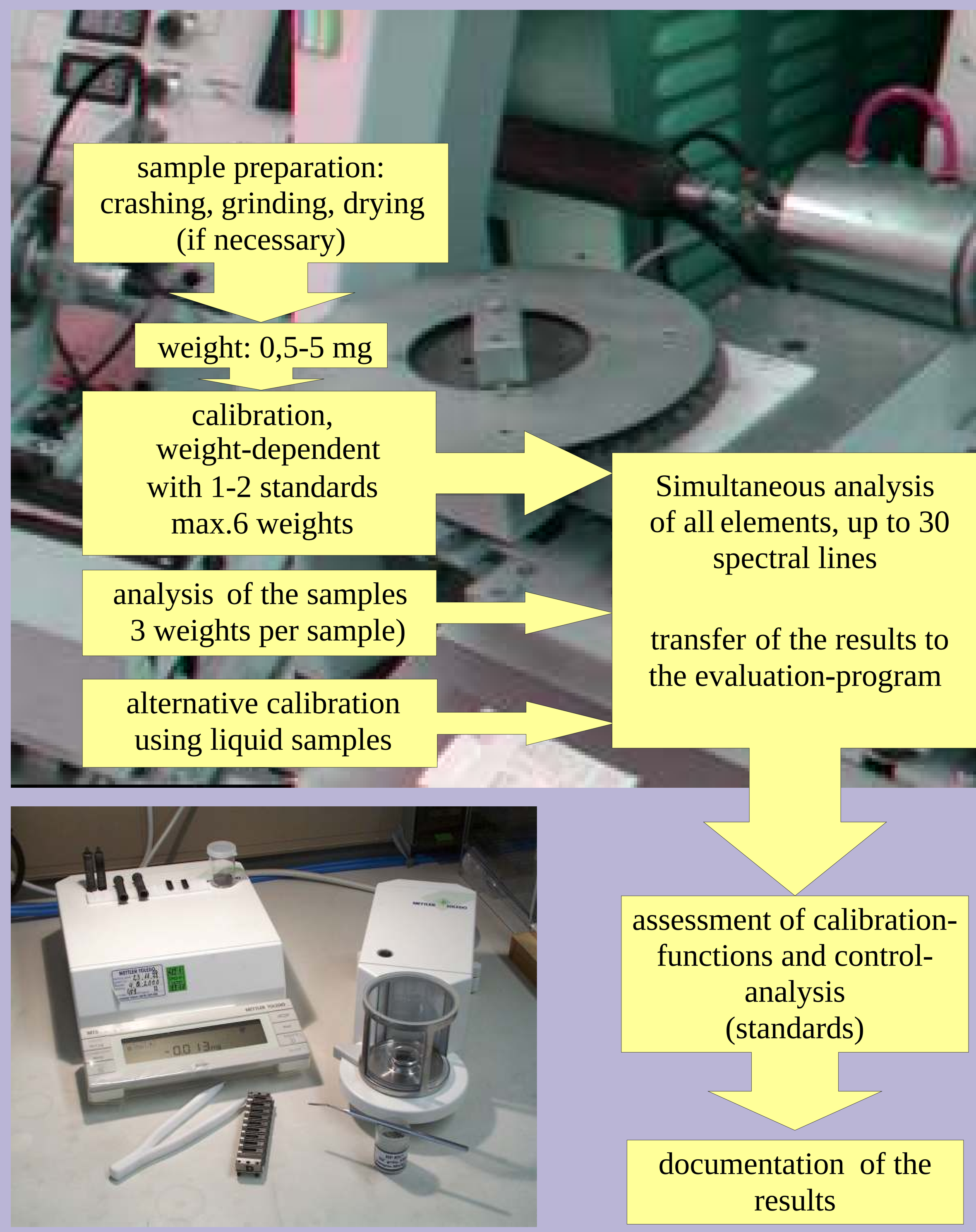


Graphite-furnace, new design

stable up to 3000°C, chemical inert materials, easy handling and maintenance,minimised seals, reduced number of working parts



ETV-analysis: example for a typical procedure



Examples of application

The results of analysed element-concentrations were calculated basing on the shown calibration functions. The points on these common calibration functions (dried liquid standards and solid sample material) show an excellent correlation and thereby prove the correctness and the convincing features of this method.

The investigated materials were:

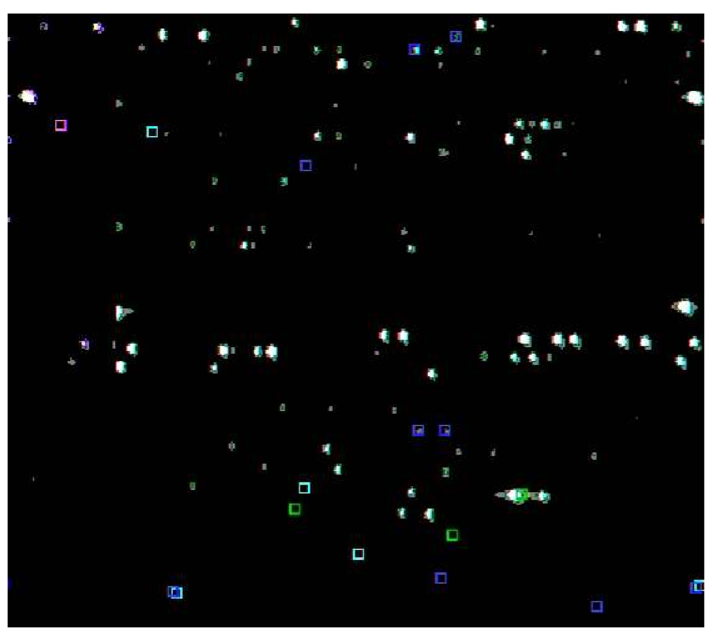
- Graphite (home standards) ©
- Ceramic Materials (BN, TiO_2, TiB_2)
- NIST SRM 1515 Apple Leaves (AL)
- Milk Powder (MP)

Example:
Gas flow and furnace-program for Iodine

Weight: 1 – 5 mg

Furnace-program:	step 1:	30s	300°C
	step 2:	2s	300°C to 1600°C
	step 3:	28s	1600°C
	step 4:		cooling 50s
Gases: Argon:	carrier 120 ml/min		
	by-pass 380 ml/min		
Freon:	2.3 ml/min		

Echelle-picture of the chip area of interest (I,S,P) between the 189th and 156th order



Analytical Lines of I,P,S

Iodine
178.276 (188) 75
179.903 (186) 5
183.038 (182) 15
206.190 (162) 3

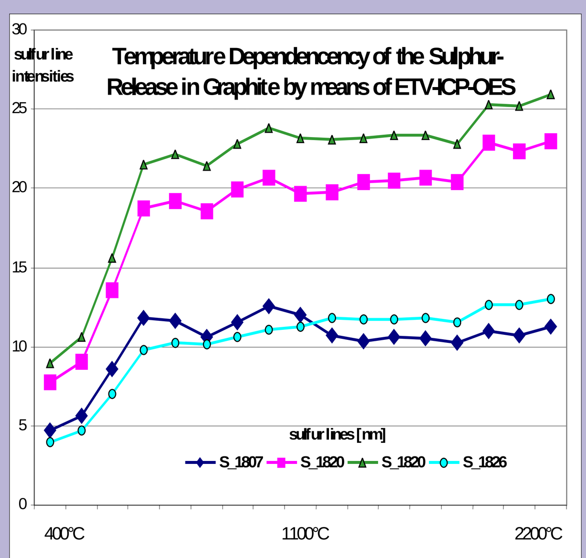
Phosphorus
177.499 (189) 100
178.287 (188) 110
178.768 (187) 60
185.891 (180) 40
185.943 (180) 65
203.349 (165) 10
213.618 (157) 90
214.914 (156) 50

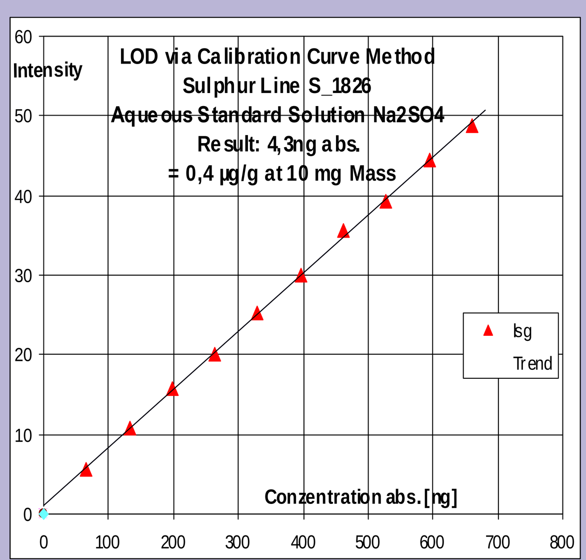
Sulphur
180.731 (185) 220
182.034 (183) 140
182.624 (183) 50

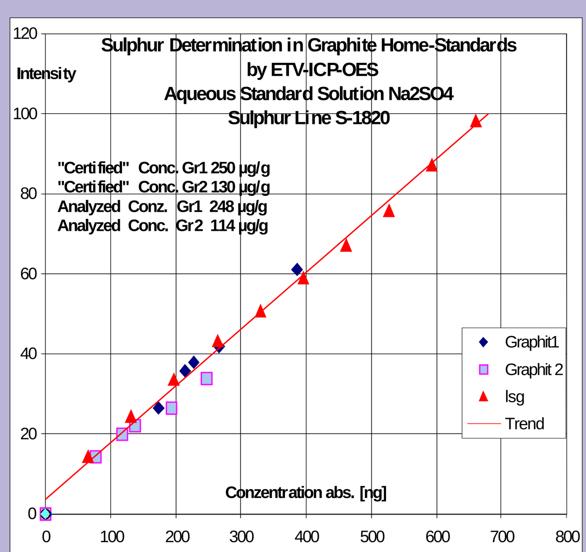
Tab. Experimental setup for ETV-ICP-OES:

ICP-Spectrometer	IRIS-AP Thermo Jarrell Ash Echelle-polychromator, Argon rinsed Echelle grating 60 grooves/mm
Spectral data	Focal distance: 381mm Resolution: at 200 nm width of one pixle 0,0035 nm Spektral range: 175-1050nm
Signal detection	CID-camera Active surface of CID chip:14,3×14,3mm (512 x 512 pixle)
ICP	axially plasma; RF generator: 1150 W at 27,12 Mhz
ETV-unit	ETV 4000 P.Perzl; Spectral Systems; Power supply: max power 400 A; end-on stream system; Furnace control: inside temperature controled

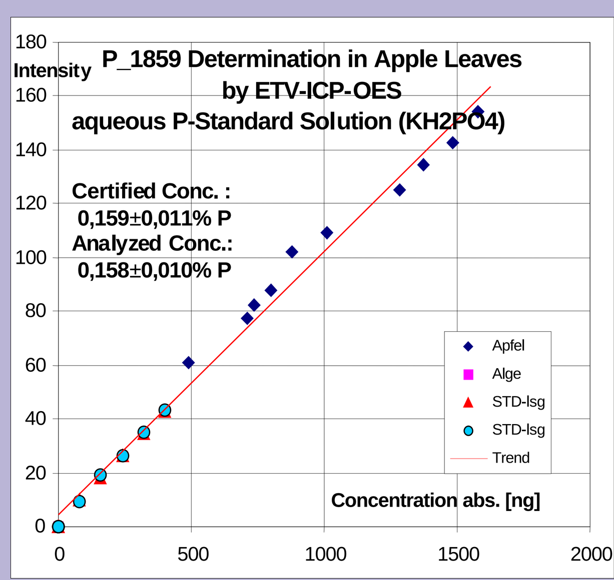
S in Graphite

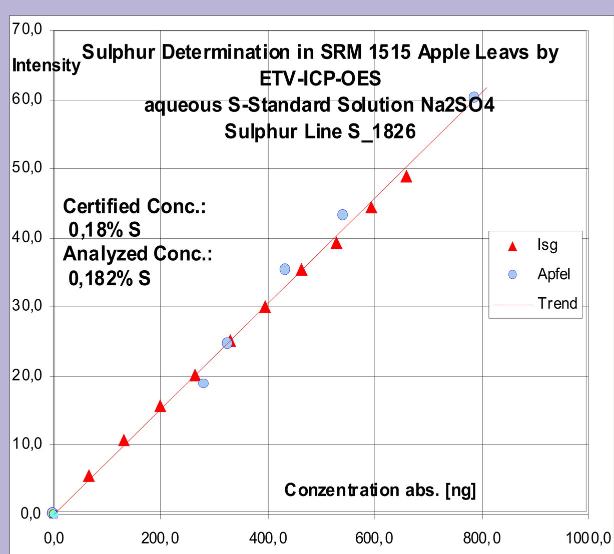




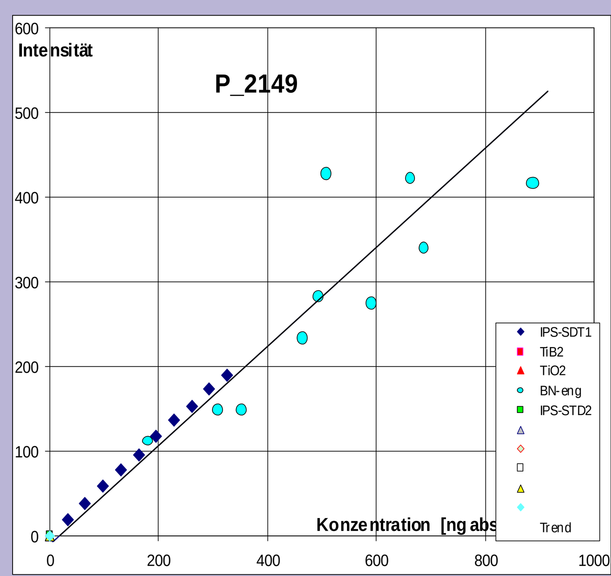


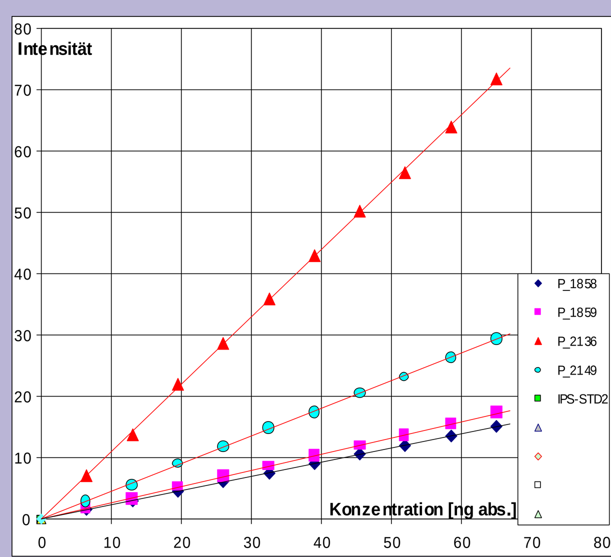
S, P in Apple Leaves



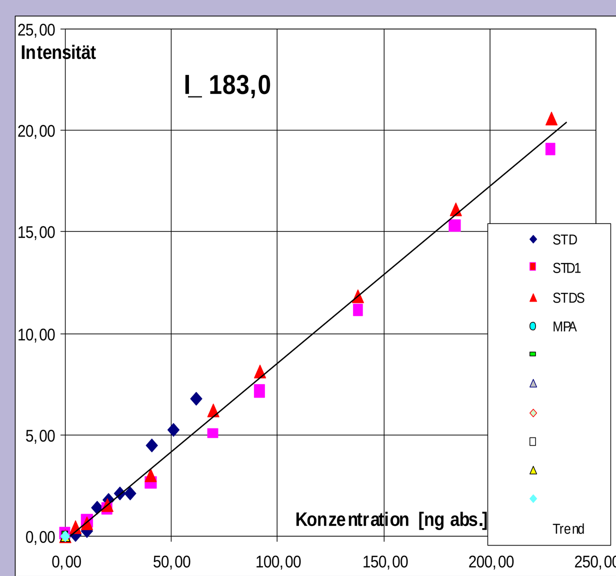


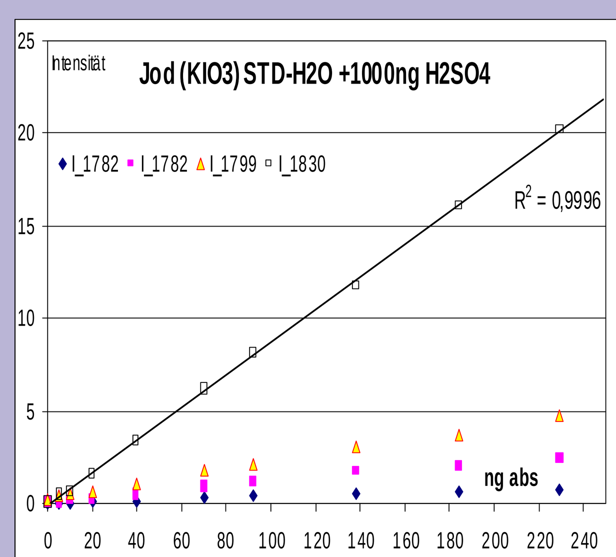
P in Ceramic Materials





I in Ashed Milk Powder





Results

Element	Line	LOD [ng abs.]	Material	Element	concentration	
					expectet	found
I	183.0	3 – 5	TiB_2	P	20 ± 5	9.5 ± 2
	179.9	7 – 11		P	510 ± 35	620 ± 40
P	185.891	0.7	BN	P	600 ± 50	550 ± 80
	185.943	0.8	Apple leafs	P	1590 ± 110	1580 ± 100
	213.618	0.5		S	1800 ± 100	1820 ± 50
	214.914	0.7	Graphite Gr1	S	250 ± 15	248 ± 10
S	182.0	1 - 2	Graphite Gr2	S	130 ± 15	114 ± 10
	182.6	4 - 5	MP	I	0.8-1.5	1.12 ± 0.25
			MP (standard addition)	I	0.8-1.05	0.95 ± 0.25

Conclusions:

As well known, modern ETV-ICP configurations are an excellent and cost-effective tool for easy, fast and precise direct solid sample multi-element analysis in a wide area of applications. The field of applications ranges from anorganic materials like ceramics and geological samples up to environmental samples and biological materials like plant materials or animal tissues and foods. The presented results demonstrate the easy and uncomplicated possibilities of calibration via liquid standard solutions compared with reference materials or home standards. The calibration with a single material standard only or even with dried fluid standard solution offers the possibility to analyse elements or materials even if no reference materials are available.
The limits of detection for the shown elements are 0.5 – 10 µg abs. and so, dependent to the weight less than 1 ppm. The reproducibility is in all cases better than 10 % rel.
The ETV-equipment is further more rationalised by an autosampler with up to 50 crucibles and integrated micro-balance.
On the basis of the presented statistical results the power of a modern ETV-ICP-OES device should be evident.