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Electrothermal Evaporation in ICP-OES; Its Development and State-of-the-art Nowadays

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Abstract. ETV-ICP-OES is a well established method nowadays. It is defined as a separate on-line tandem configuration for sample introduction. In graphite furnace a sample is being evaporated and transformed into a dry aerosol by gas phase condensation. This aerosol is being transported to the ICP-torch.
For to achieve satisfying results a lot of innovative research and development work on the furnace design itself, but also for modifier application and temperature control was necessary. Modern power-supply-electronics and microcomputer-control made compact instrumentation possible.
ETV-ICP-OES combinations using special resistance heated graphite furnaces turned out to be one of the best established and dominating method in solid sampling. Commercial solid-state automated systems are available and have proved their suitability in industrial routine labs as well as in numerous research laboratories.
In the meantime a lot of interesting applications have been carried out, one of them will be presented at the end of this article.

Key words: Solid sampling; electrothermal evaporation; ETV-furnace, ETV; ETV-ICP-OES;

Introduction

Electrothermal evaporation systems (ETV) have been object to research and develop-ment for several decades. The idea always was fascinating indeed to analyse solid samples directly without any dilution process with all its problems, possible contaminations and time consumption.

The History of ETV

The history of electrothermal vaporisation starts (Fig. 1) with the Lokyer-furnace in the 70th of the 19th century (Lokyer 1878).

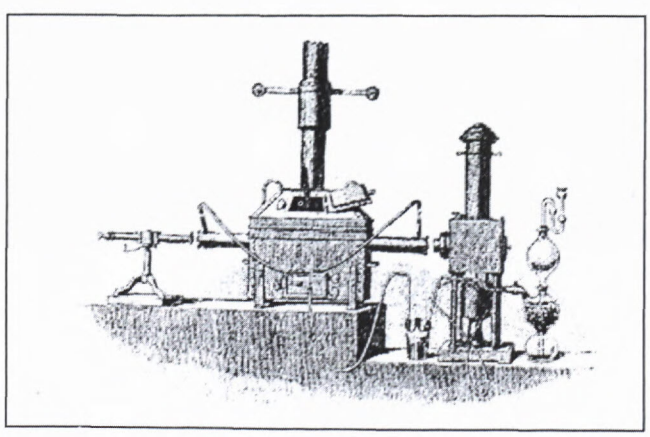

Fig. 1. Lokyer-furnace 1878

Lokyer observed phenomena of atomic absorption at his instrument. The atomiser con-sisted of a coal-heated iron-tube. Hydrogen was used as protection gas, generated by a Kipp generator.

The first real application of an ETV was done by Preuss (E. Preuss 1940). He developed an ETV-device to vaporise easy volatile metals in geological samples to analyse these elements in a DC-Arc. The coupling was made by a tube connection directly to the upper arc-electrode, shaped as a Graphite tube.

Numerous ETV-designs were derived from developments in AAS-furnace systems. So H. Massmann (Massmann 1966) may be considered as the father of graphite-tube ETV-devices and T.S.West (West 1969) as the one of the bridges-, filament- or coil- types. In the beginning of ICP-OES the ETV in first instance was meant as alternative to the sample introduction systems (nebulizers) working not satisfying at that time. By this point of view also the works of A. Fassel (Nixon at.al. 1974) concerning the evaporation by a Tantalum-filament and G. F. Kirkbright (Kirkbright at.al. 1979) concerning an ETV-device using a carbon-bridge were performed. As final stage of the graphite-bridge-furnaces the ETV-system of A.Golloch and M. Haveresch-Kock (Golloch at.al. 1990) may be considered, an ETV using a graphite-bridge and graphite-boats for high weights.

A parallel development of the graphite-bridge-type was the direct connection of the furnace to the aerosol-tube of the torch.

It was started by K. Ohls and B. Hütsch (Ohls et al., 1985) with their first experiments with a direct coupling partly by open funnel-shaped connecting parts.

It was continued by M. Reisch (Reisch et al., 1989) and for the time being finished in a technically advanced way by H. Nickel and Z. Zadgorska (Nickel et. al., 1993) by a ETV-unit with pneumatically operated furnace and direct compound with the aerosol tube.

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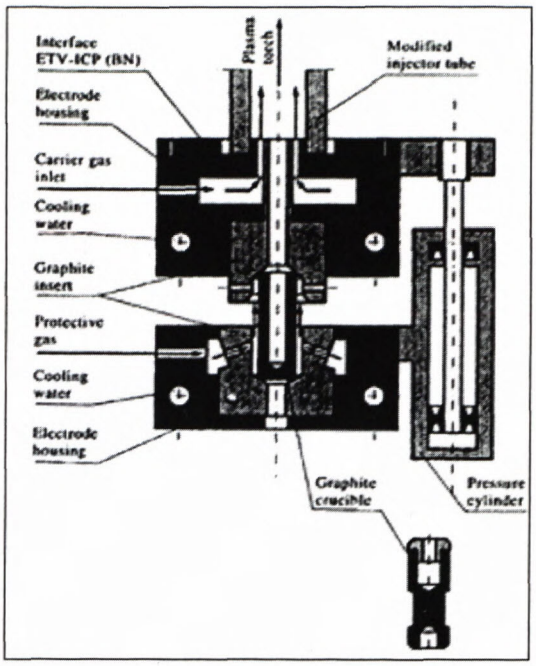

Fig. 2: pneumatic ETV-device Nickel, Zadgorska 1993

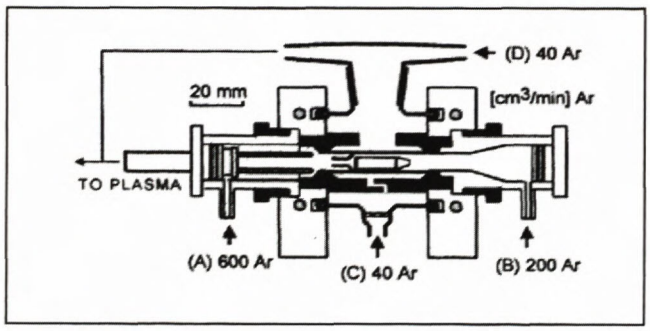

Fig. 3: Kantor-Zaray end on ETV-furnace 1992

In later phases ETV-ICP-OES configurations with graphite tube furnaces mostly used converted AAS-graphite-furnaces from Perkin Elmer for example HGA 74 (Aziz et al., 1981).

Less numerous but at least even successful were adaptations of the solid-sample-AAS-furnaces manufactured by Grün-Optik. (Schäffer et al., 1998).

Decisive pre-works for the development of the commercial ETV-System ETV 4000 (Spectral Systems) were done by T.Kantor and G.Zaray with their modified ETV-furnace (Kantor et al., 1992).

Based on this furnace in several stages of development and by numerous improvements the most modern ETV-system today was created (Hassler et al., 1999).

Development and state of the art of ETV-4000

The furnace based on the Kantor/Zaray-design is a longitudinally resistance heated type in end-on configuration. This means that a graphite tube of about 8mm diameter and 41mm length is heated by an electrical current of up to 400 Amps while a gas flow is being guided through the tube from one end to the other. The sample, that may be solid, dried liquid or dried slurry, is placed on a separate graphite support, a so called boat, in the hot centre of the heating graphite tube. The recleaned boat can be reused many times.

Halogenation: For evaporation high-boiling or carbide forming elements in many cases very high temperatures of more than 2500 °C are necessary. However, for a reasonable life time of the graphite tube the maximum temperature is limited to 3000°C and heating cycles normally should not exceed much more than 2500°C. To overcome this problem in the literature the addition of modifiers like PTFE-powder, carbon tetrachloride vapor or halocarbons has been described. Oxides and carbides by this addition are being transformed into volatile halides (Kantor, 2001). In the described system Freon 12 (CCl2F2) or Freon 22 (CHClF2) are used. These gaseous modifiers are continuously led over the sample while the evaporating process together with the carrier-argon in a con-centration of about 0.5 to 1.5%. So they are present all the time of heating and especially at higher temperatures, in contrary to solid or liquid modifiers, which evaporate and decompose at a certain temperature, mostly between 400 and 1000°C.

Transport efficiency: A transport as complete as possible of the produced aerosol into the ICP-plasma is essential for high efficiency of the process. It has been found that most of the transport losses occur in the first few millimetres downstream the end of the graphite tube. Also the end of the graphite tube itself that is hold by cooled graphite brackets and therefore cooler than the centre of the tube is affected by vapour losses. To overcome this problems a special design of this area was necessary.

A tube in tube construction was developed which the smaller inner tube (nozzle) ends some millimetres outside the end of the heating tube. The evaporated sample flows together with the carrier gas through the nozzle which is hold and connected to the hottest area in the centre of the heating tube and thereby always keeps a relatively high temperature. The end of this nozzle is separated from the end of the alumina transport tube by an alumina transition ring. A ring-shaped gap is formed between the end of the nozzle and the beginning of the transition ring. In this gap an additional argon stream is be-ing introduced (by-pass gas) that forms a boundary layer at the inside of the transport tube shielding it from the hot sample vapour. At the same time both streams are continuously being mixed and a supersaturated relatively cold aerosol is being formed. Additionally, the carbon particles originating from the decomposed Freon help to form condensed aerosol particles. This is an additional important benefit of the halogenation. The flow-relation between both argon streams is electronically controlled and adjustable by MFC´s. So under optimised conditions transport efficiencies of 80% can be achieved.

Temperature control: A graphite tube normally has a life time of several hundreds of cycles. It is clear that by sublimation losses, but also by an in-situ pyrolytic coating caused by the Freon the wall thickness and thereby the electrical resistance and the thermal behaviour of the tube are changing. To get reproducible temperatures a

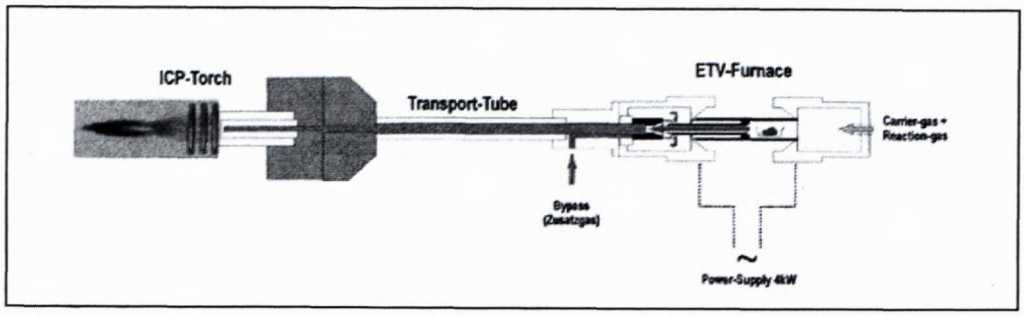

Fig. 4: ETV - ICP – connection

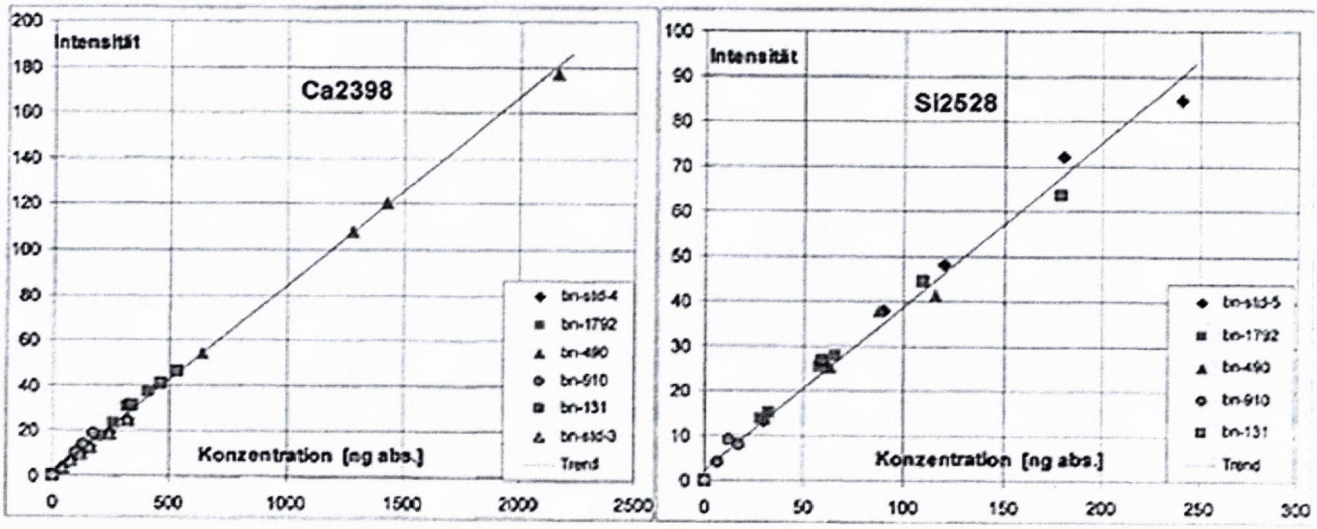

Fig. 5: Calibration functions of Ca and Si for BN-routine analysis

miniature pyrometer was developed to record the temperature of the sample-boat. It was observed that the boat temperature differs essentially from the temperature of the outside of the graphite tube (up to 500°C) so that it is necessary that the pyrometer looks directly onto the boat. The pyrometer is integrated into the control-circuit of the electrical power-supply of the furnace and therefore provides together with the PID-control not only constant temperatures independent from the furnace conditions, but also a fast and precise setting of different temperature levels by the program controller without over-shootings. The temperatures controlled by the pyrometer range between 20°C and 3000°C with a precision of 2%. The furnace thereby allows optimum and reproducible temperature steps for ashing and evaporation of low- and high-boiling elements, and even speciation analysis is possible.

Automatisation: In industrial routine analysis today with hundreds of samples time becomes more and more precious. So the modern laboratory equipment needs to be as automated as possible. For this purpose the ETV-system is equipped with an auto-sampler that is able to handle magazines with 10 or 50 boats automatically. An integrated microbalance is also available. The system is connected to the spectrometer by an interface, so that a stack of max. 50 samples can be run fully automatic.

Experimental results

The experimental results were found by routine analysis of Boron Nitride.

Hexagonal Boron Nitride is a white powder that because of its similarity with graphite in its crystal-structure and its characteristics of lubrication is also known as "white graphite". Boron Nitride is inert against water, doesn't react with acids and acid-mixtures and is not perfused by metals, metallic and non metallic slags. Boron Nitride has a very high temperature-stability in reducing gas-streams up to approximately 2400°C. Furthermore, it is resistant until 1800 °C against carbon and until 700°C against chlorine-gas. It is oxidation-resistant and has a good thermal conductivity. Boron Nitride is an electric insulator in contrast to graphite.

The shown calibration functions in figure 2 (concentrations see table 1) for Ca and Si demonstrate as an example for all other elements the simplicity and high quality of the calibration in the routine analysis of BN by ETV in a relatively large concentration range.

For quality control and statistical evaluation for routine analysis of BN a special analytical procedure was established.

Table 1: Concentrations of calibration standards (BN-home standards) [µg/g]

	fluid std	bn131	bn490	bn910	bn1792
Ca	40	145	732	55,5	127
Si	30	56	49	6,2	19,5

Table 2: Results of the evaluation of 85 runs

Element	set point [µg/g]	actual value [µg/g]	s [µg/g]	RSD [%]
Ca	145	148,1	4,7	3,2
Fe	17,5	16,4	1,3	7,5

Table 3: statistical results

	Dried standard solution				BN - home standard bn910			
element	c ng/µl solution	BM a=001	CCM a=001	RSD_{meth}	c µg/g BN-STD	BM a=001	CCM a=001	RSD_{meth}
Al3082	1	0,101	0,4	1,8	1,8	0,165	2,131	12,2
Ca2112	2	3,005	2,728	4,9	55,5	2,531	10,102	1,9
Cu3247	0,5	0,012	0,318	2,9	0,1	0,049	0,399	41,2
Fe2338	2	0,427	0,671	1,5	3,6	0,638	3,213	9,2
Mg2798	0,5	0,259	0,587	5,3	8,2	0,192	1,713	2,2
Si2528	2	2,678	1,983	4,5	6,2	4,622	3,526	5,9
Zr2734	1	0,166	0,778	3,5	0,5	0,185	0,4	8,3

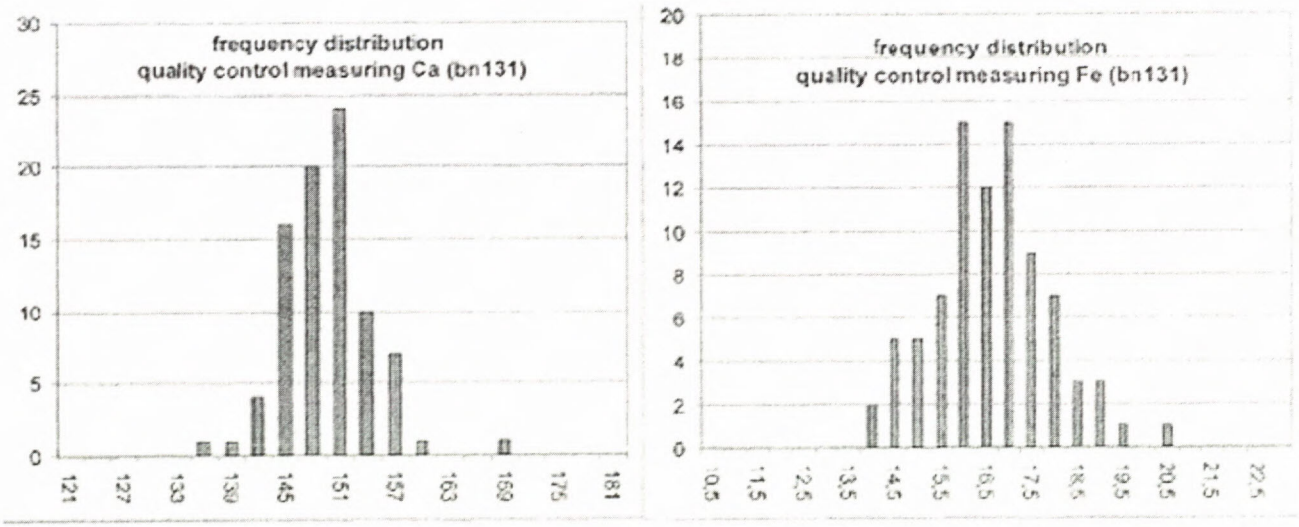

Fig. 6: Frequency distributions of Ca and Fe for 85 single results

For each analysis run of a completely provided 50-boat-sampler 20 boats are used for standards: dried standard solution (6 x) plus 4 BN home-standards (4 x bn1792, 4 x bn490, 3 x bn910, 3 x bn131). The remaining positions normally are used for 10 samples (3 x each).

After the analysis run the measurements are evaluated with an excel-program. As results the calibration functions (graphical and numerical) and statistical data (e.g. mean values, SD, RSD) of standards and samples are presented.

The standard bn131 which is included in the calibration is additionally evaluated like an unknown sample. The results of Ca and Fe (85 runs dated from 01. 03 – 07. 03) are presented as frequency distributions (concentration µg/g).

In table 3 are shown statistical results of the method for some elements/lines like limits of detection (blanc method, BM, calibration curve method, CCM, according to DIN 32645) and RSD_{method}. The values are very convenient for the demands of routine analysis of Boron Nitride.

Conclusion

A modern state-of-the-art ETV-system enables the user to achieve very short analysis times, especially with solid samples, and thereby a significant reduction of analysis costs. Further a reduced calibration expenditure is possible (standards, SRM's or home-standards). The method allows good reproducibility depending on the sample with RSD values of 2-10%. The high transport efficiencies of up to 80% provide high limits of detection (5 - 0.005 ng abs.). Of course by the high sensitivity also clean room conditions are essential for best results.

The highly automated systems (auto sampler) are also easy to handle (maintenance) and rather robust. The

field of applications is extremely wide. Some examples, where the authors have own experience with are: Si_3N_4, SiC, BN, B_4C, graphite, coal, oxides (Al_2O_3, SiO_2), sediments, sludges, plant material, apple leaves, river-cancer, green algae, milk powder (Iodine), hair samples, plastics (electric cables). Further applications are organic and inorganic slurries, tissues, blood, environmental samples, all kinds of biological samples or food, speciation analysis, volatile heavy metals, homogeneity tests. All these applications demonstrate the wide field for practical ETV-ICP analysis. Today the method is well established in numerous industrial as well as in research labs and continuously gets increasing importance in practical analytic work.

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