

Practical experience with the ETV-ICP-MS prototype

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The aim of this study was to evaluate the commercial instrumental connection of the electrothermal vaporization unit (ETV) GF 5000 and the inductively coupled plasma orthogonal acceleration time-of-flight mass spectrometer (ICP-o-TOF-MS) Optimass 9500, both from the company GBC Scientific Equipment (Braeside, Australia). The prototype of the ETV unit was borrowed by the manufacturer for the purpose of its testing in the connection with the ICP-TOF-MS. Information on this technique instrumental arrangement has not been found in the literature yet. Therefore, the facts summarized in this paper are based mainly on our observations. The analytical performance of this technique achieved in our previous work is discussed and compared to competing spectrochemical methods. The attention was paid to the software and technical shortcomings observed within three years of working with this configuration. The influence of shortcomings of the instrument found during testing has been evaluated from the point of view of potential analytical applicability in its entirety and with respect to the economic impact on routine use.

Keywords: ETV-ICP-MS; User evaluation; Software shortcomings; Technical short-comings; Switching valve; Sample dosing monitoring

Introduction

The combination of the detection power of the inductively coupled plasma mass spectrometry (ICP-MS) with the electrothermal vaporization (ETV) as a sample introduction system allows one the analysis of complicated samples in liquid, slurry, and solid form.

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A very small amount of sample (typically 5–40 μl) is sufficient for one analysis. The combination of such techniques significantly improves the already very low limits of detection of the ICP-MS due to a higher analyte transport efficiency to the plasma provided by the ETV. The improvement of operational detection limits is also associated with the ability to analyse less diluted samples. An instrumental connection of this type was firstly published by Park in 1987 [1] as a response to problems associated with traditional sample introduction system realised by a nebulizer and a spray chamber, which suffered from a high spectral background due to the high water load into the plasma. The ETV unit is mostly designed as the resistively heated graphite furnace used as an atomizer for the atomic absorption spectrometry (ETA-AAS) [2,3].

When using the ETV-ICP-MS, the sample is dosed to the graphite furnace by the autosampler. Then, the dosing orifice of the furnace is closed and the temperature program similar to that one used in ETA-AAS can be employed. The first step is a drying to remove the solvent. The pyrolysis step that then follows is used to decompose and eliminate the sample matrix. In the next step, the analyte is vaporized and transported into the ICP-MS by the flowing gas. Entering the ICP-MS, the analyte is ionized and separated by the mass analyser according to the respective mass-to-charge ratio (m/z) and detected [2,4].

Along with a sample, chemical modifiers having several function mechanisms are usually dosed into the graphite furnace. They can thermally stabilize the analyte allowing us to use higher pyrolysis temperatures that lead to a more efficient sample matrix decomposition. On the other hand, they can volatilize the analyte enabling its vaporization at lower temperatures before the vaporization of sample matrix components takes place. For the analysis of refractory elements, the use of volatilization modifiers is often required. Yet another important function of chemical modifiers is an improvement of the analyte transport efficiency [2,5].

The complicated and time demanding optimization of the ETV-ICP-MS working conditions did not allow the ETV to become a routine sample introduction system for the ICP-MS. The potential of the ETV for reducing polyatomic spectral interferences in the ICP-MS has been overcome by the arrival of mass spectrometers with the sector analyser providing a high resolution sufficient enough to eliminate most spectral interferences. The implementation of the collision / reaction cells to the design of new quadrupole-based instruments also contributes to the suppression of spectral interferences. Nebulizers with improved efficiency suitable for smaller samples analysis are also available. As well as the systems allowing to dose small and discrete volume of sample, such as the device for flow injection analysis (FIA) can be used. For the ICP-MS analysis of slurry samples, nebulizers of the Babington and Burgener design directly connected to the plasma torch are being chosen. However, the ETV is not a typical sample introduction system for routine use ICP-MS, it still plays an important role in the analysis of complicated samples. Since the ETV-ICP-MS is

not common analytical technique, its commercial availability is quite limited. Most of the instrumental connections used in the literature were home-made systems assembled from the ETV unit and the ICP-MS from different manufacturers. The ETV systems commercially available nowadays are ETV GF 5000 (GBC), ETV HGA 610 MS (Perkin Elmer) and ETV 4000C (Spectral Systems) [2,6–8].

Materials and methods

In this work, the inductively coupled plasma orthogonal acceleration time-of-flight mass spectrometer (ICP-o-TOF-MS) GBC Optimass 9500 in the connection to the electrothermal vaporisation unit GF 5000 (both GBC Scientific Equipment, Braeside, Australia) was used. The connection of these two instruments was realized using the Tygon® tube (with a length of 100 cm and inner diameter of 4 mm) from the company Saint-Gobain (Paris, France). The ETV unit was equipped with classical pyro-coated graphite tubes. For the introducing of samples, the PAL AutoSampler 3000 with the quartz dosing capillary QC-3000-Kit with the inner diameter of 500 µm was used; all this set-up being purchased from GBC Scientific Equipment (Braeside, Australia).

Results and discussion

In this study, the new and for-sale intended instrumental connection of the ETV unit with ICP-o-TOF-MS configuration was evaluated. The prototype of the ETV unit was borrowed by the manufacturer for the purpose of its testing. The analytical performance of this technique achieved in our previous work is discussed and compared to competing spectrochemical methods. During the three years' time period of working with the instrumentation ETV-ICP-o-TOF-MS from the GBC company, several shortcomings regarding the instruments control and the technical design of the ETV unit were noticed. The influence of shortcomings of the instrument ascertained during testing was evaluated from the point of view of potential analytical applicability in its entirety and with respect to the economic impact on routine use of this technique.

Analytical performance of the ETV-o-TOF-ICP-MS

The title instrumentation as a particular set-up was used in our two previous studies on the analysis of thallium [9,10]. In the first one, the analytical performance of ETV-ICP-MS was evaluated and compared to other spectrochemical methods such as classical ICP-MS equipped with a nebulizer and a spray chamber for the analysis

of solutions and the high-resolution continuum source graphite furnace atomic absorption spectrometry adapted to solid sample analysis [9]. Although the ICP-MS instrumentation is mainly used for multi-elemental analysis, Tl was used to test the analytical performance of ETV-ICP-MS in the comparative study. In ICP-MS, Tl is considered to be a problem-free element in terms of possible non-spectral interference. From the point of view of ETV and GFAAS, this element is more complicated to be analysed because of its volatility. Therefore, Tl enabled our focusing exclusively on ETV issues. In our second work [10], we dealt with the influence of the analyte transport efficiency modification on the performance of ETV-ICP-MS. The transport efficiency modifier based on carbon microparticles was newly proposed and tested. In this case, Tl was used from the above mentioned reasons. Gold was used as the analyte, too. Au is easily analysed using both ETV/GFAAS and ICP-MS and enabled to follow the analyte transport process clearly. The external calibration based on aqueous standard solutions of Tl was used for quantification for all the methods. For the solution ICP-MS analysis, the internal standard of In was added.

The figures of merit presented in Table 1 are based on experiments carried out within our previous works, i.e. for the ICP-MS and SS-HR-CS-GFAAS from the study [9], for the ETV-ICP-MS and SI-ETV-ICP-MS from [10]. Over several measurement sequences, the recovery (in percent as a ratio of the found concentration with respect to the theoretical concentration) and the reproducibility (as the relative standard deviation, RSD) were obtained from the repetitive analysis of standard solutions of Tl (ICP-MS 0.01, 0.1, 1; ETV-ICP-MS methods 0.05, 0.1, 0.5 and SS-HR-CS-GFAAS 3, 5, 10, all in $\mu\text{g L}^{-1}$). The instrumental limit of detection (LOD_i) for ICP-MS employing methods was calculated as the concentration related to the three times the standard deviation of the integrated peak area measured near the monitored ion peak for the Tl standard solution ($0.01 \mu\text{g L}^{-1}$ of Tl, $n = 10$). The LOD_i for SS-HR-CS-GFAAS was estimated as the concentration related to three-fold value of the standard deviation of the signal measured for the Tl standard solution ($1 \mu\text{g L}^{-1}$, $n = 10$). The procedural limits of detection were calculated by multiplying the LOD_i by the dilution factor coming from the sample preparation. The absolute detectable amount of analyte was calculated by multiplying the LOD_i by the dosed amount of sample ($20 \mu\text{l}$) [9]. The results obtained for Tl in the certified reference materials BCR 679 (white cabbage) and GBW 10052 (green tea) complied with the certified values [9,10]. Therefore, it was assumed that no serious non-spectral interferences occurred using the optimized working conditions.

Time demands of the entire analytical procedure (Table 1), including sample preparation and analysis of two sample blanks and three samples, were evaluated for Tl determination in spruce needles [9]. The first step identical for all the methods was a cutting and drying of the spruce needles (24 hours) which was not included in the comparison.

For the ICP-MS analysis of solution, the sample was digested (in microwave oven by 65% HNO₃) and diluted including the addition of the internal standard. The ETV-ICP-MS analysis required only the microwave digestion. For the ETV-ICP-MS analysis of slurry, the sample was homogenized (in cryogenic mill by liquid nitrogen) and slurried in 0.1% Triton X-100. The SS-HR-CS-GFAAS required only the sample homogenization step [9].

Table 1 Analytical figures of merit of four spectrochemical methods used for the analysis of thallium [9,10]

Parametr	ICP-MS	ETV-ICP-MS	SI-ETV-ICP-MS ^a	GF-AAS
Time demands [min] ^b	135	195	150	135
<i>R</i> [%] ^c	104–107		100–111	103–124
<i>RSD</i> [%] ^c	1.9–2.4		2.9–6.7	0.17–3.3
<i>LOD_i</i> [ng L ⁻¹] ^d	0.22	0.026	0.026	1200
<i>LOD_p</i> [μg kg ⁻¹] ^e	0.18	0.0021	0.0043	1.2
<i>LOD_a</i> [fg] ^f	–	0.52	0.52	1200

^a Slurry analysis using ETV-ICP-MS

^b Time demands of entire analytical procedure including sample preparation and analysis of two sample blanks and three samples

^c Recovery and relative standard deviation calculated for standard solutions of Tl under conditions of reproducibility ($n = 5$)

^d *LOD_i* – the instrumental limit of detection ($n = 10$)

^e *LOD_p* – the procedural limit of detection ($n = 10$)

^f *LOD_a* – the absolute detectable amount of analyte ($n = 10$)

Each sample was measured in two replicates using ETV-ICP-MS methods and in three replicates using ICP-MS and SS-HR-CS-GFAAS

From the analytical characteristics given in Table 1 it is evident that the main advantage of ETV-ICP-MS is its detection capability, especially, in the case of slurry analysis. On the other hand, when the sensitivity is not a crucial factor for specific analytical task, the classical ICP-MS solution analysis along with a sample decomposition seems to be a better choice. The time requirements for analysis of one-sample sequence are not very different. The time required for the method development is however dramatically different. For ICP-MS analysis, it is usually a few tens of minutes. In the case of ETV-ICP-MS, the required time is in the range of days or even weeks. The HR-CS-GFAAS for analysis of solid samples is then somewhere in the middle and, in this case, the sample decomposition step is completely avoided. The time requirements for the method development are in the range of days, too, but there is more information in the literature available to make this process more reliable and routine. It can be concluded that the analysis using ICP-MS in solution is of choice when only a small number of similar samples is to be analysed.

When there is a large number of a sample to be analysed, ETV-ICP-MS and CS-HR-GFAAS can be considered. The time invested in the method development is compensated by avoiding or simplifying the sample preparation process [9].

Software shortcomings

Several drawbacks of the software for controlling the ETV-ICP-MS, which makes work difficult and unpleasant, were observed. The Optimass 9500 2.2_b1 software is controlling the ETV-ICP-MS instrument.

Monitoring of the time resolved signal throughout the temperature programme

During the optimization of the ETV unit temperature programme and an amount of a modifier used, the intensity of selected isotopes is usually monitored in the time throughout the entire temperature programme including pyrolysis step. This approach has been used in many cases reported in the literature [11–13]. In this way, it is possible to obtain not only the optimum pyrolysis and vaporization temperatures, but also an overview on analyte losses during the temperature program before the start of the vaporization step and the signal acquisition. The ability to monitor these losses could help speed up and refine the whole optimization process. In the case of our software, the time dependent measurement of the intensity of selected isotopes throughout the entire temperature programme was not possible due to two reasons. Firstly, the total signal acquisition time for selected analytes could only be set within the analytical sequence during which ETV and ICP-MS mutually interact. Thus, the result was only the total signal intensity, the mean peak area related to one second of acquisition and the total peak area. No data describing the signal profile in time was available. Secondly, the beginning of the signal acquisition was firmly connected to the start of the vaporization step. The GBC Optimass 9500 mass spectrometer alone allows one to record the signal intensity of selected analytes in time. For this function, a separate service panel is reserved in the software where any combination of the acquisition time (minimum 0.001 s) and the number of measurements are to be made (in replicates) can be set. By combining the appropriate setting of these two parameters, an analyte signal record can be obtained over time with selectable time resolution. However, running of the ETV temperature program sequence is not possible in this mode and using this software version. ETV can only be run in the analytical mode, in which it is not possible to record the signal intensity of the analyte in time. The total duration of the vaporization step must be set as the signal acquisition time. In this case, the number of replicates was equal to the number of firings performed in the ETV, thus having had a constant value of 1 within one temperature program.

The dosing order of sample and modifier

From experiences with ETA-AAS, it is evident that the order of modifier and sample dosing may have a significant impact on the modifier proper function. A modifier can be dosed into the graphite furnace first and then dried to modify the inner surface of the graphite furnace before dosing a sample. This approach has been used, for example, in the work of Husáková et al [14].

However, the current software version for ETV-ICP-MS does not allow us gradual and multi-step modifying, as well as the sample dosing; the latter procedure having begun by aspirating of the modifier. Then, the dosing capillary is rinsed and sample sucked. Next, the aspirated material is dispensed into the graphite furnace in one step, e.g. the sample and modifier at once. The software enables repeated dosing of a sample and modifier during the sample thermal decomposition steps of the temperature programme. It was also possible to dose only a sample during the initial dosing sequence with the later dosing of a separate modifier. However, this is impossible in the opposite order. In the software, each start of new sample analysis is firmly associated with the dosing of a sample into the graphite furnace. In our previous work focused on the analysis of Tl using ETV-ICP-MS [9], it was found that the modifier (the mixture of Pd and citric acid) worked in the best way if it was dosed into the graphite furnace and dried before sample. With the current version of the ETV-ICP-MS software, such a dosing procedure is not available. To use this, it was necessary to choose a very impractical and for the operator demanding procedure. The dosing of the modifier and sample was set in the software to be done in the default way as described above. However, the sample vial was removed from the autosampler carousel before being aspirated by the dosing capillary. Only the modifier was left to come into the dosing capillary, then dispensed into the graphite furnace and subsequently dried. The surface of the graphite furnace was thus prepared for a sample to be dosed. In the meantime, the sample vial was placed back on its original position in the autosampler carousel by the operator. Afterwards, the repeated sample dosing step, which was set in the software, was performed.

Technical shortcomings of the ETV unit

The possibility of monitoring of the dosing process

From a point of view of design, there are two major drawbacks associated with the ETV unit GF 5000. The first one is the absence of the ability to control the position of the dosing capillary in the graphite furnace and the actual dosing process assisted with the built-in camera. It has a direct impact on the quality of the analysis. This function is a standard procedure in the case of ETA-AAS systems before starting a new sample sequence analysis. In our case, the ETV unit

had to be partially dismantled in order to monitor the dosing process during the optimization at least with a dental mirror. This process could hardly be performed on a daily basis and it was usually performed once a week. However, it has proven to be inadequate. Sometimes, after several successful dosing of the sample, another sample was dosed partially on the outer surface of the graphite furnace. This problem occurred when a drop of the sample was left hanging at the tip of the dosing capillary after dosing the sample was dosed. During the ejection of the capillary out of the graphite furnace, the hanging drop was captured by the edge of the dosing orifice or on the outer surface of the graphite furnace. Furthermore, the outer surface of the dosing capillary can change during longer sample sequences, a drop of a sample would climb up the outer surface of the capillary to be subsequently entrapped on the outer surface of the graphite furnace. This problem could be solved by careful cleaning the dosing capillary surface with a filter paper soaked in ethanol during analysis. Due to the absence of the built-in camera, the dosing was observed at least from above by a naked eye to check the quality of the procedure. The ETV-ICP-MS instrumentation was continuously supervised by the operator to indicate the wrong sample dosage and to exclude hardly explainable differences in the results for the same sample measured in two replicates.

The switching valve

In the ETV unit GF 5000, a switching valve at the outlet of the carrier gas from the ETV to ICP-MS disconnecting the carrier gas flow passing through the graphite furnace towards the ICP-MS is not built-in. This function is usual in the pretreatment steps of the temperature program and the cleaning step. Thus, the carrier gas from the ETV only flows into the ICP-MS system during the sample vaporization step when the signal is being acquired in the mass spectrometer. This significantly reduces the load of pyrolysis products coming from the ETV to the ICP-MS and diminishes the transport tube clogging. The switching valve is, for example, incorporated in the ETV unit HGA-600MS from the Perkin Elmer [2]. In the case of the ETV used in this work, pyrolysis products clog the transport tube. The deposit onto the inner walls of the transport tube is mainly a layer from carbon particles formed during the pyrolysis of the sample or released from the graphite furnace itself. The problem with clogging of the transport tube was, however, relatively easy to solve by its leaching in 2M HNO₃ under the simultaneous sonicating and followed by rinsing with redistilled water.

Effect of the load of pyrolytic products on sensitivity and resolution

The load of pyrolytic products coming from the ETV into the ICP-MS did not have a negative impact on the analytical performance of this technique. No undesirable deposition of carbon particles in the plasma torch injector tube was noticed. The major problems were caused by the pyrolytic products in the interface connecting the atmospheric pressure and vacuum parts of the mass spectrometer. The interface is composed of three cones (Sampler, Skimmer 1 and Skimmer 2) between which the vacuum gradually raises. The load of pyrolytic products results in a significant shortening of the life span of the third cone (Skimmer 2) due to the widening of its orifice caused by gradual abrasion by carbon particles whose motion is accelerated by the pressure gradient. The deterioration of the third cone orifice brings a gradual loss of sensitivity and resolution. The intensity 60000 counts per second and the resolution 2000 for the ^{238}U isotope measured in the uranium standard solution of the concentration $1 \mu\text{g L}^{-1}$ are considered as the optimal working conditions of the ICP-MS used in this work. It was noticed that after the first month of the connection with the ETV unit, the intensity dropped to 40000 counts per second and resolution down to 1700. These conditions remained relatively stable for about next three months. At the end of such a time period, the intensity was around 30000 counts per second and the resolution around 1500. During the next month, the intensity dropped below 20000 counts per second and the resolution decreased to 1300.

Effect of the load of pyrolytic products on a life span of cones

When liquid samples are introduced using a nebulizer and a spray chamber, the lifetime of the third cone is several years. Even a few days of the ETV unit use has a noticeable negative impact on the quality and condition of the third cone. To carry out a solution analysis using a nebulizer and a spray chamber after the mass spectrometer had been used for a long time in the connection to the ETV, it was advisable to replace the third cone for this purpose in order to obtain better analytical performance. If the mass spectrometer is to be used mainly for solution analysis, it is necessary to exchange the third cone and thus avoid its deterioration even from a short-term ETV analysis. Therefore, it is necessary to use a special third cone reserved for the ETV analysis only. It should also be noted that the access to the interface and the cone disassembly plus the subsequent assembly are not user-friendly procedures in the case of the Optimass 9500 mass spectrometer, which makes it a considerably time-consuming process.

The above mentioned effect of the pyrolysis products was not observed for the second cone (Skimmer 1), but the life span of the first cone (Sampler) was negatively affected, too.

Thermal stress due to the closeness of the ICP unit in combination with the bombardment by carbon particles had resulted in several tiny holes forming around the orifice of the cone and occurring after about one year of its usage. As a result, the signal intensity decreased due to the disruption of the ion beam formation caused by the turbulent flow in the space between the first and second cone because of the air suction through the holes. Until these holes were formed, the increased wear of this cone had no negative effect on the ICP-MS analytical performance. During the four-year work, three cones were worn in this way. Compared to traditional nebulization of liquid samples, this fact also confirms the hypothesis about the negative influence of the ETV.

Effect of the load of pyrolytic products on a high voltage discharge

The pyrolytic products also pass through the third cone into the ion optics. A high voltage of about 1000 V is applied to the third cone during analysis. Therefore, the platform on which the third cone is mounted must be isolated from the mass spectrometer body. The insulation is made of a special electro-insulating polyetheretherketone (PEEK) element. The pyrolytic products gradually form a thin layer of carbon particles onto the surface of the insulating element. As a result, a high voltage discharge causing damage to the PEEK insulating element occurred. It led to an immediate loss of voltage on the third cone, which prevented the proper focusing of the ion beam. During the four years of the use of the ETV unit in connection to the ICP-MS, this problem has settled two times, which strongly points to the ETV to be the source of this defect. There is a lot of experience with the GBC Optimass spectrometers at the workplace where this work was created. Before the Optimass 9500, the previous model Optimass 8000 was operated for a long time and a similar problem with a high voltage discharge in the ion optics was never noticed.

Effect of the pyrolytic products on the economy of the ETV-ICP-MS operation

The absence of a switching valve in the ETV does not affect the quality of analysis and the reliability of the results. However, from an economy point of view of using this technique, it leads to several problems increasing operating costs. It is necessary to change the consumable components of ETV-ICP-MS more frequently for ensuring optimal analytical conditions.

The switching valve – yes or no?

On the other hand, the absence of the switching valve causing the load of pyrolytic products to ICP-MS can be seen beneficial from the point of view of the analyte transport efficiency. The most significant analyte losses take place just in the switching valve. Gregoire and Sturgeon [15] reported on those losses to be 70 % for the ETV unit Perkin Elmer HGA-600 MS equipped with a switching valve. The entrapment of such an amount of analyte at that place can also pose a risk of the memory effects. At first glance, such high losses seem quite serious. However, a significant improvement in sensitivity provided by the ETV should be taken into account, as shown in Table 1. The procedural limit of detection for Tl using the ETV-ICP-MS for the analysis of solutions and slurries was approximately by two orders of magnitude lower (0.0021 and $0.0043 \mu\text{g kg}^{-1}$) than the limit of detection estimated for classical solution analysis using ICP-MS ($0.18 \mu\text{g kg}^{-1}$). Due to the above-mentioned serious problems caused by the absence of the switching valve, its use in the ETV unit is desirable from the perspective of the technique and its long-term and economical operability.

The decrease of sensitivity caused by the lowered analyte transport efficiency does not seem to be a sufficient reason not to incorporate the switching valve into the ETV unit.

Conclusions

The positive and negative aspects of the instrumental connection of the ETV unit GF 5000 with the Optimass 9500 mass spectrometer from the GBC were evaluated in this study. Besides the focus on the analytical performance of the technique given, a lot of experience with its practical operation has been gained. The ETV unit used was a prototype whose construction, when the control software had corresponded to the beginning of working with this technique. The beta-version of the ETV-ICP-MS control software was obtained by modifying the software designed to control the mass spectrometer itself. Shortcomings had been found on the side of the control software, which had a negative impact on exploiting the full potential of this technique under user-friendly operating conditions and on its use for routine analysis purposes. The increase of the operational costs caused by the absence of the switching valve resulting in clogging of the ICP-MS with pyrolysis products also speaks against the routine use of this technique with the ETV unit of the current design.

The facts stated in this work could not have been discussed with the literature, as this particular instrumentation had not been yet operated at any other workplace. For this reason, the study should be seen as a user's experience.

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