Analytica Chimica Acta 648 (2009) 23–44

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Review

Electrothermal vaporization–inductively coupled plasma-mass spectrometry: A versatile tool for tackling challenging samples
A critical review

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ARTICLE INFO

Article history:
Received 17 April 2009
Received in revised form 10 June 2009
Accepted 11 June 2009
Available online 18 June 2009

Keywords:
Electrothermal vaporization
Inductively coupled plasma-mass spectrometry
Solid sampling
Review

ABSTRACT

In this review, the literature on the subject of electrothermal vaporization–inductively coupled plasma-mass spectrometry (ETV–ICP-MS) published during the last decade is reviewed with a double purpose: an evaluation of the possibilities of this technique for dealing with very challenging analytical applications on the one hand, and the establishment of a reference guide for method development in ETV–ICP-MS on the other. First, a brief introduction, pointing out the milestones in the development of the technique will provide the reader with a better understanding of the present situation of ETV–ICP-MS and its future perspective. After a section on the basic processes occurring in the furnace and during analyte transport, a guide for method development for challenging analytical applications is proposed, based on the existing literature. Next, the latest contributions in the main application areas of the field are reviewed, with special attention to the most challenging ones: i.e. speciation, "thermal" resolution, enabling complex matrixes to be analyzed and spectral overlap to be avoided, and the direct analysis of slurries and solid samples. Finally, the advantages obtained by coupling an ETV unit to newer types of ICP-MS instrumentation, equipped with collision/reaction cells, time-of-flight (TOF) or sector field (SF) spectrometers, are also discussed.

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doi:10.1016/j.aca.2009.06.027

1. Introduction

Since the commercial introduction of ICP-MS, the development and improvement of sample introduction systems has been one of the main challenges for the scientists working in this field [1]. Since the beginning, sample introduction was carried out *via* pneumatic nebulization, which offered a simple and fast means of sample handling, relatively good stability, potential for automation and low cost. However, some negative aspects were also associated with this sample introduction system and, therefore, the efforts devoted to improving this part of the technique were well justified.

Very soon after the first ICP-MS paper appeared in the literature [2] (in 1980) and the first commercial instruments became available (in 1983), Gray and Date – some of the first scientists involved in the very early research in ICP-MS – pointed out the problem of high background signals coming from the water vapor introduced as a part of the nebulized aerosol and suggested that "the technique would benefit from the application of "dry" sample introduction techniques, including electrothermal atomization" [3]. Some months later, they described the coupling of an electrothermal vaporizer to an ICP-MS instrument for the first time [4], using a commercial vaporizer originally designed for coupling with an inductively coupled plasma-optical emission spectrometer (ICP-OES) [5].

ETV–ICP-MS was received with great enthusiasm by the scientific community owing to the potential advantages that the coupling could bring along. Besides the possibility to separate the volatilization of the sample matrix and that of the analyte in time (with the subsequent reduction of both spectral and non-spectral interferences), the sample introduction efficiency could be clearly improved compared to pneumatic nebulization (the efficiency of which is only about 1–2% [4]), improving even more the limits of detection (LODs) attainable. Only low sample volumes were required for analysis and the possibility for analyzing very demanding samples such as organics, slurries and even solid materials existed. This encouraged scientists to work on and with ETV–ICP-MS.

In 1985, the first ETV device specifically designed for working with an ICP-MS was presented by C.J. Park in his PhD thesis [6]. From this moment on, some publications related to ETV–ICP-MS started to appear in the literature. They mainly contained general descriptions of the technique's features and some applications, using Park's device or other in-house modified atomic absorption spectrometry (AAS) or ETV–ICP-OES vaporizers. A nice overview of the situation and papers presented in this first period can be found in [7].

Attracted by the optimistic conclusions reported in these works, some scientific manufacturers developed and commercialized ETV devices for combination with ICP-MS in the beginning of the 1990s [7]. This had a dramatic influence on the number of papers published on the topic in the following yeas, as can be seen in Fig. 1A. In 1992, the number of publications per year was doubled with respect to the papers published in 1991; and in 1994, the number of publications was five times higher (at that moment it was estimated that more than 100 commercial electrothermal vaporizers had been sold worldwide [8]). From this moment on, the rate of ETV–ICP-MS publications per year has only undergone few changes, with a limited but steady number of contributions in-between 20 and 30 per year. However, by considering the tremendous increase in the number of ICP-MS-related publications in the same period [9], one can easily see that ETV–ICP-MS has been attracting less attention from the scientific community than in the period in which it was first introduced.

This situation contrasts with the highly optimistic predictions of most of the scientists actively working in the field of ETV–ICP-MS in the beginning of the technique's life. On the 4th Surrey Conference on Plasma Source Mass Spectrometry in 1991, e.g., D.C. Grégoire foresaw an "unusually rapid popularization of ETV–ICP-MS among ICP-MS users" [10]. In fact, this "rapid popularization" never took place. The reasons were many. On the one hand, scientists realized that working with ETV–ICP-MS was not so straightforward and required a higher level of expertise. The work presented by D.J. Gray and coworkers in 1994 [11], stressing the need for careful optimization of the working conditions in ETV–ICP-MS in order to compensate for the different factors affecting stability and sensitivity with this technique, illustrates this statement. On the other hand, and also in the same period, important improvements in other sample introduction systems for ICP-MS were also accomplished (as reflected, for instance, in a special issue of Spectrochimica Acta Part B published in 1995, entirely devoted to advances in sample introduction in spectrochemistry [12]). As a result, some of the former "unique" ETV features, such as the capability of analyzing small sample volumes, were then matched and even surpassed by the newly developed introduction devices (e.g., microflow nebulizers), which, additionally, were in most cases easier to use than ETV. In fact, the actual market trends reflect this situation quite clearly, as several companies now produce these "alternative" introduction systems and, to the best of the authors' knowledge, only one company is still manufacturing ETV units [13]. Also the evolution of ICP-MS instrumentation has contributed to the decline of ETV, as the feasibility of ETV systems to reduce some polyatomic interferences in ICP-MS was no longer a prime advantage since sector field ICP-MS instruments and quadrupole-based units equipped with collision/reaction cells were introduced onto the market. A combination of all these factors caused the analytical domain of ETV–ICP-MS to be considerably reduced in favor of some competing techniques, as summarized in Table 1.

These circumstances led to a noteworthy change in the original perspective on the position of ETV–ICP-MS in the beginning of the 2000s. ETV was no longer considered as a potential "standard" sample introduction system for ICP-MS, but its use was rather reserved to cope with particularly challenging analytical problems that could not be tackled easily with other strategies. This consideration is still valid today. An excellent review in this direction was written by Sturgeon and Lam in 1999 [14]. In their paper, also the feasibility of using chemical modifiers or other reagents used in electrothermal atomic absorption spectrometry (ETAAS) and ETV–ICP-OES to alter the volatility of either the analyte or the concomitant matrix in ETV–ICP-MS was highlighted, presenting the ETV as a *thermochemical reactor* for ICP-MS sample introduction. As indicated by these authors, this approach might alleviate space–charge matrix effects, minimize polyatomic ion interferences, permit direct speciation of trace element fractions in samples, as well as serve as a crucible for sample preparation. These outstanding features can explain why, in spite of the new sample introduction systems cited in Table 1 and