

# Linearization of calibration curves by aerosol carrier effect of CCl<sub>4</sub> vapor in electrothermal vaporization inductively coupled plasma mass spectrometry<sup>☆</sup>

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## Abstract

Carbon tetrachloride vapor as gaseous phase modifier in a graphite furnace electrothermal vaporizer (GFETV) converts heavy volatile analyte forms to volatile and medium volatile chlorides and produces aerosol carrier effect, the latter being a less generally recognized benefit. However, the possible increase of polyatomic interferences in inductively coupled plasma mass spectrometry (GFETV–ICP–MS) by chlorine and carbon containing species due to CCl<sub>4</sub> vapor introduction has been discouraging with the use of low resolution, quadrupole type MS equipment. Being aware of this possible handicap, it was aimed at to investigate the feasibility of the use of this halogenating agent in ICP–MS with regard of possible hazards to the instrument, and also to explore the advantages under these specific conditions. With sample gas flow (inner gas flow) rate not higher than 900 ml min<sup>-1</sup> Ar in the torch and 3 ml min<sup>-1</sup> CCl<sub>4</sub> vapor flow rate in the furnace, the long-term stability of the instrument was ensured and the following benefits by the halocarbon were observed. The non-linearity error (defined in the text) of the calibration curves (signal versus mass functions) with matrix-free solution standards was 30–70% without, and 1–5% with CCl<sub>4</sub> vapor introduction, respectively, at 1 ng mass of Cu, Fe, Mn and Pb analytes. The sensitivity for these elements increased by 2–4-fold with chlorination, while the relative standard deviation (RSD) was essentially the same (2–5%) for the two cases in comparison. A vaporization temperature of 2650 °C was required for Cr in Ar atmosphere, while 2200 °C was sufficient in Ar+CCl<sub>4</sub> atmosphere to attain complete vaporization. Improvements in linear response and sensitivity were the highest for this least volatile element. The pyrolytic graphite layer inside the graphite tube was protected by the halocarbon, and tube life time was further increased by using traces of hydrocarbon vapor in the external sheath gas of the graphite furnace. Details of the modification of the gas supply for HGA-600MS furnace and the design of the volatilization device are described.

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## 1. Introduction

The effects of halocarbon vapors (Freons, CCl<sub>4</sub>, etc.) mixed to the internal argon flow of a graphite furnace

electrothermal vaporizer (GFETV), that is coupled to inductively coupled plasma (ICP) excitation–ionization source, have been recently reviewed in [1]. Accordingly, the most generally observed effect of these gaseous phase modifiers manifested in the production of halogenating species from about 500 °C that convert the analytes and/or matrices from heavy volatile chemical forms to volatile and medium volatile fluorides or chlorides.

In an earlier work [2], with the use of a GFETV–Flame atomic absorption spectrometry (AAS) system, increase of transport efficiency for Zn with the use of CCl<sub>4</sub> vapor in the

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furnace gas was observed, and explained by the generation of carrier aerosol particles from the halocarbon. This interpretation was based on the studies with  $\text{CCl}_4$  vapor in a plasma reactor, reported by Kana'an et al. [3]. They elucidated a partial polymerization of halocarbon radicals in the cooler parts of the reactor that yielded yellow colored solid particles, from which perchloro benzene ( $\text{C}_6\text{Cl}_6$ ) was identified. It can be expected that this kind of processes take also place in a graphite furnace with increasing temperature from 500 to 600 °C, the final decomposition product being carbon soot above 1000 °C. The mixture of these solid particles has been supposed to be an effective carrier in the observed improvements of transport efficiency [2,4]. Increase of the transport efficiency with the use of different Freons found for GFETV–ICP optical emission spectrometry (OES) [5,6] and GFETV–ICP mass spectrometry (MS) systems [7–10], have also been related in part to the generation of carrier particles.

Although it is logically supposed that improvements in the transport efficiency are manifested also in improved linearity of the calibration curves, it seems worthwhile to study this relationship more explicitly, which is the subject of the present paper with the use of  $\text{CCl}_4$  vapor. Non-linear characteristics of the calibration curves with the use of ETV sample introduction obtained in the absence of matrix or modifier have been observed in the early work of Millard et al. [11], and was further investigated and explained in [2,9,12–14]. Accordingly, the bending of the calibration curve to the signal axis is the result of the increasing transport efficiency with increasing amount of vaporized substance, which is typically the case when matrix-free solution standards are applied in at least two orders of magnitude concentration ranges. The non-linearity is the most severe for MS signals in the available lowest concentration ranges, but it is also significant in higher concentration ranges covered by flame-AAS and ICP-OES detection.

Roles of the chemical modifiers in ETV can involve the covaporization of the analyte and the modifier thus yielding a carrier effect. This effect is explained by considering that the vapor of the modifier nucleates to a higher extent (due at least to its higher vapor concentration) than the analyte vapor and the latter can physically condense onto the modifier nuclei. Ediger and Beres called this phenomenon a *physical carrier effect* [9].

In aerosol science, the term *chemical condensation* is used to the case when a less volatile compound is formed by a chemical reaction in the vapor phase, which results in a significant increase of self-nucleation–condensation of vapor. The possible role of this kind of process in the ETV methods is discussed in [2,13] and the term *aerosol carrier effect* has been suggested for a more general use, if the physical or chemical nature of the process is unknown or not to be described [1,14].

The above mechanism with respect of the limited nucleation of the analyte vapor applies typically to the relatively volatile elements (especially to As, Cd, Zn, etc.)

[2], for which the cooling of the vapor–gas mixture within the graphite tube (considering end-on streaming of the vapor) is not sufficient for an effective nucleation of the vapor. However, bending the calibration curve to the signal axis has been observed also to medium volatile elements, such as, e.g. Co, Ni, Fe, Mn, Cu, Ga [9,15]. As proved by Schäffer and Krivan [15] and studied further in [16] for low volatile elements (e.g. Cr, Ba, Ti, V), the vapors of these elements partially undergo physical condensation or chemical deposition in the cooler end of the graphite tube (end-on streaming). It is a question whether any change is required in the interpretation of calibration curve bending for these less volatile elements.

In the present work, the linearity of the calibration curves will be investigated for five elements including volatile (Pb), medium volatile (Cu, Fe, Mn) and heavy volatile (Cr) elements under conventional GFETV–ICP–MS conditions, in comparison with the use of  $\text{CCl}_4$  vapor in the furnace internal gas (Ar).

## 2. Experimental

### 2.1. ICP-MS equipment

The Elan 5000 Perkin-Elmer ICP-MS instrument (Perkin-Elmer Sciex, Concord, Ontario, Canada) was used. The data acquisition was made by means of the ICP-MS software, version 2.2. The experimental parameters are shown in Table 1. The ion optics lens settings were adjusted by following the manufacturer's instructions to provide the optimum signal for Rh with  $\text{CeO}^+/\text{Ce}$  and  $\text{Ba}^{2+}/\text{Ba}^+$  ratios below 3%. A cross-flow nebulizer coupled to a Ryton double pass spray chamber was employed for the conventional ICP-MS set-up procedure prior to the ETV sample introduction.

### 2.2. ETV sample introduction system

The electrothermal vaporizer was a model HGA-600MS (Perkin-Elmer Sciex, Concord, Ontario, Canada). The ETV unit was equipped with an autosampler (Model AS-60), the dispensed volume was 20  $\mu\text{l}$ , if not stated otherwise. The ELAN 5000 ICP-MS computer controlled the operation of the graphite furnace. Standard pyrolytically coated graphite tubes without platform were used (Perkin-Elmer part number 091 504). The thermal program employed is summarized in Table 1 for the conventional conditions (A) and for the modified conditions (B) with  $\text{CCl}_4$  vapor introduction (see details below). It is to be noted that *sample gas* is provided by the ICP gas supply unit, and the *furnace internal gas* is provided by the furnace power and gas supply unit. Further terms with regard of the branching of these gas flows will be explained below.

The gas flow system of the HGA-600MS unit is shown in Fig. 1, depicting the difference between the conventional

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