Application of the ligand vapour technique to the volatilization of unstable chelate compounds (particularly iron(III) trifluoroacetylacetonate) in AAS

J. R. Castillo, J. M. Mir, M. E. García-Ruiz, and C. Bendicho
University of Zaragoza, E-50009 Zaragoza, Spain

Summary. This paper describes a method for volatilizing chelate complexes in AAS using a carrier gas containing ligand vapour in order to prevent chelate decomposition on heating. The method is evaluated with iron(III) trifluoroacetylacetonate. The sample containing chelate is injected into an electrically heated system, and is carried by nitrogen gas containing trifluoroacetylacetone H(TFA) to a silica tube where atomization occurs. This system increases the reproducibility of atomic absorption signals and decreases the high blanks which occur with the conventional method as a result of chelate decomposition. The characteristic mass of the combined analytical procedure is 1.30 ng Fe, the detection limit 12.0 ng Fe, and the relative standard deviation is 4.7% ng Fe (n = 10). Sensitivity is improved 16-fold with respect to the system involving conventional nebulization and atomization of aqueous solutions in air-acetylene flame.

Introduction
Sample introduction in Atomic Spectrometry (AS) has been considered as an inefficient step of this analytical technique. Certainly, the yield of the liquid sample introduction step is low, and the solid sample introduction poses special problems, with lack of reproducibility and calibration. These circumstances make it interesting to work with other types of samples. Volatile phases have been widely studied; covalent hydrides [1], mercury vapour [2], and, to a lesser extent, volatile compounds such as methyl boric ester [3], nickel tetracarbonyl [4] and some organometallic compounds [5].

The advantages of such combined procedures have led to the study of other volatile compounds such as chelate complexes which require sophisticated vapour generation systems since their sublimation temperatures are normally above 100°C.

Many studies have been performed on the volatility and thermal stability of metal complexes, basically β-diketone derivatives, using gas chromatography (GC) [6, 7]. However, anomalies are often detected in GC signals which can be attributed to decomposition, adsorption etc. in the column, and these tend to reduce the efficiency of this technique [8]. These effects can be avoided by using the ligand vapour technique [9–11].

Apart from the advantage of gas phase introduction, the determination of metals by volatilizing their complexes with different ligands preconcentrates the metal by extraction with different organic phases, thereby providing a degree of selectivity in the face of other metals present in the matrix, which might interfere in the determination. Its application to complex matrices reduces the sample pre-treatment required, and eliminates potential sources of error due to losses or contamination. Work has been done using ICP-AAS [12, 13], AFS [14] and AA [15–18] as determination methods.

In some cases where the complex is thermally unstable, the volatile complex may not form completely, or may decompose. Likewise, there may be ligand exchange phenomena, and adsorption on the walls of the volatilization system. These interferences can be avoided by forming the volatile phases in the presence of a gas containing the ligand vapour [13].

This paper evaluates a technique for volatilizing thermally unstable chelates, such as Fe(TFA)₃, and determines the metal by AAS.

Experimental

Apparatus
The following apparatus were used: Perkin Elmer 3030 atomic absorption spectrophotometer, with graphics software and a deuterium lamp background corrector; Perkin Elmer PR-100 printer; Perkin Elmer 2380 atomic absorption spectrophotometer; Perkin Elmer Fe hollow cathode lamp; Perkin Elmer TGS-2 thermobalance; Perkin Elmer 283 IR spectrophotometer; Hamilton 5 μl microsyringe; volatilizer.

Volatile system and ligand vapour generator
The volatilization system is similar to that used in previous studies [16 – 18]. It consists of a glass tube with a carrier gas inlet; one end of this system is connected to the silica tube heated by an air-acetylene flame; the other end serves either as the direct inlet for carrier gas, or is connected to a ligand
Fig. 1a–d. Atomic absorption and blank signals, when the chelate is volatilized in the absence and presence of H(TFA) vapour. a and b correspond to the blank and atomic absorption signals, respectively, for 0.15 µg of Fe, when volatilization occurs in the absence of ligand vapour (absorption signal/non-specific absorption). c represents the blank and d the atomic absorption signal for 0.025, 0.05, 0.1, 0.2 and 0.4 g of Fe when volatilization occurs in the presence of a carrier gas with 0.5% of H(TFA) at a volatilization temperature of 194°C.

vapour generation system. This system contains a solution of H(TFA) in ethanol, and is heated in a thermostat bath at 35°C. The entire volatilization system is heated by electric blankets, controlled by a thermo-regulator, and the temperature is measured using a thermometer.

Reagents
All reagents were of Analytical Reagent grade.
H(TFA) distilled before use, FeCl₃ and Fe metal, sodium acetate. Methanol, ethanol, ethyl acetate and MIBK were used as solvents for the chelates.

To synthesize Fe(TFA)₃, to a solution of FeCl₃ add the stoichiometric amount of H(TFA) dissolved in ethanol. Shake until the chelate precipitates. After filtering and drying, the chelate thus prepared is taken as a secondary standard of Fe.

Solutions of the pure chelate in various organic solvents are prepared, at a concentration of 100 mg l⁻¹.

Procedure
Under optimum conditions, inject 5 µl of chelate solution Fe(TFA)₃ in ethanol into the volatilization system through