PART XII: TERMS RELATED TO ELECTROTHERMAL ATOMIZATION

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1 INTRODUCTION

Part I and Part II are concerned mainly with general recommendations in the field of emission spectrochemical analysis. Part III deals with the nomenclature of analytical flame spectroscopy and associated procedures. Part IV concerns X-ray emission (and fluorescence) spectroscopy. Part V deals with the classification and description of radiation sources. Part VI covers molecular luminescence spectroscopy. Part VII is concerned with molecular absorption spectroscopy (UV/VIS). Part VIII proposes a new nomenclature system for X-ray spectroscopy. Part IX deals with instrumentation for the dispersion and isolation of optical spectra and Part X is concerned with the preparation of materials for analytical spectroscopy. Part XI deals with radiation detectors. This report, Part XII, deals with the techniques of *electrothermal atomization* (*ETA*) used in optical atomic spectrometry to introduce the sample into a sampling or excitation source (See Part V of this series).

1.1 General

An *electrothermal atomize* ris here narrowly defined as a device which is heated to the temperature required for analyte atomization by the passage of electrical current through its body. This technique has largely been developed for use in atomic absorption spectrometry for which the terms *electrothermal atomic absorption spectrometry*, *electrothermal AAS* and the abbreviation *ETAAS* are defined. It has also been applied in optical emission and atomic fluorescence spectrometry, with appropriate analogous terms, such as *electrothermal optical emission spectrometry* and *electrothermal atomic fluorescence spectrometry*, being defined.

This document is, then, mainly concerned with the application of electrothermal atomizers in AAS with the assumption that similar usages for other applications can be derived by analogy.

In many cases, as in tubular electrothermal atomizers used for atomic absorption spectrometry, the atomizer itself prescribes and confines the *observation volume* and in others the observation volume is immediately adjacent to the atomizer. In these cases, where the atomization/excitation and vaporization stages are not separated, including the case of the graphite furnace with additional excitation by, for example, a glow discharge, the term atomizer applies. If, however, an electrothermal atomizer is combined with an excitation source, such as a plasma discharge, so that the device's function is to vaporize the sample into a clearly separated atomization/excitation stage then it should be termed an *electrothermal vaporizer* (*ETV*).

2 ATOMIZERS

2.1 Electrothermal Atomizers

An electrothermal atomizer is heated by the passage of electricity through the body of the device. Samples may be heated by conductive, convective and radiative processes within the atomizer. Different types of electrothermal atomizer can be distinguished according to the method used to cause the flow of current. As an alternative to the use of a conventional voltage supply for the

resistively heated atomizer, a *capacitive discharge* may be used. *Inductively heated atomizers* are also used. If the current flows through resistance wires round the atomizer, as in the *silica tube atomizer*, the device should not be termed an electrothermal atomizer and the more general term *furnace atomizer* should be used. This last term encompasses atomizers using other forms of heating, e.g. the flame-heated furnace and the *graphite furnace atomizer*, heated electrically by external coils, as well as the electrothermal atomizer.

2.1.1 Protective devices for atomizers

To minimize oxidation of the atomizer material at high temperatures the atomizer must be isolated from the atmosphere, almost always by a *protective gas*. *Enclosed atomizers* are situated in a housing flushed with the protective gas, usually an inert gas. With *unenclosed atomizers* the protective gas forms a freely flowing sheath enveloping the atomizer body. Postcombustion flame gases are sometimes used as the protective gas, in order also to improve atomization, or excitation, or both as in the *capsule-in-flame* and the *graphite rod-in-flame atomizers*. The protective gas may be at pressures higher than atmospheric or at the reduced pressure required, for example, to sustain a glow discharge for additional excitation as in the technique referred to as *Furnace Atomic Non-thermal Excitation Spectrometry* (*FANES*).

2.1.2 Types of atomizer

In AAS a distinctive feature of the atomizer is its geometry in relation to the *measuring beam*.

In *open atomizers* the sample vapour, together with analyte atoms, leaving the atomizer surface may move freely into the surrounding space. Analyte atoms thus pass through the observation volume, i.e. the space within the vapour cloud defined by the dimensions of the measuring beam. Depending on the actual physical form of the atomizer body, open atomizers have been referred to as *rods*, *cups*, *filaments*, *boats*, *loops*, *strips*, *wires*, *braids*, etc. This category also includes *exploding wire* atomizers.

In *confined atomizers* the sample vapour is restricted by the atomizer wall except for the openings where the optical beam enters and leaves the atomizer and the *sample introduction hole*. The residence time of the analyte atoms within the observation volume is thus prolonged compared with open atomizers. The protective gas flow in enclosed, confined atomizers is divided into the *outer-* and the *inner flows*, only the latter passing through the observation volume. By stopping the internal protective gas flow during the atomization stage, *stopped-flow* operation, removal of analyte atoms due to *forced flow* operation is eliminated and sensitivity increased. Confined atomizers are generally in the form of tubes. *Graphite tube atomizers* are often referred to as graphite furnace atomizers, though the term furnace does not necessarily imply electrothermal atomization (see Section 2.1).

2.1.3 Atomizer material

The material used for the atomizer body must be electrically conductive and able to withstand high temperatures. This limits the possible materials to different kinds of carbon, i.e. *graphite* (*polycrystalline electrographite*), *pyrolytic graphite* and *glassy carbon* and a few metals with high melting points.

The surface of carbon-based atomizers is sometimes treated to enhance its analytical performance by deposition of a pyrolytic graphite layer or by forming a layer of a refractory metal carbide on the original carbon surface. This *pyrolytic graphite coating* or *carbide coating* generally limits soaking of the sample solution into the graphite and can enhance the atomization efficiency and

tube lifetime and reduce the reactivity of the carbon surface, etc. An atomizer can be specified by indicating the material and form, e.g. *glassy carbon tube, tantalum carbide-coated tube, tungsten strip*, etc.

2.1.4 Atomizer surface

That part of an atomizer on which the sample is placed is the *sample support*. It may be an integral part of the atomizer, e.g., the *wall* of a tube atomizer or it may be inserted into the atomizer as a *platform*, a *boat*, a *metallic foil* lining the inner surface of the tube, an inner tube (*tube-in-tube atomizer*), etc.

If the sample support can readily be inserted into (and withdrawn from) a preheated atomizer for the atomization and measurement stage or, optionally, for the drying and pyrolysis stages, the support is called a *probe*.

The surface from which the sample is atomized, the *atomization surface*, is usually that of the sample support. Exceptionally, prior to atomization the analyte may be transferred from the support by vaporization and condensation on to a *secondary atomization surface*.

Since conditions of atomization depend strongly on the atomization surface it is common to specify this surface by the terms *graphite platform atomization, tungsten-*, or *graphite probe atomization*, etc. If the atomization surface is not specified *wall atomization* is assumed.

2.2 Processes In Atomizers

2.2.1 Sample treatment

Heating of the atomizer is regulated by a control unit which allows programming of a succession of temperature steps and corresponding time intervals. This *temperature programme* defines the *thermal treatment* of the analytical sample prior to, during and after atomization.

A liquid sample generally undergoes three stages of heat treatment i.e. *drying pyrolysis* and *atomization*. During the drying stage liquid from the sample, most often the solvent, is evaporated and driven off. In the pyrolysis stage some of the concomitants in the sample are removed and other desirable chemical and physical processes may occur which ultimately enhance the analytical performance.

The temperature and time intervals of the particular steps of the temperature programme are called the *drying, pyrolysis, atomization* and *cleaning temperatures* and *times*, with the notation T_{dry}, T_{pyr}, T_{at}, T_{cl} and t_{dry}, t_{pyr}, t_{at}, t_{cl}, respectively.

The temperature may be increased continuously by *ramp heating*, or incrementally by *stepwise heating* within each of the three major stages. In those cases T_{dry}, T_{pyr}, and T_{at} correspond to the highest values reached during any particular stage.

Pyrolysis of samples containing organic matter is sometimes referred to as *charring*, or in presence of oxygen as *ashing*. The corresponding terms *charring temperature* and *charring time* or *ashing temperature* and *ashing time* may be used. A cooling stage may be used after the pyrolysis stage as well as at the end of the cycle after the atomization or cleaning stage.

As commonly used T_{dry}, T_{pyr}, and T_{at} are temperature values set on the control unit. They generally do not correspond to temperatures at which the particular processes start and may not even correspond to the actual temperature of, or in, the atomizer at the particular step. Authors should therefore specify whether these values are instrumental settings or measured quantities.

If the sample is introduced by the *sample injector* of an automatic sampler or by Some other sample introduction technique such as the *aerosol deposition technique*, sample introduction is quantified by the terms *sample deposition temperature*, T_{dep} and *deposition time*, t_{dep}.

2.2.2 Parameters characterizing atomization conditions

When describing conditions of atomization the following parameters may conveniently be used.

The *atomization surface temperature*, T_s, is the temperature of the support from which the sample is atomised and may be the *wall temperature* T_w (in tubular atomizers). The *gas temperature*, T_g, (Part V, Table V.2 and section 2 3.2) is the temperature in the observation volume.

In open atomizers $T_w$is synonymous with T_s; T_g however, while applicable, is difficult to specify.

If the gas temperature does not change when the analyte atomizes, *constant temperature atomization* is said to take place. This may be achieved by using, for example, very high heating rates, or by introducing the analyte into a preheated atomizer by means of a probe or an independent volatilizer.

When platform, probe, secondary surface or similar mode of atomization is used the time-dependent change in gas temperature occurring during analyte vaporization/atomization can be reduced, but not eliminated and the term *stabilized temperature atomization* has been applied. The sample may be deposited on a preheated atomization surface, a *preheated platform* or *preheated probe*.

2.2.3 Parameters characterizing analyte atomization

The behaviour of the analyte is conveniently characterized using the following terms.

Appearance temperature, T_{app}, is the temperature of the atomization surface at which the analyte signal/noise (r_{SN}) ratio reaches a value of 3 when the quantity of analyte in the atomizer is one hundred times the characteristic mass for peak high absorption (See 2.3). *Vaporization temperature*, T_{vap}, is the temperature of the atomization surface at which analyte loss becomes statistically significant. The vaporization and appearance temperatures may be derived from the *pyrolysis*- and *atomization curves* (See Section 2.3). The *pyrolysis curve* expresses the dependence of the analyte signal on the *pyrolysis temperature*, with the *pyrolysis time*, atomization temperature and all other parameters being held constant. The atomization curve expresses the dependence of the analyte signal on the atomization temperature using an already established and constant pyrolysis temperature.

The analyte can also be described by the *activation energy of atomization*, E_a. This is the enthalpy of the reaction or process controlling the atomization rate. It is usually derived from simultaneous recordings of the *temperature profile*, i.e. the time-dependence of the atomization surface temperature, and the *absorbance profile*, i.e. the time-dependence of the analyte absorbance, from which the supply function can be deduced. The shape of the absorbance peak results from variations in the rate of supply of analyte atoms to, or their *removal* from, the observation volume.

The supply is mainly controlled by the heating rate and processes of analyte atomization; the removal is mainly the result of diffusion and of convection by thermal expansion of the gaseous phase and/or by forced flow of the protective gas.

2.3 Analytical Aspects

In order to influence processes taking place in the atomizer in the desired way, reagents called *chemical modifiers* may be added. These can help to retain the analyte to higher temperatures during pyrolysis, to remove unwanted concomitants or improve atomization in other ways.

For measurements in ETAAS, a *peak height absorbance*. A_p, and an *integrated absorbance*, $Q_A = \int_{t_1}^{t_2} A \, dt$ may be used. The first is controlled by supply and removal processes. The second is, ideally, not controlled by the supply process, so it is much less dependent on matrix variations and experimental conditions.

Sensitivity of determination in ETAAS may conveniently be expressed in terms of *characteristic mass*, m_c, i.e. the mass of analyte which, when atomized electrothermally, produces the uniquely defined absorption signal. The *characteristic mass for peak absorption*, m_p, is that mass of analyte which provides a defined peak absorbance of 0.0044 (or 1% absorptance). The *characteristic mass for integrated absorption*, m_o, is that mass of analyte which produces an integrated absorbance signal whose net area is equal to 0.0044 seconds. This latter characteristic mass is a function of the *residence time* of atoms in the observation volume but is much less dependent on other instrumental factors.