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SCIENTIFIC COMMITTEE, ANALYTICAL SECTION
EXPERT PANEL ON QUANTITIES AND UNITS†

QUANTITIES AND UNITS IN CLINICAL CHEMISTRY: NEBULIZER AND FLAME PROPERTIES IN FLAME EMISSION AND ABSORPTION SPECTROMETRY

(Recommendations 1986)

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Quantities and units in clinical chemistry: Nebulizer and flame properties in flame emission and absorption spectrometry (Recommendations 1986)

A classification of quantitative concepts, a unification of nomenclature, and suggestions for the introduction and implementation of recommended units for quantities relating to the nebulizer and flame components of emission and absorption spectrometers are presented. The purpose is to provide users of this form of instrumentation for clinical chemical determinations with a complete, systematic description of the quantities involved in the use of the instruments, so that the data generated from such instruments for patient care purposes is applied correctly. For all quantities listed, the kind of quantity, the symbol for the kind of quantity and a practical unit, the systematic name, the system and the component, and the definition of the quantity are given. Nebulizer quantities defined include the minimum nebulization time, to ensure the analysis provides data of require precision, the efficiency of nebulization and of atomization, and the fractions of a component desolvated. volatilized and atomized are distinguished. Flame properties defined include temperature, observation height, path length and volume, and the times taken for the component to travel through the flame compared to the observation space are characterized. Finally, quantities for gas flow rates through the flame are listed.

1. INTRODUCTION

1.1 The Commission on Quantities and Units in Clinical Chemistry (CQUCC) is part of the Clinical Chemistry Division (CCD) of the International Union of Pure and Applied Chemistry (IUPAC). The titular members also serve as the Expert Panel on Quantities and Units (EPQU) of the Scientific Committee (SC) of the International Federation of Clinical Chemistry (IFCC). General recommendations on quantities[1] and units in clinical chemistry have been published (IUPAC-CQUCC & IFCC-EPQU 1974, 1979). Certain terms defined there are used here without further explanation. The present document is based primarily on recommendations already published by the IUPAC Commission on Physicochemical Symbols, Terminology and Units (IUPAC-CSTU, 1979) and the IUPAC Commission on Spectrochemical and Optical Procedures for Analysis (IUPAC-CSOPA 1972, 1976), and is specifically addressed to clinical chemistry.

1.2 Spectroscopy is the study of physical systems[2] by the electromagnetic radiation with which they interact or that they produce. Spectrometry is the measurement of such radiations as a means of obtaining information about the systems and their components[3]. In certain types of optical spectroscopy, the radiation originates from an external source and is modified by the system, whereas in other types, the radiation originates within the system itself.

1.3 In many applications where the radiation originates within the system itself, the original material is converted into a mist or droplets by nebulization. The solvent is evaporated, leaving the solute as a dry aerosol (desolvation). With further heating, the solute itself is evaporated and sometimes decomposed to form a molecular vapour (volatilization). The molecules are then partially or totally dissociated within the physicochemical plasma[4] to yield neutral atoms (atomization). In some cases (for instance with alkaline earth elements) ions are also formed (ionization).

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(1) In this recommendation, the term "quantity" is used in its broad meaning and includes the concepts called "quantity" and "kind of quantity" in the recommendation IUPAC-CQUCC and IFCC-EPQU, 1979.

(2) Representative parts of the system (for example, serum) may be treated (for example, diluted) before measurement. In analytical chemistry, the instrumentation or parts of it may also be considered as systems.

(3) "Component" may be a chemical compound (e.g. ethanol), an ion (e.g. Na^+), a chemical group within one or more compounds (e.g. amino group), or any of several chemical species sharing one common property (e.g. alkaline phosphatase). In this document, the word "component" is also used to designate a neutral atom whose concentration in a physicochemical plasma is proportional to the concentration of the original component in the material being analysed.

1.4 In emission spectroscopy, the processes of energy transfer within the flame excite the atoms, molecules and radicals, resulting in the emission of radiant energy in the form of atomic lines and molecular and radical bands. Ionization is usually undesirable and can be minimized by lowering the temperature of the flame or by adding electron donors, for instance caesium derivatives. The intensity or radiant power of a line or band of the component to be analysed depends critically on the physicochemical properties of the flame such as temperature, chemical composition, redox properties, etc. For a given flame, the intensity of a line or band depends on the concentration of the component in the material analysed and is related to it by a calibration function. This function is established by using a series of reference solutions, called calibrators, which contain the component at known concentrations.

1.5 In atomic absorption spectroscopy, a background source, usually a hollow cathode lamp, sends a spectrum of radiation through the flame, but atomic absorption of that radiation takes place only at the resonance lines [5] of the element considered. In the process, energy is taken up from the background radiation by a neutral atom in the ground state, and then dissipated in various ways, e.g. as a rise in flame temperature. At the low flame temperatures that are commonly used (below 3 300 K), only a few resonance lines can occur as absorption lines because of the small number of electrons occupying the higher energy levels. Thus, if Mg, for example, is to be measured the cathode lamp will emit all the spectral lines of Mg, but absorption will take place only at 285.2 nm, a resonance line of Mg, when Mg is present in the flame. One measures the intensity of the radiation at the resonance line. The absorbance is proportional to the concentration of the element under observation in the observed space in the flame. Molecular bands give no useful signals for analysis. A full classification of all types of instruments and methods of the different branches of flame spectroscopy is given in IUPAC-CSOPA, 1976. Measurements of the emitted light from atomic fluorescence are rarely used in clinical chemistry and will not be considered in this document.

1.6 With some instruments, an internal reference component (also called internal standard) having a distinct line or band can be added to the prepared material in order to reduce variations resulting from differences in the sample, such as surface tension, volumic mass (mass density) and viscosity. The reference element method is based on the comparison between the intensities of the two different spectral lines or bands whereas the direct method takes the intensity of one spectral line or band as a measure of the concentration of the component.

2. KINDS OF QUANTITIES AND UNITS

Quantities and units are presented as follows:

Name of quantity	symbol of kind of quantity	symbol of a practical unit
Systemic name of quantity: System-- Component, kind of quantity		
2.1 Rate of fluid consumption	q_V	$\mu L\ s^{-1}$

Systematic name: Nebulizer - - Fluid consumed, volume rate.
Definition: The volume of fluid consumed by the nebulizer divided by time.

(4) A physicochemical plasma is any system at a high temperature (e.g. part of a flame, a high-frequency torch, an electrically heated furnace), that is generally characterized by its degree of ionization. Flames are at the lower limit of the temperature range, and therefore the constituents of such a plasma are ionized to a low degree.

(5) The emission of an atomic line is the result of a transition of an atom, from a state of higher excitation to a state of lower excitation. When the lower state of the transition is the ground state, the line is called a resonance line. When the ground state is a multiplet, only a transition to the lowest multiplet state should be called a resonance line. (IUPAC-CSOPA, 1976).

Notes: 1. Volume rate has also been called volume flow, flux, aspiration rate, aspiration flow or aspiration flux.

2. The fluid consumed is either aspirated or injected.

3. The volume rate of fluid consumption by nebulizers is usually between 10 and 100 $\mu L\ s^{-1}$.

4. Several factors influence the rate of fluid consumption, such as:
   a. physicochemical properties of the fluid in its environment: viscosity, density (volumic mass), surface tension and pressure.
   b. properties of the instrument: design of nebulizer nozzle, length and diameter of the capillary, ageing and partial clogging of these parts.
   c. operating factors: pressure adjustment for the nozzle, kind of gas used in the nebulizer, temperature of the gas nebulizer and nozzle.
   d. vertical distance between the free surface of the fluid and the opening of the nozzle.
   e. change in ambient pressure.

5. The amount of component used in one analysis is equal to rate of fluid consumption multiplied by consumption time, multiplied by concentration of the component in prepared sample.

6. In IUPAC-CSOPA, 1976, the trivial name is rate of liquid consumption.

2.2 Total consumption time t_{tot} s

Systematic name: Prepared sample - - Consumption (total), time.
Definition: Time necessary to consume the prepared sample completely.
Note: Total consumption time is equal to the volume of the prepared sample divided by the rate of fluid consumption.

2.3 Minimum consumption time t_{min} s

Systematic name: Prepared sample - - Consumption (minimum), time
Definition: Time during which nebulization must be carried out in order to perform one analysis with a given precision.
Note: Minimum consumption time is equal to the minimum volume consumed of the prepared sample divided by the rate of fluid consumption in order to obtain a given precision. Minimum consumption time can be reduced by means of integrating the signal or measuring the signal increments (kinetic methods).

2.4 Efficiency of nebulization ε_n 1

Systematic name: Component consumed - - Component entering the flame, substance fraction.
Definition: The substance fraction of component entering the flame in the amount of component consumed.
Notes: 1. The efficiency of nebulization is related to the amount of component and not to the amount of solvent. It cannot be calculated directly from the ratio: volume rate of sample drained from the spray chamber divided by volume rate fluid consumed. Corrections usually have to be made to take account of differences in component concentrations in the drained and consumed solutions respectively because of evaporation of some solvent from mist droplets deposited on the walls.

2. Some of the component is further lost by deposition as solid in the spray chamber, the burner tip and the tubings. Efficiency of nebulization reflects the operation of the whole nebulizer-burner assembly, not of the nebulizer alone. With direct-injection burners, droplets may be ejected from the flame by turbulence of gases leaving the burner.

3. Heating the nebulizer-chamber helps to diminish the losses.

4. Typical values of ε_n for different kinds of instruments are:

- chamber-type nebulizer: 0.01 - 0.1
- heated chamber: 0.1 - 0.5
- injection burner: 0.9

2.5 (Local) fraction desolvated χ_s 1

Systematic name: Component entering the flame - - Component desolvated, substance fraction.
Definition: The substance fraction of component in desolvated state in the amount of component entering the flame.
Notes: 1. This quantity is measured in a defined part of the flame, usually the observation space.

2. Because it varies with height in the flame as a result of progressive evaporation of aerosol droplets, it is appropriate to call it local.

3. The fraction desolvated does not account for losses by incomplete volatilization of the dry aerosol (which largely depends upon the nature and concentration of the component). Such losses are described by local fraction volatilized (see 2.6), which usually depends on the solute.

4. Since χ_s varies markedly with the height in the flame, its observed value represents an average.

5. Local fraction desolvated depends on the solvent, the temperature of the flame and the time the component takes to travel from the tip of the burner to the height in the flame considered.

2.6 (Local) fraction volatilized χ_v 1

Systematic name: Desolvated component - - Volatilized component, substance fraction.
Definition: The substance fraction of the volatilized component in the total desolvated component. The gaseous state includes free atoms, molecules and radicals.
Notes: 1. This quantity is measured in a defined part of the flame, usually the observation space.
2. The fraction volatilized can be increased by adding certain dispersing agents, such as lanthanum salts, to the sample.
3. The interference of phosphates in emission and atomic absorption spectrometry of alkaline earth elements is the result of a decrease in the fraction volatilized.
4. The fraction volatilized varies inversely with the size of the desolvated particles.
5. Since χ_v varies markedly with the height in the flame, its observed value represents an average.

2.7 (Local) fraction atomized χ_a 1

Systematic name: Volatilized component - - Atomized component, substance fraction.
Definition: The substance fraction of the atomized component in the total volatilized component.
Notes: 1. This quantity is measured in a defined part of the flame, usually the observation space.
2. The fraction atomized is the result of chemical reactions in the gaseous state. It depends on the bond strength of the compounds that the component may form within the flame and on the composition and temperature of the flame.
3. When analysing elements that tend to become oxidized in the flame, it may be advisable to use as fuel gas mixtures with a reducing component such as C_2H_2 or N_2O.

2.8 (Local) efficiency of atomization ε_a 1

Systematic name: Component consumed - - Atomized component, substance fraction.
Definition: The substance fraction of atomized component in the component consumed.
Notes: 1. The efficiency of atomization is measured in a given part of the flame, usually the observation space.
2. $\varepsilon_a = \varepsilon_n \cdot \chi_s \cdot \chi_v \cdot \chi_a$
3. The signal is a function of the product $q_V \cdot \varepsilon_a$. But ε_a is also a function of q_V usually decreasing at high volume rates.

2.9 (Local) flame temperature T_l K

Systematic name: Flame - - Observation space, temperature.
Definition: The effective thermodynamic temperature in the observation space (2.12) as measured by a specific sensor for a specified element.
Notes: 1. The temperature of a flame (or other plasma) is not homogeneous. It is usually lower at the borders of the flame. It is therefore appropriate to speak of an effective temperature which represents an average value of all temperatures throughout the observation space.
2. The flame temperature depends on several factors such as: kind of plasma, kind of gas or gas mixture and concentration gradient of the thermometric species in the observation space.

2.10 Observation height h_{obs} mm

Systematic name: Flame - - Observation space, height.
Definition: The difference in height between the axis of the observed space (optical axis) and the burner tip. The optical axis of the instrument should be the same as the optical axis of the observation space.
Notes: 1. Other definitions which express the observation height as a fraction of the whole flame height are not recommended because the height to the tip of the flame is not well defined.
2. The observation height should be stated in the method.

2.11 Observation pathlength l_{obs} mm

Systematic name: Flame - - Observation space, pathlength.
Definition: The intersection of the optical axis and the observation space.

2.12 Observation volume V_{obs} µL

Systematic name: Flame - - Observation space, volume.
Definition: The volume of that portion of the flame that is observed through the optical device. The observation space is the intersection of the optical beam and that part of the flame where the net signal is at least half of the maximum net signal.

Notes: 1. The characteristics of the observation space depend on the temperature of the flame, stoichiometry of the gases and the properties of the processed fluid (presence of proteins for instance).
2. The observation space in atomic absorption is analogous to observation space of a cuvette in molecular absorption spectrometry.

2.13 Travel time t_{tv} s

Systematic name: Flame - - Component transport, time (burner tip to lower limit of observation space).
Definition: The time needed for the component to be carried from the burner tip to the observation space.
Note: Travel time depends on the observation height and the flame rise velocity.

2.14 Transit time t_{ts} s

Systematic name: Flame - - Component transport, time (through observation space)
Definition: The time needed for the component to pass through the observation space.
Note: Transit time depends on the geometry of the observation space, the flame temperature and the solute nebulized.

2.15 (Vertical) rise velocity v_f mm s^{-1}

Systematic name: Observation space - - Component volatilized, (upward) velocity.
Definition: The vertical component of the velocity of the volatilized component in the observation space.
Note: Vertical rise velocity depends on the flame temperature, the solute nebulized, the observation height and the gas flow rate.

2.16 Burning velocity (of flame front) v_b mm s^{-1}

Systematic name: Flame - - Burning front, (backward) velocity.
Definition: The mean velocity of the flame front towards the unburnt gas mixture (usually vertically downwards).
Notes: 1. The quantity applies to gas mixtures and not to injection burners.
2. Burning velocity depends on the flame temperature and the solvent nebulized.

2.17 Flow rate of unburnt gas mixture q_u µL s^{-1}

Systematic name: Burner - - Gas mixture, volume rate
Definition: The volume rate of the gas mixture of the burner tip.
Note: Flow rate of unburnt gas mixture depends on operating conditions such as gas pressure. The ambient temperature and pressure should also be stated.

2.18 Flow rate of X (e.g. air, O_2) q_X µL s^{-1}

Systematic name: Burner - - Component of gas mixture, volume rate.
Definition: Volume rate of one component, X, of the unburnt gas mixture (such as C_2H_2, O_2, etc.) in the burner tip.
Notes: 1. Ambient temperature and pressure must be stated.
2. Most instruments are equipped with flow-meters to measure the quantity.

3. REFERENCES

1. IUPAC-CQUCC/IFCC-EPQU (International Union of Pure and Applied Chemistry- Commission on Quantities and Units in Clinical Chemistry, and International Federation of Clinical Chemistry- Expert Panel on Quantities and Units); 1979. Quantities and units in clinical chemistry, Recommendation 1978. Prepared by R. Dybkaer. Pure and Applied Chemistry 51: 2451-2479, Clinica Chimica Acta 96: 157F-183F, and Journal Clinical Chemistry Clinical Biochemistry 17: 807-821.

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