

# MINISTRY OF HEALTH OF THE RUSSIAN FEDERATION

## GENERAL PHARMACOPOEIA MONOGRAPH

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**Atomic emission spectrometry**

**GPM.1.2.1.1.0004.15**

Replaces the State Pharmacopoeia of the Russian Federation XII, Part 1 Monograph, GPM 42-0044-07

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Atomic emission spectrometry is a combination of methods based on measurement of electromagnetic radiation emitted by excited atoms or single-atom ions.

**General principles.** During atomic emission spectrometry, a sample is exposed to high temperatures inducing evaporation of the substance, molecular dissociation into atoms, ionization, and atom excitation. These are equilibrium and temperature-dependent processes. Following thermal excitation of an atom or ion, valency electrons switch from their principal level to levels of higher energy. During a back transition of a valency electron to a lower energy level, electromagnetic radiation of a certain wavelength ( $\lambda$ ) is emitted as reflected by the following equation:

$$\Delta E = hc/\lambda, \text{ where}$$

$\Delta E$  is the difference in the energies of the two energy levels, J;

$h$  is the Planck constant ( $6.626 \cdot 10^{-34}$  J · s);

$c$  is the speed of light (299,792,458 m/s).

The relationship between the intensity of emitted electromagnetic radiation and the wavelength is called *the emission spectrum*. The number of lines in an element's emission spectrum is determined by the number of valency electrons and the number

of allowed inter-level atomic transitions. There are few lines in the spectra of atoms with a small number of valency electrons (alkaline, alkaline earth metals). Atoms with a complex external electron shell pattern (particularly elements of the side subgroups in the periodic table) produce spectra with a large number of lines. Lines corresponding to transitions to the principal energy level are called resonance lines. In an emission spectrum, resonance lines are observed in the visible and ultraviolet regions. The line intensity ( $I$ ) of an element's emission spectrum is in direct proportion to the number of excited atoms or singly charged ions ( $N^*$ ). Excited and non-excited atoms and singly charged ions are in a thermodynamic equilibrium described by the Boltzmann distribution equation:

$$N^*/N_0 = (g^*/g_0)e^{-E/kT}, \text{ where}$$

$N_0$  is the number of non-excited atoms or singly charged ions;

$g^*$  and  $g_0$  are the statistical weights of the excited and non-excited states;

$E$  is the excitation energy, J;

$k$  is the Boltzmann constant, ( $1.381 \cdot 10^{-23}$  J/K);

$T$  is the absolute temperature, K.

At constant temperature, the spectral line intensity of an element is in direct proportion to the number of non-excited atoms of the element, which is proportionate to the concentration of the element being determined in the sample under given atomization conditions ( $C$ ). Therefore, there is a direct proportion between the spectral line intensity in the emission spectrum of an element and the concentration of the element being determined:

$$I = k \cdot C, \text{ where}$$

$I$  is the intensity of the spectral line of the element;

$k$  is the coefficient of proportionality;

$C$  is the concentration of the element being determined in the solution, %.

The  $k$  coefficient is an empirical value, which depends on the source of atomization and excitation (atomizer). The main characteristic of any atomizer is its

temperature. Temperature determines the overall equilibrium of processes going on in the atomizer and, as a result, the intensity of the spectral lines and the metrological characteristics of the method. The equilibrium of the processes of evaporation and molecular dissociation into atoms is altered by the effects of competitive chemical reactions (such as anion-promoted production of hardly volatile and weakly dissociating compounds: phosphates, silicates, borates, production of oxides and carbides of metals, etc.). The interfering influence of anions becomes noticeable upon a temperature decrease. A presence of easily ionizable cations tips the balance of excitation and ionization towards the formation of excited atoms. Cation interference increases with elevating temperature. The change in the intensity of the element being determined as a result of influences of other elements co-existing in the sample is called the matrix effect. The matrix effect is eliminated by adding chemical modifiers or ionization buffers to the tested sample.

The major types of atomizers and their temperature and metrological characteristics are shown in Table 1.

Table 1

Temperature and metrological characteristics of different types of atomizers

Atomizer	t, °C	Sample state	C min, % mass	Relative standard deviation (S <sub>r</sub> )
Flame	1500 – 3000	Solution	10 <sup>-7</sup> – 10 <sup>-2</sup>	0.01 – 0.05
Electric arc	3000 – 7000	Solid	10 <sup>-4</sup> – 10 <sup>-2</sup>	0.1 – 0.2
Electric spark	10000 – 12000	Solid	10 <sup>-3</sup> – 10 <sup>-1</sup>	0.05 – 0.10
Inductively coupled plasma	6000 – 10000	Solution	10 <sup>-8</sup> – 10 <sup>-2</sup>	0.01 – 0.05

**Flame** is the lowest-temperature atomizer used in atomic emission spectrometry. Temperatures achieved with flame are optimal for the determination of the most easily atomized and excitable elements, alkaline and alkaline earth metals.

For these elements, the sensitivity of the flame atomic emission spectrometry method is  $10^{-7}$  mass %. For the majority of other elements, the lower limits of detection are higher by a few orders. An important advantage of flame as a source of excitation is its high stability and the resulting good reproducibility of measurement results [relative standard deviation ( $S_r$ ): 0.01 – 0.05]. To produce a flame, a gas mixture consisting of an inflammable gas and an oxidizing gas should be prepared. The choice of components for a gas mixture should be made based on the required flame temperature, which depends on the excitation energy of the element being determined. Table 2 contains information concerning the most frequently used types of flame.

Table 2

Temperature of the most frequently used gas mixtures

Inflammable gas	Oxidizer	t, °C	Burning rate, cm/s	Type of flame	Excited elements
methane	air	1800	55	laminar	alkaline metals
acetylene	air	2200	266	laminar	alkaline and alkaline earth metals
hydrogen	oxygen	2800	3680	turbulent	alkaline, alkaline earth, and heavy metals
acetylene	oxygen	3100	2480	turbulent	Ag, Cu, Mn etc.
acetylene	nitrous oxide	3200	120	laminar	heavy metals

When in a flame, many metals tend to produce high-melting, dissociation-resistant oxides. To increase the free atom production level, a reducing atmosphere should be created in the flame by increasing the flow rate of the inflammable gas.

Such flame is called an enriched flame. The main limitation to the use of a flame atomizer is its low capacity for inducing an emission required for testing many elements.

**Electric arc.** Arc discharges of constant and alternating current are used as a source of excitation for the atoms of the tested substance during atomic emission spectrometry. An electric discharge is generated between two electrodes (usually made of charcoal). A solid sample is placed in the socket in one of these electrodes. The temperature of the arc discharge is 3000 to 7000 °C. These temperatures are sufficient to atomize and excite most elements, except for the most hardly excitable non-metals, halogens. Therefore, the limit of detection for the majority of elements is lower for arc discharge than for flame (Table 1). Unlike flame atomizers, arc atomizers do not display high stability, and therefore the reproducibility of obtained results is low ( $S_r$ : 0.1 ÷ 0.2).

**Electric spark.** A spark atomizer is designed in the same way as an arc atomizer, and its principal use is analysis of solid samples at the qualitative level.

**Inductively coupled plasma** is a state-of-the-art atomizer possessing all necessary analytical potential and metrological characteristics. An inductively coupled plasma atomizer is a burner containing argon plasma, which is initiated by a spark discharge and stabilized with a high-frequency induction coil. The temperature of argon plasma varies with the burner level, being in the range of 6000 – 10000 °C. The majority of elements are excited at these high temperatures. This method has a sensitivity of  $10^{-8}$  -  $10^{-2}$  mass %, depending on the element. The characteristics of an argon burner are highly reproducible, which permits quantitative analysis with a reproducibility in the range  $S_r$ : 0.01 ÷ 0.05 over a broad concentration interval.

The atomic emission spectrometry methods are designed for the detection and quantification of elements. Qualitative analysis is performed by the positions of lines in the spectrum. For quantitative analysis, line intensity is the reliable concentration measure for the element being determined.

**Apparatus.** The main constituents of an atomic emission spectrometer are:

- a sample feeding system and a dispersion system;
- an atomizer (a flame burner for flame atomic emission spectrometry; a high-frequency generator and a plasma burner for inductively coupled plasma atomic emission spectrometry);
- a dispersion device consisting of diffraction gratings, prisms, filters, or interferometers;
- a detector transforming emitted radiation into electrical energy;
- a data collection system.

The apparatus should be operated exclusively as required by the manufacturer's Instructions for Use. The atomic emission spectrometer should be checked for proper functioning. This check should consist of appropriate tests, which usually include diffuser efficacy and stability checks; determination of the resolution of the optical system by measuring the peak width at its half-height; and calculation of the limits of detection for the elements over the chosen wavelength range.

**Procedure description.** The sample preparation procedure depends on the type of atomizer. For flame spectrometry and atomic emission spectrometry with an inductively coupled plasma, the sample preparation procedure includes dissolution of the tested sample and obtaining a tested solution concentration corresponding to the working range of the apparatus. Water is recommended as the solvent. Water to be used should be deionized on ion-exchange resins and meet the requirements established for purified water. Some sample introduction systems permit use of high-concentration acids, provided that the solvent has been demonstrated to exert no effect on flame stability; organic solvents may be utilized in some cases. If organic solvents are used, the need for oxygen supply to prevent formation of organic layers should be taken into consideration. To eliminate the matrix effects, a control solution is prepared and a chemical modifier or ionization buffer is added to the tested solution if necessary. Quantitative measurements necessitate preparation of reference solutions,

i. e. standard solutions of the element being determined that should have a known concentration. Unless otherwise specified in the Pharmacopoeia Monograph, all reagents used for the preparation of the tested solution should be added to the standard solutions of the element being determined and to the control solution at the same concentrations. The tested, control, and standard solutions should be prepared as specified in the Pharmacopoeia Monograph. Plastic laboratory ware is recommended for the preparation of test solutions. If the solid sample introduction technique is used, the analytical conditions should be described in the Pharmacopoeia Monograph.

The atomic emission spectrometry is switched into the working mode in accordance with the Instructions for Use of the manufacturer, and the operating parameters of the device are set at the levels specified in the Pharmacopoeia Monograph (rate at which the sample is fed into the atomizer, wavelength, emission viewing position (radial or axial), integration time, i. e. time to emission intensity measurement at each wavelength; number of repeated emission measurements, etc.). The control solution is then introduced into the atomizer, and the registering device is zeroed. The control solution, the tested solution, and the standard solutions are introduced into the apparatus in the same quantity of repeats. For quantitative measurements, the number of replicates should be not less than 5. The relative standard deviation of obtained response values should not exceed 1.0 %. The apparatus is washed after each measurement, and the operator should make sure that the device reading has returned to the baseline value obtained during the control solution measurement. Measurement of the content of the element being determined is done by comparing the emission of the tested solution with the emission of standard solutions with a known concentration, using the calibration curve method or the standard additions method.

*The calibration curve method.* Not less than three standard solutions of the element being determined should be prepared so that the concentration range of these solutions includes the expected concentration values of the element being determined

in the tested solution. The standard solutions of the element being determined are injected, and a calibration curve is plotted to reflect the relationship between the mean emission values of the standard solutions and the concentration of the element being determined. The calibration curve is calculated using the least squares regression method for all data obtained in the calibration test. This graph is used to obtain the concentration of the element being determined in the tested solution.

*The standard additions method.* Equal volumes of the tested solution are transferred into at least three volumetric flasks of the same capacity. Proportionately increasing volumes of the standard solution with a known concentration of the element being determined (standard additions) are transferred into all the volumetric flasks but one; the volume of the contents in each volumetric flask is brought to the mark with the solvent used, and mixing follows. The emission values of the solutions containing the standard additions (reference solutions) should lie within the linear region of the calibration curve. The least squares method is then used to calculate the parameters of the linear equation reflecting the relationship between the mean obtained emission value and the concentration of the solution, and the concentration of the determined element in the tested solution is calculated. The concentration calculation may be done graphically. To do this, a graph is plotted showing the relationship between the mean obtained emission value and the added quantity of the element being determined. The line connecting these points on the graph is extrapolated until it crosses the axis of abscissas. The distance between the origin of the coordinates and the obtained point shows the concentration of the element in question in the tested solution.