Electronics And Instrumentation

8th Semester

Subject: Analytical Instrumentation
Subject code: BT 808

Unit-3

Flame Photometers

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8. INTERFERENCES IN QUANTITATIVE DETERMINATIONS

As mentioned above, the success of the quantitative determination depends on how accurately the intensity of the emitted radiation represents the concentration of the analyte. It has been found that number of factors besides the analyte, affect the intensity of the emitted radiation. The analytical signals measured often include contributions from constituents other than the analyte. The constituents are called the **matrix constituents.** The contributions are known as **interferences** and are found to influence the outcome of the analytical procedure. These can be corrected by subtracting their contributions to the signal. The contribution of the interferent can be calculated from the magnitude of the interference and the concentration of the interferent. The interferences encountered can be classified as follows.

- Spectral interferences
- Ionised interferences
- Chemical interferences

Let us learn about different types of interferences encountered in quantitative determinations by flame photometry.

8.1 Spectral Interferences

These refer to the interferences that affect the spectral intensity or resolution. There are several types of spectral interferences which are explained below.

- The **first type** of interference arises when two elements exhibit spectra, which partially overlap, and both emit radiation at some particular wavelength. The detector cannot distinguish between the sources of radiation and records the total signal, thus resulting in incorrect answer. Such interferences are more common at high flame temperatures because numerous spectral lines are produced at high temperatures. For example, the Fe line at 324.73 nm overlaps with the Cu line at 324.75 nm. Such interference can be overcome either by taking measurements at an alternative wavelength which has no overlap, if available, or by removing the interfering element by extraction. Alternatively, one may make a calibration curve, which is prepared from a solution having similar quantities of the interfering element.
- The **second type** of spectral interference deals with spectral lines of two or more elements which are close but their spectra do not overlap. This type of interference becomes a problem when a filter is used as the device to isolate spectral lines. A filter may allow spectral lines separated by 5.0-10.0 nm to pass through, thus resulting in an error in the analysis. Such interferences can be reduced by increasing the resolution of the spectral isolation system. However, the interference cannot be eliminated entirely due to the finite width of the spectral isolation system and the finite slit width in such systems.
- A **third type** of spectral interference occurs due to the presence of continuous background which arises due to high concentration of salts in the sample, especially of alkali and alkaline earth metals. Some organic solvents also produce a continuous background. This type of interference can be corrected by using suitable scanning technique.

8.2 Ionisation Interferences

In some cases, high temperature flame may cause ionisation of some of the metal atoms, e.g., in case of sodium, it can be given as follows.

Na -$Na^+ + e^-$

The Na+ ion possesses an emission spectrum of its own with frequencies, which are different from those of atomic spectrum of the Na atom. This reduces the radiant power of atomic emission. This interference can be eliminated by adding a large quantity of a potassium salt to the standards as well as sample solutions. The addition of potassium salt suppresses the ionisation of sodium, as the potassium atom itself undergoes ionisation due to low ionisation energy. Thus, the sodium atom emission is enhanced. This type of interference is restricted to alkali metals.

8.3 Chemical Interferences

The chemical interferences arise out of the reaction between different interferents and the analyte. These are of different types. Some of these are given below.

- **Cation-anion interference**

The presence of certain anions, such as oxalate, phosphate, sulphate and aluminate, in a solution may affect the intensity of radiation emitted by an element, resulting in serious analytical error. For example, calcium in the presence of phosphate ion forms a stable substance, as Ca3(PO4)2 which does not decompose easily, resulting in the production of lesser atoms. Thus, the calcium signal is depressed. Another similar example is that of determination of barium in presence of sulphate forming insoluble BaSO4. This type of interference can be removed either by extraction of the anion or by using calibration curves prepared from standard solutions containing same concentrations of the anion as found in the sample.

- **Cation-cation interference**

In many cases, mutual interferences of cations have been observed, resulting in reduced signal intensity of the element being determined. These interferences are neither spectral nor ionic in nature and the mechanism of such interferences is not well understood. Thus, for example, aluminum interferes with calcium and magnesium. Also, sodium and potassium show cation-cation interference on one another.

- **Interference due to oxide formation**

This type of interference arises due to the formation of stable metal oxide if oxygen is present in the flame, resulting in reduced signal intensity. The alkaline earth metals are subject to this type of interference. This type of interference can be eliminated by either using very high flame temperature to dissociate the oxides or by using oxygen-deficient environment to produce excited atoms.

8.4 Other Factors

A number of other factors affect the intensity of light emission from a given sample solution. For example, the organic solvents in a sample may also influence the intensity of the emission line by changing the viscosity and surface tension of the liquid, which in turn alter the rate at which the sample is aspirated into the flame. They also affect the flame temperature through their contribution to the heat of combustion. An increase in the line intensity is usually observed.

9. MERITS AND LIMITATIONS OF FLAME PHOTOMETRY

You have learnt that flame photometry is suitable for qualitative and quantitative determination of several cations, especially for metals that are easily excited to higher energy levels at a relatively low flame temperature. The metals mainly are Na, K, Rb, Cs, Ca, Ba and Cu. The salient features of analysis by flame photometry can be summarised as follows.

- Propane-air or natural gas-air mixtures that give good flame with strong heat and minimal background light emission are used for the atomisation.
- A solvent blank is run for setting zero emission.
- As the concentration intensity relationship is not valid for all concentrations, the solutions are suitably diluted to fall within linear part of the calibration curve.
- The use of solutions of very low concentration of Na+ and K+ solutions are avoided as these may encounter problems of contamination; especially in case of Na+, which leaches slowly from glass and on contact with skin.
- The interference effects of anions and cations can cause errors and need to be suitably accounted for.
- The random flame instability and random dilution errors can be minimised by using an internal standard (lithium). Let us learn about the merits and limitations of the flame photometry method.

Merits

Flame photometry, coupled with simple read-out devices, provides high sensitivity and high reliability for the determination of elements in the first two groups of the periodic table. Among these elements are sodium, potassium, lithium, calcium, magnesium, strontium and barium. The measurement of these elements is very useful in medicine, agriculture and plant science. The two important merits of flame photometry are as follows.

- The sensitivities of the flame photometry for most alkali and alkaline earth metals lie in the ppm and sub-ppm range.
- Flame photometry is also successful in determining certain transition elements such as copper, iron and manganese.

Limitations

The flame photometric methods like many other techniques have some limitations also. These are given below.

- As natural gas and air flame is employed for excitation the temperature is not high enough to excite transition metals, therefore the method is selective towards detection of alkali and alkaline earth metals.
- The low temperature renders this method susceptible to certain disadvantages, most of them related to interference and the stability of the flame and aspiration conditions. Fuel and oxidant flow rates and purity, aspiration rates, solution viscosity, affect these. It is therefore very important to measure the emission of the standard and unknown solutions under identical conditions.
- The relatively low energy available from the flame leads to relatively low intensity of the radiation from the metal atoms, particularly those that require large amount of energy to become excited.
- Flame photometry is a means of determining the total metal concentration of a sample; it tells us nothing about the molecular form of the metal in the original sample.
- Only liquid samples can be used. In some cases, lengthy steps are necessary to prepare liquid samples. Despite the limitations, the flame photometry is extensively used due to its portability,

ease of operation, etc. Let us summarise what have we learnt in this unit.

10. SUMMARY

Atomic spectroscopy is the oldest instrumental method of elemental analysis. The origin of these techniques dates back to the times of Bunsen and Kirchhoff in the mid- 19th century wherein they showed that the optical radiation emitted from flames is characteristic of the elements present in the flame and the intensities of the emitted radiation were dependent on the amount of elemental species present.

The atomic spectroscopic methods are based on the transitions amongst the quantised electronic energy levels caused by the absorption of radiation by the atoms in vapour phase or by the emission of radiation by the excited atoms. As the transitions manifest in terms of absorption, emission or fluorescence emission. Accordingly, we have atomic absorption, emission or fluorescence spectroscopies. The type of atomic spectroscopic method is determined both by the method of atomisation as well as the nature of the analyte radiation interaction. In contrast to the molecular spectra, the atomic spectra consist of a number of sharp absorption lines, characteristic of the atomic species. The signals in an atomic spectrum are also characterised in terms of the position, intensity and the band width. Flame photometry is a method for the determination of elements which can be easily excited and is based upon the measurement of intensity of radiation emitted, in the visible region, when a metal is introduced into a flame. The wavelength of the emitted radiation, tells us what the element is, and the intensity of the radiation tells us how much of the element is present. The sensitivity of the flame photometric method depends on the number of excited atoms, which in turn depends on the flame temperature. The flame temperature is a function of the type of fuel and oxidant used. In a typical flame photometric experiment, a solution of the analyte is aspirated into the burner and dispersed into the flame as a fine spray in a process called nebulisation. A number of processes occur in the flame to generate the gaseous atoms and ions in the excited state. The intensity of the emitted radiation is then measured for the qualitative and quantitative determination of the analyte.

A flame can be described as a steady state gas phase reaction which takes place with emission of light. These are produced by burning a mixture of fuel and air or oxidant in a burner. The maximum operating temperature of the flame is determined by the identity of fuel and oxidant whereas the exact temperature is fixed by the ratio of fuel and oxidant. Either pre-mix (or laminar) or unpremix (or turbulent) flames are used in flame photometry. In the former, the fuel and oxidant are well mixed before combustion, whereas in later these are mixed in the flame itself. The instrument used in flame photometry is called flame photometer; it consists of a flame atomiser, flame burner, monochromator, detector, amplifier and readout device. A simple inexpensive flame photometer employing glass filters, is sufficient for routine analysis of alkali and alkaline earth metals though more expensive sophisticated instrument using monochromator may be required for analysis of other elements.

The quantitative analysis can be carried out using standard calibration curve, by standard addition or internal addition method. The method is subject to various interferences such as spectral, ionisation, and chemical interferences. The major applications of flame photometry include qualitative and quantitative analysis especially of Group I metals (Li, Na, K) and Group II metals (Mg, Ca, Sr, Ba). It is very useful in routine determination of these metals in medicinal, biological, agricultural and industrial fields. Merits of the technique include high sensitivity and reliability, inexpensive instrumentation and advantages in analysis of alkali and alkaline earth metals. On the other hand, the method is chiefly restricted to these elements, liquid samples, and is subject to different types of interferences, and gives no information on chemical form of the element present.