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Application of flame photometry in the detection of main group metals (Na, K, Li & Ca)

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Abstract
Flame photometer has a high resolution for the detection of alkali and alkaline earth metal ions such as sodium, potassium, lithium, and calcium. Flame photometry separates the characteristic spectra of an element while also measuring emission by atomizing a solution sample into a flame. Alkali and alkaline earth metals, such as Na, K, Ca, and Mg, play important functions in the human body. They are crucial in physiology, industry, and pharmaceuticals as well. In a wide range of applications, routine, accurate, and reliable qualitative and quantitative assessment of these metals is critical. Since the beginning of time, flame photometry has been the most widely utilised technology for this purpose. This resurrected paper discusses the numerous applications of flame photometry that have been carried out to date.

Keywords: flame photometer, alkali and alkaline earth metal, emission, detection

Introduction
Flame photometry is an indispensable tool in the field of analytical chemistry. Flame atomic emission spectroscopy (FAES) is another name for it. "The first flame photometer was developed and became available commercially in the 1940s".(Barnes *et al*.) Bunsen and Kirchhoff were the first to investigate the idea of using distinctive emission from energetic electrons of the atom in quantitative element analysis for analytical chemical research. (Banerjee and Prasad) The concentration of metal ions of group- I and group-II such as sodium, potassium, lithium, calcium, and caesium can be determined using a flame photometer. In flame photometer spectra the metal ions are used in the form of atoms. When alkali (Group I) and alkaline earth metal (Group II) compounds are exposed to flame, they disintegrate into atoms. Some of these atoms are subsequently excited, reaching even higher levels of excitation. However, at higher levels, these atoms are unstable. Hence, these atoms emit radiations when returning back to the ground state. These radiations generally lie in the visible region of the spectrum. Each of the alkali and alkaline earth metals has a specific wavelength as given in table 1. The intensity of the emission is directly proportional to the number of atoms returning to the ground state and the light emitted is in turn proportional to the concentration of the sample. (Rich)

Table 1: Color of flame and characteristic emission wavelength of some elements

Elements	Color of Flame	Emission Wavelength (nm)
Na	Yellow	589
K	Violet	766
Ba	Lime green	554
Ca	Orange	622
Li	Red	670

Instrumentation
The instrument possesses the same basic components as a spectroscopic apparatus has flame (burner), monochromator, slit system and detector system. Various components of the instruments are described as follows:

Source of flame
A burner in the flame photometer is the source of flame. There are significant disparities in the absolute ease with which the elements in a flame are stimulated. The most readily excited element is Na. During sodium and potassium analysis, a low-temperature flame is suitable, however a high-temperature flame is usually required for calcium and magnesium analysis. Natural gas-air, Propane-Air, Hydrogen- Air, Acetylene -Air, Acetylene- oxygen, Hydrogen -Oxygen, Acetylene- Nitrous oxide etc. are the combination of fuel and oxidants that are generally used in flame photometer for flame. The acetylene-oxygen flame, with a temperature of 31,00°C, is the most often used flame. It has highest temperature. (Rich) The temperature of the flame fluctuates with its position, and the area "seen" by the recorder can be changed by modifying the burner's height. (May *et al*.)

Nebuliser
It is used to send homogeneous solution into the flame at a balanced rate.

Optical System
It consists convex mirror and convex lens. The convex mirror transmits the light emitted from the atoms. The convex lens helps to focus the light on a point or slit.

Filter
The reflection from the mirror passes through the slit and reach to the filters. Filters will isolate the wavelength to be measured from that of irrelevant emissions.

Photo-detector
The intensity of radiation emitted by the flame is measured by the photo- detector. Here the emitted radiation is converted to an electrical signal with the help of photo

detector. These electrical signals are directly proportional to the intensity of light.

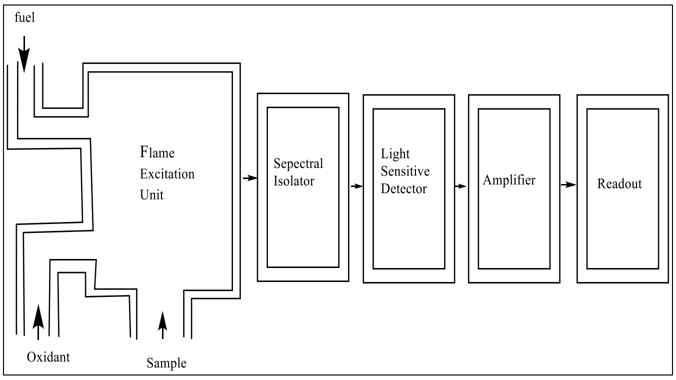

Fig 1: Block diagram of Flame Photometer

Various Applications of the Flame Photometry

1. Application of Flame Photometry in Water for determination of elements of group-I and group-II

1.1 Determination of Na and K in surface and groundwater

A Flame Photometer can both qualitatively and quantitatively determine group-I and group-II elements in the water. Banerjee, P.; and Prasad, B. (Banerjee and Prasad)determined the total potassium and sodium concentration in the groundwater and surface water in and around Dhanbad City of Jharkhand, India. This city is located in India's coal mining belt. The Water Quality Index was also calculated by the authors to see if the surface and groundwater samples were appropriate for human consumption by residents of the study areas. The authors gathered 18 water samples from various bodies of water, 12 of which were underground water samples (taken from several tube wells throughout Dhanbad) and 5 were surface water samples (collected from different ponds and dam of the city).

After that, the Flame Photometer was calibrated using Na and K stock solutions. The gadget then evaluated the samples. All of the samples were taken during the dry winter season when the average temp. was 20°C. Following the instrument's analysis, all of the samples' Na and K concentrations were confirmed to be within the WHO's admissible limits. (Yamamura *et al*.) However, there were some differences in sodium and potassium concentrations between samples. Based on all the study's findings, the scientists determined that the water from Maithan Dam is the best for daily consumption due to its appropriate sodium and potassium content. "The presence of sodium in surface water can be linked to the time-dependent wear-out of sodium-containing mineral rock and salt deposit erosion, as well as surface filtrations".(Abowei) Road salt irrigation, (Eaton; Boyd) sewage effluent, (Theroux *et al*.) and filtering of leachate from industrial locations (Chaurasia and Pandey; Dwivedi and Pandey) are further sources of sodium in surface water. Potassium in groundwater might come from hard water treatment using potassium permanganate or from a big amount of potassium accidentally discharged.

1.2 Analysis of Sodium and Potassium in Rainwater

Sugawara, K. *et al*. (Sugawara *et al*.) developed a method for detecting group-I and group-II metals by employing positive interference phenomena for one element in a way that drastically reduces the observable amount of that element. According to the authors, surface-active agents (such as lauryl amine hydrochloride and isooctyl phenol) and solvents (such as acetone, ethyl alcohol, methyl ethyl ketone, butyl alcohol, and formaldehyde) can be used to increase the emission intensity of Na and K elements at low concentrations of those elements in the sample. The intensity of the element's emission can be boosted by adding a single solvent or a combination of solvents and a surface-active agent. The authors concluded that: 1. Acetone gives the highest emission intensity for sodium and potassium when individually added to Na and K samples in comparison to other solvents, 2. Acetone-propyl alcohol gives the best results among different solvent combinations, 3. In the presence of surface-active agent lauryl amine hydrochloride, propyl alcohol can be replaced by ethyl alcohol in the above combination, and this new combination i.e. Acetone-Ethyl Alcohol- Lauryl amine hydrochloride gave the highest emission intensity of 110 for 0.05 ppm Na and 100 for 0.4 ppm K. The authors also analysed a sample of rainwater and used a flame photometer to identify the Na and K levels in the sample based on the experimental results of positive interference.

1.3 Determination of Ca and Sr in rainwater

According to Hinsvark, Wittwer and Sell, 1953 and Chow and Thompson, 1955, stroncium emission can be boosted by Na, K, and Ca but calcium emission is unaffected. (Sugawara *et al*.) used a flame photometer to determine the Ca and Sr in rain water samples that were free of Na and K. Ca is initially found at 5600 A°, followed by Sr at 4607 A°. During the processing of a rainwater sample, calcium and strontium were precipitated out as oxalates of Ca and Sr by adding ammonium oxalate and urea.

2. Application of Flame photometry in Manufacturing

2.1 Detection of Na, K and total alkalies in Fly Ash, Admixtures, Protland Cement and Water of Concrete by FIA-FES

Concrete is the most widely utilised construction material on the planet. Concrete is made up of cement, fly ash, aggregates (such as crushed rock, sand, and gravel), slag cement, and water admixture.(Askarian *et al*.) Cement has the ability to bond. Cement paste is made by combining cement and water. The aggregates are held together by this paste. Reinforced concrete is formed by mixing glass fibres, steel bars, and steel fibres into concrete. Admixtures are components that are added to concrete mixes to provide specific qualities that are not available in standard concrete mixes. They may aid in improving the durability and workability of concrete. Among all the reactions in concrete, some are unfavourable, especially the alkali-silica reaction (ASR). It's the reaction between reactive amorphous silica and alkaline cement paste that neutralises it. Bumping gel products result from this interaction. This type of product put a broad range of pressure on concrete. Concrete cracking can occur as a result of persistent ASR, which can lead to a variety of structural issues. Limiting the reactive silica content of the aggregates, neutralising the excessive alkalinity of cement at the early stage of cement setting by adding extremely fine siliceous materials, and limiting the 1st group metal contents of the cement are three strategies to make this reaction less harsh. In cement, the alkalies KOH and NaOH are extremely reactive. Flame photometry has been approved as a standard method for detecting Na and K in concrete and cement products. (Assaad *et al*.) For rapid and accessible procedures and on-line sample preparation, flow injection analysis has been introduced to these devices.(Almeida *et al*.; Basson and Van Staden; Bautista *et al*.) For the examination of Na and K in materials, Jaroon Junsomboon *et al* devised a simple FIA-FES detection. With flow injection analysis, the performance of the flame emission spectrometer (FES) improves in terms of keeping the burner and nebulizer clean and boosting sample throughput. The Flow injection analysis- Flame emission spectrometer (FIA-FES) was also connected to an amplification circuit in order to improve the flame emission spectrometer's sensitivity and detection limit. The developed technique was effectively employed to detect aggregrates, cement, and concrete admixtures. As a result, this enhanced system would be suitable for routine material quality checking. This developed system was used by the authors(Junsomboon and Jakmunee) to determine Na and K in concrete components such as cement and admixtures.

2.2 Determination of Sodium, Potassium, Lithium and Calcium Traces in the Cr-Ni Steel

The determination of K, Na, Li, and Ca traces in Cr-Ni steel is another use of flame photometry. (Sobkowska and Basińska) After separating the main component of steel, these alkali and alkaline earth metals were identified (Cr, Fe, Ni and partly Mn by electrolysis and Titanium and remaining Mn by precipitation with ammonia). Initially, a 1 g sample of steel was taken for this metal determination. For this investigation, a flame atomic emission spectrometer with a monochromater SPM-2 and a diffraction grating was used.

At 624.0 nm, 670.8 nm, 588.9 nm, and 766.5 nm, respectively, the intensity of calcium, lithium, sodium, and potassium emission was measured. Table no. II shows the results of two different steel samples.

Table 2: Ca, Li, Na, and K determination in steel

Sample,(g)	Ca	Li(µg)	Na	K
I 0.2	1.5	0.07	12.0	8.3
0.5	1.2	0.09	12.5	8.3
	1.6 3.5	0.07 0.20	11.5 30.0	8.0 19.0
II 0.2	6.5	0.10	9.0	6.5
0.2+20µg each of Ca, Li, Na, K	5.7 7.5 7.0 28.0 26.0	0.12 0.12 0.13 20.1 20.1	7.0 8.5 8.6 28.0 29.0	5.7 7.5 7.0 28.0 26.0

3. Application of Flame Photometry in Food

3.1 Determination of salt concentration in Soy Sauce

Soy sauce is a widely used and well-liked cooking ingredient. The salt content of soy sauce was determined by the authors.(Hiu and Spencer) The authors looked studied Li, Na, K, and Ca ions in six different brands of soy sauce that were available in the UK at the time. For their research, they employed a BWB XP flame photometer. As a fuel, propane gas was used. Six product samples (see Table III) were diluted with deionized water, and the flame photometer was calibrated with standard Li, Na, K, and Ca ions solutions. Following that, the samples were inspected. Each diluted soy sauce sample was examined in the same way that standard solutions were used to calibrate devices. The content of lithium was below the detection limit (0.1 mg/l for all cations), according to the authors. Table IV summarises the Na ion concentration data from six soy sauce samples and compares them to the nutrition tag provided by the manufacturer on the product packaging.

Table 3: Soy Sauce samples: kind and origin

Soy Sauce Sample	Origin	Kind
A	China	Light
B	China	Dark
C	Korea	Light
D	Malaysia	Light
E	Hong Kong	Light
F	The Netherlands	Light

Table 4: Conc. of sodium Calculated using the manufacturer's nutrition labelling and flame photometry results.

Soy Sauce Sample	Sodium conc. From flame photometry (mg/L)	Sodium conc. From manufacturer's Tag (mg/L)
A	98670	67693
B	86730	40537
C	81230	63000
D	45198	45900
E	42535	44500
F	45817	45600

3.2 Determination of Salt content in Processed Food

In the human diet, sodium chloride (NaCl) is a vital component. The intake of sodium chloride (NaCl) in the diet is still linked to the development of cardiovascular disease and hypertension.(Robinson) It has been reported that Na^+ ions, rather than Cl^- ions, induce such severe consequences.(HERLITZ *et al*.) NaCl is a key element in processed foods for increasing flavour and extending shelf life. As a result, the amount of salt in foods is important for food processing and health. In comparison to the Mohr's titration method, flame photometry is a simple and better method for determining the concentration of Na^+ ions in processed foods. The salt level of 48 food samples was examined by Chen, M.-J.; *et al*.(Chen *et al*.) The Na^+ concentrations (salinity) measured using Mohr's titration and flame photometry methods were statistically compared for each sample. The salinities measured by Mohr's titration and flame photometry were favourably associated, with a squared correlation coefficient of 0.9995 for both procedures.

The measured metal ion concentrations by the two methods did not differ significantly. However, the flame photometric direct measurement of metals is a better alternative than Mohr's titration since sodium concentration in Mohr's method is estimated by titration with $AgNO_3$ to determine the concentration of chloride ions. The disadvantage of this procedure is that it requires de-coloration preparation for foods with dark colours.(Skoog *et al*.) Flame photometry, on the other hand, does not require such a decolorization process, that is why it is superior to Mohr's titration.

4. Application of flame photometry in biological samples

4.1 Determination of Na^+ and K^+ in blood serum

The flame photometer is the most used potentiometric method for measuring the concentrations of K, Na, and Li in blood and urine samples. Electrolytic disorders are common in many surgical scenarios and it may cause death if not treated. The most serious electrolyte disturbance involves abnormalities in the level of sodium, potassium or calcium. This examination of plasma potassium and sodium is particularly significant in determining the fairness of various illnesses.(Peres *et al*.) Sodium is an extracellular fluid.(Vieira Neto and Moysés Neto; Mata *et al*.; Rocha; Arampatzis *et al*.) Hypernatremia and Hyponatremia are the disorders that are caused by change in Na^+ conc. Hypernatremia can be easily treated by simple therapeutic procedures.(Gusmão and Abdulkader; de Freitas Dutra *et al*.) Hyponatremia is a major disorder. Hyponatremia can induce neurological disorders and even death.(Rocha) Potassium is present in intracellular fluid and it is 2nd most abundant cation in the cell. Hypokalemia and Hyperkalemia are the disorders caused by low and high level of K^+ ion respectively in blood serum. (Daly and Farrington) Garcia, R. A.; *et al*. (Garcia *et al*.) analysed 175 serum samples from patients using three different methods for the determination of Na^+ and K^+ conc., as the distribution of these electrolytes in the blood serum, in particular conc., is highly crucial for healthy cell functioning. The results of the flame photometer were in close agreement with those of the other methods used.

4.2 Determination of Na and K conc. in mammalian subcutaneous tissue fluid

Dogs of both the sexes and mixed breed, and albino rabbits were used for this determination by Hengo Haljamae.(Haljamäe) The sample was tissue fluid present in the subcutaneous tissues of the hind leg of the dog. Ultra-micro flame photometric method was used to analyse the samples where the conc. of potassium and sodium of nanolitre samples of solution could be determined. Thin Pt-Ir wire was used by author to dry the sample. The wire holder was abode in a slit of instrument i. e. flame photometer (flame atomic emission spectrometer) and was pushed into the flame. On opposite side of the flame two photocells were placed. Sodium and potassium emission were detected by these cells. The integrating units which were connected to the photocells gave the value of total amount of the Na and K of the samples. The average Na conc. in tissue fluid was 153.4 meq/L and average K conc.was 4.67 meq/L.

5. Application of Flame photometry in Pharmaceuticals

5.1 Determination of metal ions in drugs

Humans are exposed to various metal ions either through different environmental factor like metal contaminated water or through diet.(Guna *et al*.) Some metals are essential for our good health and some are toxic if present in higher concentrations. When drug molecules combine with metal ions, complex formation takes place and this complexation may affect the outcome of chemical reaction because their pharmacokinetics may get changed upon complexation with metal ion. This change may occur in number of ways like change in drug distribution, drug interaction and in drug absorption properties. Hence controlling and decreasing the side effects of these meta ions from medicine is important to maintain the safety of drug therapy. Drug therapy can be maintained by the use of instrumental methods. Prabhu *et al* studied Ca, Na and K metal ion concentrations from various commercial formulations of tablets by flame photometric method.(Prabhu *et al*.) Authors evaluated 10 different formulations in their study. For this analysis, authors prepared 1000ppm standard solution of $CaCO_3$ by dissolving 0.2528 g of $CaCO_3$ in 100 ml of water and 6 ml dilute hydrochloric acid was added into this solution. From this standard solution 6 solutions of 40, 50, 60, 70, 80, and 100 ppm were prepared. Distilled water was used as blank and reading of these prepared solutions was taken by flame photometer on calcium filter. For sample preparation, 0.3035 gm of formulation 1 was weighed and putted into 100 ml beaker and then 6 ml dilute hydrochloric acid added to the beaker to dissolve all the $CaCO_3$. Prepared sample solution was sonicated for 15 minutes. After that solution was made to 100 ml y adding water up to the mark. This prepared sample was of 1000 ppm conc. Five different solutions of 40, 60, 70, 80, 100 ppm were made from this sample solution and aspirated into the flame. Instrumental readings for sample as well as standard solution was showing linearity in their results.

6. Application of Flame photometry in determination of Alkaline Earth Oxides Dissociation Energies

Dissociation energies of alkaline earth oxides were determined by flame photometric method by Kalff, P. J.; *et al*.(Kalff *et al*.) In their experiment the flames used were carbon monoxide flame with air and the visual sodium-D-line reversal method was used to measure the flame temperature. The salt under study were placed into the moist- CO-air flames. The sodium -D- line emission was measured as the SrO 6050 A° and 6660 A° bands, the CaO 5415 A° and 6220 A° and the BaO 5350 A° and 5087 A° as a function of temperature. In table no. V the average value of the dissociation energy of the three different measurement methods is shown that is reported by the Kalff, P. J.; *et al* in their result.

Table 5: Dissociation energy values of alkaline earth oxides (in ev).

Sample molecule	Self- absorption method	Line-line ratio method	Line- band ratio method
CaO	3.96±0.1	4.08±0.1	3.90±0.1
SrO	4.09±0.1	3.98±0.1	4.13±0.1
BaO	…………..	5.00±0.1	4.98±0.15

Conclusion

After looking at the flame photometry-based literature, it is predicted that the use of flame photometry in pharmaceutical, forensic, health, manufacturing will become increasingly more important in future.

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