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Modern instrumentation and practical application of flame atomic emission spectrometry

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Abstract

The modern instrumentation for flame atomic emission spectrometry (FAES) is overviewed: the main technical (composition of the fuel gas used, dispersing element, number of analytical channels, reference channel, detecting element, sampling method) and analytical (determined elements, range of determined concentrations, limits and the accuracy of their determination, the duration of a single measurement, the equired amount of the analyzed sample) characteristics of flame photometers for industrial and clinical use as well as spectrophotometers currently made by various manufacturers such as Sherwood Scientific Ltd., BWB Technologies UK Ltd., Labtron Equipment Ltd., Labnics Equipment Ltd. and JENWAY Ltd (UK); A.KRÜSS Optronic (Germany); Cole Parmer Instrument Company and Labfon Equipment Inc. (USA); Inesa Analytical Instrument Co., Ltd (China); OJSC Zagorsk Optical and Mechanical Plant, Unico-SIS LLC and VMK-Optoelectronics LLC (Russia); Manti Lab Solutions, Labtronics, Systonic, Globe Instruments, Electronics India, Lasany (India). The main areas of application of FAES are presented – bioenergy, agriculture (analysis of plants, soil extracts and fertilizers), mineral raw materials (geology), clinical medicine and pharmaceuticals, food industry, environmental control (analysis of drinking, technical and waste water), nuclear energy, metallurgy and chemical industry, as well as some features and problems associated with the preparation of samples for analysis by the FAES method. The review includes references to works on the practical application of FAES, published mainly from 1998 to 2023.

Keywords

flame
flame spectrometry
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Key findings

• Despite the advent of atomic absorption spectrometry and inductively coupled plasma, FAES as an analytical tool continues to be efficiently used for the determination of alkali and alkaline earth metals: the method is characterized by simplicity and speed of implementation, and its implementation requires simple and inexpensive equipment. The fields of application of the FAES method are very diverse: these are environmental control, food industry, agriculture, geology, medicine, pharmacology, nuclear and bioenergy, metallurgy and the chemical industry.

1. Introduction

Despite more than a century and a half of the rapid development of inductively coupled plasma and atomic absorption spectrometry, FAES, as one of the most reliable, simple, convenient and economically available methods of analysis, continues to be used and retains its priority in the control of alkaline and alkaline earth elements, the need to assess the content of which in a wide variety of objects is still quite high [1]. To a large extent, this is facilitated by the technical improvements introduced in the FAES in recent decades, aimed at automating the method, increasing its reliability and safety.

The purpose of this work is to review the current state of the FAES instrumentation and its main areas of application.

2. Modern instruments for FAES

To implement the method, flame photometers and spectrophotometers made by various manufacturers such as Sherwood Scientific Ltd., BWB Technologies UK Ltd., Labtron Equipment Ltd., Labnics Equipment Ltd. and JENWAY Ltd (UK); A.KRÜSS Optronic (Germany); Cole Parmer Instrument Company and Labfon Equipment Inc. (USA); Inesa Analytical Instrument Co., Ltd (China), OAO Zagorsk Optical and Mechanical Plant, OOO "UNIKO-SIS" and OOO "VMK-Optoelectronics" (Russia) were used. The main technical and analytical characteristics of the devices are given in Table 1–4.

Most devices for FAES use propane, butane, propane-butane mixture in cylinders or natural gas from the gas network as fuel gas. The only flame photometer on the market that can work with acetylene, which allows maintaining a higher flame temperature (2050 °C) and, accordingly, providing more accurate measurements of calcium, is offered by A.KRÜSS Optronic (Germany): the company recommends using propane to determine alkali metals (with butane as a possible substitute for propane), and acetylene for alkaline earth metals. The fuel gas flow rate is 0.4 l/min. Fuel gas regulators and fuel filters are required to control the pressure of the fuel supplied to the flame photometer and prevent particulate matter from entering the mixing chamber from the fuel source.

To achieve flame stability, constant sample supply and good accuracy of results, all flame photometers use dry, clean (oil-free) compressed air as an oxidizing agent, supplied at a pressure of 1 kgf/cm^2 by an oil-free air compressor connected to the photometer. Some photometers (eg BWB-XP from BWB Technologies UK Ltd.) have built-in compressors (or a low-noise built-in air pump) and electronic airflow control for optimal results. The air flow is 6 l/min.

Water separators are recommended to remove residual water from the compressed air source; they are especially needed at high humidity. The air humidity determines the amount of condensate and thus the size of the water separator (drain trap). Some photometers (eg BWB-XP from BWB Technologies UK Ltd.) have a full water separator detector.

The sample flow rate generally varies between 2 and 6 cm^3/min. The analyzed samples should be aqueous solutions, homogeneous and not too viscous.

Modern flame photometers have up to five measuring channels, providing the possibility of simultaneous determination of up to five elements, respectively (photometers from BWB Technologies UK Ltd., A.KRÜSS Optronic and Labnics Equipment Ltd.).

A number of photometers have a reference channel that registers the emission line of the so-called internal standards: lithium (lithium standard) or cesium (cesium standard). The use of the reference channel makes it possible to increase the stability of the photometer readings and eliminate deviations associated with the state of the flame, zero drift and dilution errors, i.e., ensure reproducible and accurate measurement results. The lithium reference channel is provided in photometers from Sherwood Scientific Ltd. (UK) and Cole Parmer Instrument Company (USA). In Sherwood Scientific Ltd. photometers, in addition to lithium, there is a model (photometer model M420Cs) with a cesium reference channel.

Photometers manufactured by most companies have a modular design. This makes it possible to equip the devices with additional automation components: automatic samplers (autosamplers) for working with large flows of analyzed samples (for example, DV-704 and DV-710 photometers are equipped with autosamplers for 12 and 20 positions, respectively, with a sample volume of 50 μl; Sherwood Scientific Ltd. completes its photometers with autosamplers for 40 tubes with a minimum sample volume of 200 μl; photometers from BWB Technologies UK Ltd. and A.KRÜSS Optronic can include autosamplers for 89 and 72 positions, respectively); built-in automatic dilution devices (so-called thinners) necessary when working with high concentrations requiring dilution (Sherwood Scientific Ltd., BWB Technologies UK Ltd. and A.KRÜSS Optronic) with a choice of dilution factor. A number of photometers provide: the possibility of pre-selection of the flame size (Labnics Equipment Ltd. and Labtron Equipment Ltd., UK); automatic filter selection (in Flame Photometer Superspec S20-F photometers from Spectrolab, England); built-in syringe holder for cleaning the nebulizer capillary from clogging with solutions with a high salt content (in BWB-XP photometers from BWB Technologies UK Ltd.).

In order to ensure safe operation, modern photometers are provided with the following devices: flame protection and automatic detection of flame failure (JENWAY Ltd.), flame failure detector and automatic shutdown (BWB Technologies UK Ltd., Globe Scientific Instruments): the automatic gas shutdown mechanism is activated if the flame spontaneously extinguishes.

Photometers are supplied with digital displays. For example, the BWB XP Performance Plus photometer is equipped with a four-line display, which allows calibration and determination of all elements without using a PC.

Photometers from a number of companies (for example, the BWB XP photometer from BWB Technologies UK Ltd.) feature the data transfer to a PC and the software for displaying and printing analysis results. For example, in devices from BWB Technologies UK Ltd. (BWB-XP) the software provides: mathematical signal processing (as a result, the need to use an internal standard is eliminated); calibration by two or more points; selection of the type of calibration dependences (linear and quadratic); conversion of concentrations (ppm, mg/l, meq/l and mmol/l); recalculation of concentration units of calibration curves.

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Table 1 Flame photometers for laboratory applications. Technical characteristics.

Country	Manufacturer	Type (model) instrument	Fuel gas composition	Number of channels	Reference channel	Sample supply		Note
						Manual	Automatic (number of positions)	
Great Britain	Sherwood Scientific Ltd. [2]	M360	LPG (propane, butane or propane/butane mixture), or natural gas from the gas network	1	–	+	–	–
		M410	–“–	1	–	+	–	–
		M420	–“–	2	Li	+	–	–
		M420Cs	–“–	2	Cs, Li	+	–	–
		M425	–“–	2		+	+	–
	JENWAY Ltd. [3]	PFP-7	Propane, butane, propane-butane or natural gas	1		+	–	Add. Filters for Li, Ca and Ba
	BWB Technologies UK Ltd. [4]	BWB-XP	Propane, butane, LPG[a] Flow rate 0.4 l/min.	5		+	+(89)	Built-in: automatic. diluent and air compressor
		BWB XP Performance Plus	Propane, butane or natural gas. Up to 19 mbar. Consumption 0.4 l/min.	5		+	+(89)	Available with automatic sample diluent
	Spectrolab [5]	Flame Photometer Superspec S20-F	Propane, butane or natural gas. LPG[a]	4		+	–	Automatic LF[b] selection
	Labnics Equipment Ltd. [6]	Series NFP 100, 101	LPG[a]	2	–	+	–	Flame size selection
		Series NFP 102, 103, 104	–“–	3	–	+	–	–“–
		Series NFP 105	–“–	4	–	+	–	–“–
		Series NFP 106	–“–	5	–	+	–	–“–
	Labtron Equipment Ltd. [7]	Series LFP A10, A11, A20, A21, A22, A30, A40	Propane/butane or propane/butane mixture. Air supply 6 l/min.	2	–	+	–	Flame size selection
Germany	A.KRÜSS Optronic [8]	FP8000 FP8400, FP8500, FP8600 FP8700	Propane, butane, acetylene	5	–	+	+	–
USA	Cole Parmer Instrument Company [9]	Series ML 02655-00	Propane, butane, acetylene or propane/butane mixture; natural gas	1	–	+		Add. filter for Li
		Series ML 02655-10	Propane/butane or propane/butane mixture. Air supply 6 l/min	2	Li	+	–	–
		Series ML 02655-15	–“–	4	Li	+	–	–
	Labfon Equipment Inc. [10]	F-FPM106		2	–	+	–	-
India	Manti Lab Solutions [11]	MANTI MT 125	LPG[a] and dry oil-free air	2	–	–	–	Dual display; oil-free mini compressor block with pressure regulator

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Table 1 Flame photometers for laboratory applications. Technical characteristics.

Country	Manufacturer	Type (model) instrument		Fuel gas composition	Number of channels	Reference channel	Sample supply		Note
							Manual	Automatic (number of positions)	
India	Labtronics [12]	Series LT	65	–“–	–	–	–	–	2.5 digit LED display
			671	–“–	1	–	–	–	For industrial and clinical applicable. Automatic ignition and filter selection
	Systonic [13]	S-931		–“–	1	–	–	–	2.5 digit LED display. Automatic ignition system
	Globe Instruments [14]	Globe Scientific Instruments 038-G		LPG[a] and dry oil-free air	–	–	–	–	–
		1600-G		–“–	–	–	–	–	For industrial and clinical applicable. Embedded microprocessor
	Electronics India [15]	381		–“–	–	–	–	–	–“–
Russia	OJSC Zagorsk Optical and Mechanical Plant [16]	FPA-2		Propane butane	–	–	+	–	Embedded microcomputer
China	Inesa Analytical Instrument Co., Ltd [17]	Series FP	640	Propane butane	2		+	–	7" LCD touch screen. Flame size selection.
			6410	–“–	2				7" LCD touch screen. Automatic calculation of the correlation coefficient. Flame size selection. Optional built-in printer
			6430	–“–	3				
			6431	–“–	3				
			6440	–“–	4				
			6450	–“–	5				

[a] mixture of liquefied hydrocarbons;

[b] light filter.

Table 2 Flame photometers for laboratory applications. Analytical characteristics.

Country	Manufacturer	Type (model) instrument	Element concentration range (ppm) Detection limits of elements (ppm)								Precision, %	Duration single measurements, s
			Na	K	Li	Cs	Ca	Ba	Sr	Rb		
Great Britain	Sherwood Scientific Ltd. [2]	M360	1 0.1	0.5 0.1	1 0.1	–	20 2	300 20	–	–	2	≤20
		M410	0.5–10 0.02	0.5–20 0.02	0.5–20 0.02	20–100 0.2	10–100 0.2	1000 20	1000 20	1–100 0.1	<2	≤20
		M420	–“–	–“–	0–20.0 0.05	–	–	–	–	–	<2	≤20
		M420Cs	–“–	–“–	–“–	–	–	–	–	–	≤0.5	–
		M425	–“–	–“–	–“–	–	5.0–100 0.2	–	–	–	<2	≤20
	JENWAY Ltd. [3]	PFP-7	0.50–10 0.2	0.50–10 <0.25	–	10–200 <15	50–200 <30	–	–	–	≤60	–

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Table 2 Flame photometers for laboratory applications. Analytical characteristics.

Country	Manufacturer	Type (model) instrument	Element concentration range (ppm) Detection limits of elements (ppm)								Precision, %	Duration single measurements, s
			Na	K	Li	Cs	Ca	Ba	Sr	Rb		
Great Britain	BWB Technologies UK Ltd. [4]	BWB-XP	0.05–1000 0.02		0.1–1000 0.05	–	2.5–1000 1	30–3000 10	–	–	–	–
		BWB XP Performance Plus, Calibration: one point	0.1–60 0.03	0.05–100 0.02	0.05–50 0.02	–	1–100 0.03	5.0–100 –	–	–	–	30
		BWB XP Performance Plus, Calibration: multi point	0.1–1000 0.03	0.05–1000 0.02	0.05–1000 0.02	–	1–1000 0.03	5–3000 1.6	–	–	–	–
	Spectrolab [5]	Flame Photometer Superspec S20-F		0–199.9 0.2		–	0–199.9 <10		–	–	–	–
	Labnics Equipment Ltd. [6]	Series NFP 100	0–160 0.01	0–100 0.01	–	–	–	–	–	–	<3	8
		Series NFP 101	0–160 0.1	0–100 0.1	n/n[b]	–	–	–	–	–	–“–	–“–
		Series NFP 102	0–160 0.01	0–100 0.01	0–100 0.1	–	–	–	–	–	–“–	–“–
		Series NFP 103	0–160 0.01	0–100 0.01	–	–	0–1000 2	–	–	–	–“–	–“–
		Series NFP 104	0–160 0.01	0–100 0.01	–	–	–	0–3000 6	–	–	–“–	–“–
		Series NFP 105	0–160 0.01	0–100 0.01	0–100 0.1	–	0–1000 2	–	–	–	–“–	–“–
		Series NFP 106	0–160 0.01	0–100 0.01	0–100 0.1	–	0–1000 2	0–3000 6	–	–	–“–	–“–
	Labtron Equipment Ltd. [7]	Series LFP A10	0–160 0.184	0–100 0.156	–	–	–	–	–	–	–	–
		Series LFP A11	–“–	–“–	opt.[a]	–	–	–	–	–	–	–
		Series LFP A20	–“–	–“–	0–100 0.1	–	–	–	–	–	–	–
		Series LFP A21	–“–	–“–	–	–	0–1000 2	–	–	–	–	–
		Series LFP A22	–“–	–“–	–	–	–	0–3000 6	–	–	–	–
		Series LFP A30	–“–	–“–	0–100 0.1	–	0–1000 2	–	–	–	–	–
		Series LFP A40	–“–	–“–	–“–	–	–“–	0–3000 6	–	–	–	–
Germany	A.KRÜSS Optronic [8]	FP8000 8400, 8500, 8600	0.01–45000 0.01	0.02–45000 0.01	0.01–45000 0.01	–	0.5–45000 0.03	–	–	–	0.06	–
		FP8000 8700	–	–	–	–	–	–	–	–	–	–

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Table 2 Flame photometers for laboratory applications. Analytical characteristics.

Country	Manufacturer	Type (model) instrument	Element concentration range (ppm) / Detection limits of elements (ppm)								Precision, %	Duration single measurements, s
			Na	K	Li	Cs	Ca	Ba	Sr	Rb		
USA	Cole Parmer Instrument Company [9]	Series ML 02655-00	0–1999 / < 0.5		0–1999 / <2	–	0–1999 / 5	–	–	–	–	–
		Series ML 02655-10	1.00–9.99 / 0.5		1.00–9.99 / 2	–	–	–	–	–	–	–
		Series ML 02655-15	1.00–9.99 / 0.5		1.00–9.99 / 2	–	0–1999 / 5	–	–	–	–	–
	Labfon Equipment Inc. [10]	F-FPM106	0–160 / 0.184	0–100 / 0.156	0–100 / 0.1	–	0–1000 / 2	–	–	–	1	<8
India	Manti Lab Solutions [11]	MANTI MT 125	–	–	–	–	–	–	–	–	<2300 ppm: ±2%; >2300 ppm: ±5%	–
	Labtronics [12]	Series LT 65	0–100 / 5		10–100 / 10	–	20–100 / 10	–	–	–	<40 ppm: ±2%; >40 ppm: ±5%	–
		Series LT 671	0–100 / 5		10–100 / 10	–	20–100 / 10	–	–	–	–	–
	Systonic [13]	S-931	0–100 / 5		10–100 / 10	–	15–100 / 10	–	–	–	±2%	–
	Globe Instruments [14]	Globe Scientific Instruments038-G	0–100 / 5		10–100 / 10	–	15–100 / 10	–	–	–	±2%	–
		1600-G		0–100 / 0.5		–	0–100 / 15	50–1000 / 50	–	–	<2%	–
	Electronics India [15]	381	0–100 / 5		10–100 / 10	–	15–100 / 10	–	–	–	< 40ppm ±2%; >40 ppm ±5%	–
Russia	OJSC Zagorsk Optical and Mechanical Plant [16]	FPA-2	0.5–23 / –	0.2–40 / –	0.1–4.0 / –	–	0.5–40 / –	–	–	–	–	–
China	Inesa Analytical Instrument Co., Ltd [17]	Series FP 640	0–160 / 0.01	0–100 / 0.01	–	–	–	–	–	–	3	<8
		Series FP 6410	0–160 / 0.01	0–100 / 0.01	–	–	–	–	–	–	–“–	–“–
		Series FP 6430	0–160 / 0.01	0–100 / 0.01	0–100 / 0.1	–	–	–	–	–	–“–	–“–
		Series FP 6431	0–160 / 0.01	0–100 / 0.01	–	–	0–1000 / 2	–	–	–	–“–	–“–
		Series FP 6440	0–160 / 0.01	0–100 / 0.01	0–100 / 0.1	–	0–1000 / 2	–	–	–	–“–	–“–
		Series FP 6450	0–160 / 0.01	0–100 / 0.01	0–100 / 0.1	–	0–1000 / 2	0–3000 / 6	–	–	–“–	–“–

[a]optional;
[b]not necessary.

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Table 3 Flame photometers for clinical use. Technical and analytical characteristics.

Country	Manufacturer	Type (model) instrument	Fuel gas composition	Number of channels	Sample supply: Manual	Sample supply: Automatic (number of positions)	Range of determined concentrations (ppm) / Limits of detection (ppm): Na	K	Li	Ca	Ba	Note
Great Britain	Sherwood Scientific Ltd. [2]	M410C	LPG[a] (propane, butane or propane/butane mixture), or natural gas from the gas network	1			Urine 0–4600 – Serum 2530–3910 –	Urine 0–4600 – Serum 0–230 –	0–70 –	–	–	–
		M360C	–"–	1			0–1 0.1	0–0.5 0.1	0–1 0.1	0–20 2	0–300 20	–
		M420C	–"–	2			0.5–20 0.02		0.0–20 0.05	–	–	–
	JENWAY Ltd. [3]	PFP7/C	Propane, butane, propane-butane (LPG[a]) or natural gas	1	+	–	0.50–10.0 <0.2		0.50–10.0 <0.25	–	–	–
Italy	Lab Service sas [18]	DIGIFLAME COMPACT Model DV-704	LPG[a], propane or butane Compressed air: 14 l/min	3	–	+ (20)	0–5750 3200	Serum 0–230 – Urine (0–4600) 115	0–230 69	–	–	Microprocessor. Internal valve stops gas exit when air pump is off Air pump is automatically arrested in case of lack of flame
		DIGIFLAME 2000 Model DV 710	–"–	3	–	+ (12)	0–5750 –	Serum 0–230 – Urine (0–4600) –	0–230 –	–	–	–"–
India	Manti Lab Solutions [11]	MT-126	LPG[a] and dry oil-free air	2	+	–	0–100 5		10–100 10	15–100 10	–	Ca, Li, opt.[b]
	Labtronics [12]	LT-66	–"–		+	–	0–4600 –	0–2300 –	0–230 –	0–46 –	–	Dual 2.5 digit LED display. Ca and Li opt.[b]
	Systonic [13]	S-932	–"–	1	+	–		0–100 0.5		0–100 15	–	Dual 2.5 digit LED display. Automatic ignition system. Ca, Li, opt.[b]
		S-935	–"–	4	+	–	0–100 0.5		0–100 50	0–100 15	–	Embedded software. Automatic filter selection. USB port. Ca, Li, opt.[b]
	Globe Instruments [14]	Globe Scientific Instruments 039-G	LPG[a] and dry oil-free air	2	+	–	0–100 5		10–100 10	15–100 10	–	Dual display Ca, Li, opt.[b]

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Table 3 Flame photometers for clinical use. Technical and analytical characteristics.

Country	Manufacturer	Type (model) instrument	Fuel gas composition	Number of channels	Sample supply		Range of determined concentrations (ppm) Limits of detection (ppm)					Note
					Manual	Automatic (number of positions)	Na	K	Li	Ca	Ba	
India	Electronics India [15]	1385 1382	–“–	–	+	–		0–100 0.5		0–100 15	0–100 50	Built-in microprocessor Ca, Li, Ba
		1381		–			0–100 0.1		0.5–100 0.1	15–100 0.1	–	For industrial and clinical applications
		391		2			Urine, Serum 0–4600 –	Urine 0–2300 – Serum 0–230 –	0–46 –	0–230 –	–	–
	Lasany [19]	Model 1307	–	–	+	–		0–100 0.5		0–100 15	–	–

[a]mixture of liquefied hydrocarbons;
[b]optional.

Table 4 Flame spectrophotometers. Technical and analytical characteristics.

Country	Manufacturer	Type (model) instrument	Fuel gas composition	Operating wavelength range, nm	Analyzed elements and ranges of determined concentrations (ppm)					Number of simultaneously controlled elements	Precision, %	Single measurement duration, s	Sample consumption of the analyzed sample, cm^3	Notes
					Na	K	Li	Ca	Sr					
Russia	OJSC Zagorsk Optical and Mechanical Plant [16]	FPA-2-01	Propane butane Pressure created by the compressor, atm, no more than 0.6–1.5	580–780	0.5–23	0.5–40	0.1–4.0	0.2–40	2.5–500	1; 2; 3; 4	≤ 2.5	–	≤ 2.5	Embedded microcomputer
	OOO „UNIKO-SIS” [20]	PFA-378	Propane butane	–		0.5–100.0		15–100	–	–	±(0,036C+0,004) (C — measurement result, mg/dm^3)	≤5	≤2.5	Ba, Sr, Rb, Cs – optional
	VMK-Optoelectronics LLC [21–23]	Flame spectrometer «Pavlin»	Acetylene-air Acetylene consumption 0.3–1 l/min	390–860		0.001–10^5 mg/l			–	–	–	–	0.5–1.5 ml/min	Ba, Rb, Cs

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JENWAY Ltd (PFP7/C photometer) and Sherwood Scientific Ltd. (photometers models M410C, M360C and M420C), in constrast to industrial (laboratory) photometers are produced for clinical use (Table 3): the display of these photometers is calibrated directly in units of Na and K concentration in biological samples (urine and blood serum); only one external standard is needed for this. Firms Globe Scientific Instruments and Labtronics (India) produce photometers designed both for laboratory and clinical use (Table 1, 3).

A number of firms (Electronics India, Manti Lab Solutions, Labtronics, Systonic, Lasany) specialize only in the production of photometers for clinical purposes (Table 3).

Flame spectrophotometers (Table 4) use a propane-butane mixture as a fuel gas. The decomposition of radiation into a spectrum and its registration are carried out using diffraction gratings and a photodiode ruler (out of 512 photodetectors), respectively. The latter provides simultaneous determination of the group of elements Na, K, Li, Ca, Ba, Ce, Rb, Sr. The processing of current information and control of the operation of photometers with the help of built-in microcomputers are provided.

The Pavlin flame spectrometer manufactured by VMK-Optoelectronics LLC (Novosibirsk, Russia) uses an air-acetylene flame, a three-slit torch made of chemically resistant stainless steel, and a stainless steel concentric atomizer similar in design to a Meinhard atomizer; the spectrum registration process is controlled using the Atom program [21–24].

3. Practical applications of FAES

A real publication boom associated with the use of flame photometry was observed in the forties and eighties of the last century. However, at present, the need for FAES is quite high.

Below is a review of the areas of application of FAES most frequently mentioned in the modern literature with a brief description of the features of sample preparation, a stage that plays an important role in analysis in general, and in analysis by the FAES method, in particular. The main emphasis is placed on works published in the last two decades.

3.1. Application in geology

Mineral raw materials are considered one of the most difficult objects for the simultaneous determination of alkali metals [25] and this is due to the fact that their content in natural samples differs by thousands of times [26]. The process of preparing samples of mineral raw materials for analysis is also time-consuming. Most often, acid decomposition with hydrofluoric acid is used for these purposes, and the resulting fluoride complexes are destroyed by evaporation, for example, with perchloric [26–30] or hydrochloric acid [31]. In [32], to determine potassium by FAES, samples of silicate rocks (basalt, monzogranite, and slate fines) are dissolved using an ultrasonic bath in a mixture of HNO_3, HCl, and HF acids.

3.2. Applications in clinical chemistry and pharmaceuticals

3.2.1. In clinical chemistry

The flame photometry method, due to its ease of implementation, rapidity and availability of equipment, is widely used in clinical laboratories to determine in the blood: sodium and potassium, the concentration ratio of which controls the functioning of muscles, including the heart [33–38]; total calcium is one of the numerous indicators of the state of human blood [39].

The FAES method has also shown its suitability for determining the concentration of Li administered for therapeutic purposes in biological fluids, for example, in bipolar disorders [40, 41]; sodium concentration and osmolality in plasma and cerebrospinal fluid (the so-called water-salt homeostasis of the brain) [42]; concentrations of sodium and potassium ions to study the physiological state of the kidneys [43]; levels of Ca, K, and Na in oral fluid [44], potassium levels in the vitreous body of the eye [45]; metals in hair [46]; calcium in urine [47], sodium and potassium in blood serum and urine [48, 49]; level of magnesium in blood plasma in patients with chronic alcoholism during withdrawal syndrome [50].

FAES method determines the intracellular content of Na^+ and K^+ cations to assess the functional state of erythrocytes [51].

Flame photometry examines the sodium content in dialysates and selects sodium dialysate for patients on hemodialysis [52–57]. Using flame emission photometry calibration of brain samples with a micropunch, quantitative [Na(+)] and [K(+)] maps of the brain are obtained [58].

3.1.2. In pharmaceuticals

FAES is also used in pharmaceuticals to control the sodium content in parenteral solutions used in rehydration therapy [59], sodium and potassium in powders for oral rehydration therapy [60]; potassium in complex solutions administered intravenously to replenish its intracellular losses [52], sodium in sodium diclofenac [61]; sodium and potassium in infusion solutions, such as, for example, sodium chloride solution, Ringer's solution and Reamberin [62, 63]; sodium in albumin [64].

3.3. Application in food analysis

Demand for the use of flame photometry for food analysis has grown significantly in recent years.

Since food products are complex multicomponent systems, the procedure of sample preparation is of great importance in their analysis. For liquid samples (e.g. water, beverages) direct determinations are possible with minimal sample processing such as dilution, degassing or evaporation of matrix components. Solid samples are decomposed by dry or wet ashing [65–69] as well as microwave decomposition [70].

As for the actual analysis of food products, the FAES method is known to be used to determine Li^+, Na^+, K^+ and Ca^{2+} in soy sauce [71]; sodium in processed foods and bread

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to assess their salinity [72–74]; Na and K in beer using microwave processing of samples [75]; calcium, magnesium and potassium in canned tomatoes [76]; rubidium in some drinks (beer, wine, vegetable and fruit juices) using a platinum wire loop for spraying in a methane-air flame [77]; sodium, potassium, lithium and rubidium in honey [78]; in the analysis of the main elements of the mineral composition of wine products [79].

3.4. Applications in the analysis of drinking, industrial and waste water

Flame photometry methods are successfully used to determine cesium and rubidium in mineral and well water using a methane-air flame [80, 81]; sodium, potassium, calcium and magnesium in natural waters [82, 83]; sodium and potassium in samples of surface, underground and river waters [84]; sodium in sea water [85]; lithium in wastewater from the production of metallic lithium and its compounds [23].

3.5. Application in bioenergy

Demand for renewable fuels has been on the rise in recent decades as fossil fuel sources are limited and, in addition, burning biodiesel results in lower emissions of carbon monoxide and hydrocarbons than burning petroleum fuels.

As with any fuel, the determination of metals in biodiesel is important because they can contribute to fuel degradation or corrosion of engine parts, reducing engine performance and life. Of particular importance is the monitoring of Na, K, Ca and Mg, whose salts and hydroxides (or their corresponding alkoxides) are used as catalysts in the biodiesel production process. These elements may be present in the form of abrasive solids or soluble soaps and contribute to engine wear due to deposit formation. In this regard, restrictions on the maximum levels of metals allowed in biodiesel have been established: for example, the maximum combined concentration of Na and K is 5 mg/kg [86].

The analysis of biodiesel is not a trivial task: its characteristics such as viscosity (11–17 times higher than that of diesel fuel), immiscibility with aqueous solutions, and high carbon content can affect the sensitivity and accuracy of the determination. FAES successfully copes with the task of monitoring the content of Na, K, Ca and Mg in biodiesel fuel.

The analysis of biodiesel by the FAES method using various types of sample preparation is widely presented in the literature: acid decomposition using HNO_3, H_2SO_4, HCl, and H_2O_2, as well as their mixtures with simple or microwave [87, 88] heating; dry decomposition, which makes it possible to preconcentrate the analyte, reduce the volume of strong acids at the stage of dissolution, exclude the use of organic solvents, and shorten the stages of sample preparation, thereby contributing to a decrease in the error [89]; rapid, easy-to-implement sample dissolution in organic solvents such as ethyl alcohol [90, 91] and methyl oleate [92], which replaced xylene or n-hexane and made it possible to use aqueous spectroscopic standards that improved the spraying process; dissolution by emulsification of a biodiesel sample with HNO_3, n-butanol (as a co-solvent) and an aqueous solution of a surfactant (Triton X-100) [93] or by microemulsification with n-propanol and an aqueous acid solution [94]; as well as a method based on reverse-phase dispersive liquid microextraction [95].

The currently used methods for preparing biodiesel samples for elemental analysis (including the FAES method) are considered in detail in [96, 97].

3.6. Application in agriculture

The analysis of agricultural materials – plants, soil extracts and fertilizers – is another area in which FAES has been successfully applied. Traditionally, in order to determine the optimal amount of fertilizers and develop recommendations for their application, analysis of the soil and nutrient content in the foliage of plants is carried out.

3.6.1. Soil and plant analysis

Potassium and sodium are the most important elements for the vegetative growth of plants, so the control of their content in the soil and in crops is very important.

To determine the content of nutrients using the FAES method, soil samples are treated with ammonium acetate [98–103], and plant samples are treated with acids (either one ($HClO_4$), or a mixture of two (HNO_3 + $HClO_4$) or three (HNO_3 + H_2SO_4 + $HClO_4$) acids) [104], ultrasonic radiation [105] or subjected to extraction with a mixture of solutions of ammonium acetate – magnesium acetate [106], HCl solution [106–108], or water (since potassium in plant tissues is not bound to organic compounds and is in a soluble form) [109, 110]. Issues related to the determination of analytical elements in soil hydrolysates, soil extracts and soil solutions are discussed in sufficient detail in the book [111].

3.6.2. Fertilizer analysis

In modern agriculture, a wide range of potash fertilizers is used. FAES is employed to determine the content of potassium oxide K_2O in the production of complex fertilizers [112, 113] and organic fertilizers [114], using extraction with an ammonium oxalate solution and treatment with a mixture of nitric and perchloric acids, respectively, to decompose the samples.

3.7. Application in nuclear power, metallurgy and chemical industry

FAES has found application in the nuclear power industry for the determination of potassium in sodium used as a coolant in a fast neutron reactor [115], and alkali metals and calcium in chemical concentrates using an air-acetylene flame [24], in the chemical industry for the analysis of trace amounts of potassium in some oil samples after selective preconcentration by a centrifuge-free method of dispersive liquid microextraction, based on the use of a new target magnetic polymeric ionic liquid as a chelating and extraction solvent [116], and in metallurgy for the determination of lithium, potassium, sodium and calcium in solutions of

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technological processes for the production of metallic lithium and its salts [22, 23], for determination of lithium in lithium-born alloy in the range from 59.0 to 96.0% with a relative total error of no more than 2.7% [117], and measuring the amount of rhenium in highly reducing acetylene-oxygen and acetylene-dinitrooxide flames [118].

4. Limitations

The presented review does not consider problems associated with the preparation of samples for analysis, the influence of the matrix and third elements on the results of analysis and methods for reducing this influence.

5. Conclusions

Despite the advent of atomic absorption spectrometry and inductively coupled plasma, flame emission as an analytical tool continues to be efficiently used for the determination of alkali and alkaline earth metals: the method is characterized by simplicity and high throughput (for example, the A.KRÜSS Optronic flame photometer allows up to 300 measurements per hour), its implementation requires relatively simple and inexpensive equipment. The fields of application of the FAES method are very diverse: these are environmental control, food industry, agriculture, geology, medicine, pharmacology, nuclear and bioenergy, metallurgy and the chemical industry.

In many ways, the successful use of FAES is facilitated by extensive automation of analysis, involving the automatic samplers (autosamplers) for 12–89 samples for working with large flows of analyzed samples, built-in automatic dilution devices for working with high concentration solutions, built-in syringe holder for cleaning the spray capillary from clogging with solutions with a high salt content, the possibility of pre-selection of the flame size and automatic selection of filters, an automatic detection of the loss of the flame and an automatic shutdown of the gas, which is triggered if the flame goes out, the use of digital displays that allow calibration and determination of all elements without using a PC, the ability to transfer data to a PC and print the results of the analysis, and the possibility to define up to five elements at the same time.

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