

Determination of magnesium by flame AAS detection with flow injection analysis

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A simple arrangement of the flow injection analyzer (FIA) was applied to the determination of magnesium by flame atomic absorption spectrometry (FAAS) in samples of luminophores of the type of aluminates. The influence of carrier medium and other parameters on absorption signal of magnesium has been discussed and the calibration methods have been assessed for the FIA—FAAS method.

Простая модификация проточного инжекционного анализатора (FIA) была применена для определения магния с помощью пламенной атомной абсорбционной спектроскопии (FAAS) в образцах люминофоров типа алюминатов. Обсуждается влияние среды носителя и других параметров на абсорбционный сигнал магния, а также оцениваются калибрационные методы, применяемые в методике FIA—FAAS.

The flow injection analysis (FIA) is one of the modern analytical techniques that very rapidly develop at the present time and work their way into different regions of analytical chemistry. The connection of FIA with FAAS (flame atomic absorption spectrometry) made possible to achieve increased sample throughput, permitted to analyze samples with high inert salt contents, enabled reduction in the interfering matrix effect, and gave new possibilities of calibration [1—6].

The FIA—FAAS method has been applied to determination of a great number of elements including alkaline-earth metals. In this study the above method was used for the determination of magnesium. As a matter of fact, the determination of magnesium in the acetylene—air flame is impaired by the presence of three- and multivalent elements, such as Al, Si, Ti, Zr, and others and by the formation of thermostable compounds. Nevertheless, this influence can be removed by an addition of releasing agents [7]. The interfering influence of aluminium can be suppressed by the releasing elements in the form of salts (chlorides or nitrates) of Sr, La, Ca, Ba, Sc, Y, Ce, Ni or by some chelate-forming agents [7].

In this paper the influence of carrier medium, volume of the injected sample, length of dispersing coil, and flow-rate of carrier and sample is described and different calibration methods are compared with each other. A simple

FIA—FAAS equipment was built up for the determination of magnesium in luminophores of the type of aluminate as major component.

Experimental

The standard solution of MgCl_2 ($\rho(\text{Mg}) = 1.02 \text{ g dm}^{-3}$ in 0.1 M-HCl) was prepared by dissolving metallic magnesium, anal. grade (Lachema, Brno), in excess 6 M-HCl and diluting with bidistilled water to the volume of 1000 cm^3 . The solution was standardized by chelatometric titration with EDTA using eriochrome black T as an indicator. Working solutions were prepared by diluting the standard solution with 0.1 M-HCl. Other chemicals were commercial products of anal. grade or high purity (Lachema, Brno). Water was twice redistilled in a quartz apparatus.

The single-channel FIA—FAAS system [4] consisted of a transport unit, an injecting device and a FAAS detector connected with recorder and/or integrator. The capillary dispersing system FIA comprised teflon capillaries of inner diameter of 0.6 or 1.0 mm (Norton Chemplast, Wayne, U.S.A.). A pulse-free continuous flow of the carrier medium in the necessary range of flow-rate Q_c was provided by hydrostatic pressure of the liquid in an infusion bottle of 250 cm^3 volume placed above the nebulizer, in conjunction with the natural suction rate of the nebulizer.

The rotatory loop injector with changeable sample loop of the volume $V_s \geq 20 \text{ mm}^3$ comprised a teflon rotor and stator as well as injecting and supplying teflon capillaries (i.d. 0.6 or 1.0 mm). The dosing loops were filled with an injection syringe.

The measurements were performed on an atomic absorption spectrometer PE 306 (Perkin—Elmer, Norwalk, U.S.A.) equipped with a Mg hollow cathode lamp (Pye—Unicam, Cambridge) at the wavelength of 285.2 nm by using slit width of 0.7 nm (current 4 mA). 10 or 5 cm one-slot burners were used for measurements in the acetylene—air flame. The volume flow-rates were 3.7 or $2.4 \text{ dm}^3 \text{ min}^{-1}$ for acetylene and 22.5 or $15.0 \text{ dm}^3 \text{ min}^{-1}$ for air, respectively. The absorption signal was scanned on a TZ 4100 recorder or on an IT 2 integrator (Laboratorní přístroje, Prague) in the form of peaks.

The calibration graphs and other relationships were obtained in most cases by measuring the peak heights, and occasionally by measuring the peak area or peak width. The calibration curves were evaluated by a linear least-squares method and the slope of these curves was also determined from the quotient of y and x coordinates in the reference point ($\lim c \rightarrow 0$).

Decomposition of luminophore samples

The weighed amounts (0.3 g) of luminophore samples of the aluminate type $\text{Ba}_{0.9}\text{Mg}_2\text{Al}_{16}\text{O}_{27}\text{Eu}_{0.1}$ were poured on the mixture containing 0.5 g Na_2CO_3 and 1 g of crystalline sodium tetraborate in a platinum crucible. The sample was melt in the flame of a Meker burner. After cooling the melt was dissolved in 20 cm^3 of warm 2 M-HCl and the solution was diluted with water to 100 cm^3 . The resulting solution was then diluted

to tenfold volume with 0.1 M-HCl and injected by the loop of the volume of 20 mm³ into pulseless continuous flow of the solution of sulfosalicylic acid ($\rho = 10 \text{ g dm}^{-3}$). The dilution degree equal to 1 : 13 was obtained using a dispersing coil of the length $L_r = 135 \text{ cm}$ (i.d. = 1 mm).

Results and discussion

Influence of the carrier medium

The sample zone dispersion is much higher for injection of a sample ($\rho(\text{Mg}) = 1 \mu\text{g cm}^{-3}$) into water stream when compared with injection into gaseous medium (air). For this reason, the absorption signals obtained by injecting the sample into gaseous medium are higher (by 50 % for a sample of 20 mm³ volume or by 10 % for a sample of 100 mm³ volume) than the corresponding signals obtained for the liquid medium (Fig. 1). For a sample volume over 50 mm³, the absorption signal for gaseous medium exceeds the corresponding signal in steady state provided the Mg(II) sample of the equal concentration is directly and continuously atomized. This increase in the sensitivity of the determination of about 10 % might be due to higher efficiency of sample atomization in the nebulizer.

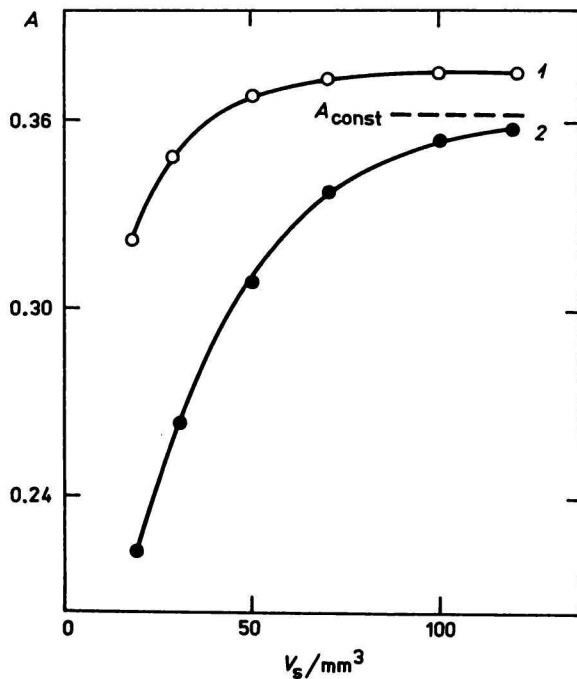


Fig. 1. Variation of Mg(II) absorbance with sample volume, $A = f(V_s)$. Carrier medium, $Q_c / (\text{cm}^3 \text{ min}^{-1})$: 1. air, 4.4; 2. water, 5.4. $\rho(\text{Mg}) = 1 \mu\text{g cm}^{-3}$, 10 cm burner, $L_r = 15 \text{ cm}$.

Influence of the injected sample volume

The absorption signal of the sample solution ($\rho(\text{Mg}) = 1 \mu\text{g cm}^{-3}$) rapidly increases with the injected volume of the sample up to the limit of 100 and 50 mm^3 for water and air as carrier media, respectively. Further increase in the sample volume changes the absorption signal only slightly. The dispersion of the sample zone is suppressed in gaseous carrier medium and the zone of liquid sample forms a sharply limited discrete zone. That is why further parameters of the FIA—FAAS system were optimized only for the liquid carrier medium.

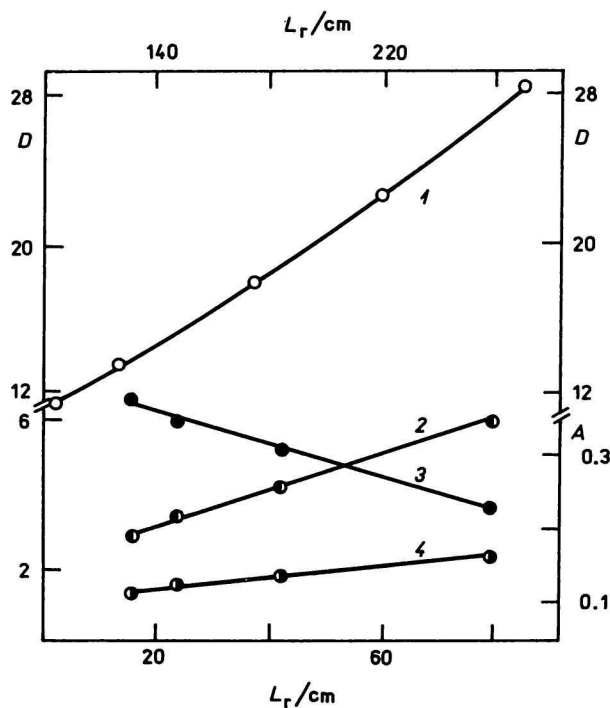


Fig. 2. Variation of Mg(II) absorbance or dispersion coefficient with dispersion coil length, $A = f(L_r)$ or $D = f(L_r)$.

$Q_C = 5.4 \text{ cm}^3 \text{ min}^{-1}$, $\rho(\text{Mg}) = 2 \mu\text{g cm}^{-3}$, 5 cm burner.

Curve	i.d./mm	V_s/mm^3	L_r	Relation
1	1.0	20	100—268	D
2	0.6	20	15—80	D
3	0.6	50	15—80	A
4	0.6	50	15—80	D

Influence of the length of dispersion coil

The absorption signal decreases as much as by 40 % with the length of the dispersion coil over the range $L_r = 15\text{--}80$ cm for the constant injected sample volume of 50 mm^3 at constant capillary inner diameter of 0.6 or 1.0 mm (Fig. 2). In order to ascertain the necessary degree of sample dilution it is convenient to plot the dispersion coefficient D [1–6] against the length of dispersion coil (Fig. 2, curves 1 and 2). It is evident that small volumes of samples are better dispersed than larger volumes and a higher dispersion can be achieved by using capillaries with wider inner diameter and longish length. For instance, if 20 mm^3 of sample are injected and a capillary of i.d. = 1 mm is used, the dispersion coefficient $D = 11\text{--}28$ can be achieved by using capillary length over $100\text{--}270$ cm range (Fig. 2).

Influence of the flow-rate

If 100 mm^3 of the sample solution are injected and the flow-rate of sample in liquid carrier medium increases over the range $Q_c = 0.5\text{--}8.5\text{ cm}^3\text{ min}^{-1}$, the peak height monotonously increases up to the maximum at $Q_c = 5\text{ cm}^3\text{ min}^{-1}$, and afterwards it monotonously decreases (Fig. 3). The maximum of absorption signal corresponds to the flow-rate optimum of liquid carrier medium in the FIA—FAAS system. This rate is by $0.6\text{ cm}^3\text{ min}^{-1}$ higher than the inherent suction effect of the nebulizer. The increase in peak height is likely due to the increased transport of the sample solution into the atomizer at the constant

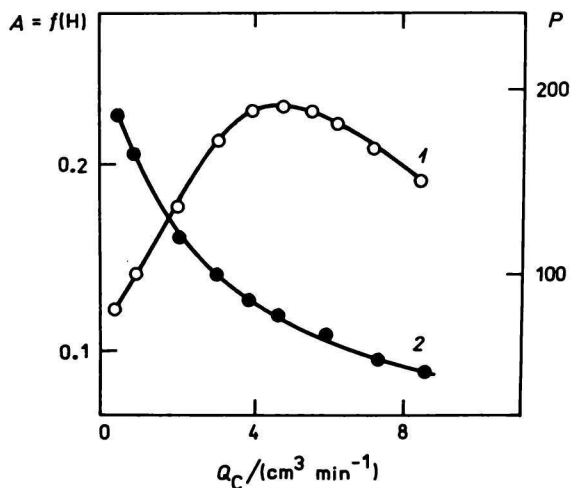


Fig. 3. Absorption signal of Mg(II) as a function of flow-rate of carrier medium Q_c by measuring the peak area P (curve 2) or peak height H (curve 1). $V_s = 100\text{ mm}^3$, $L_r = 15$ cm, $\rho(\text{Mg}) = 1\text{ }\mu\text{g cm}^{-3}$, 5 cm burner, sucking rate of nebulizer $4.4\text{ cm}^3\text{ min}^{-1}$, P is expressed in relative units.

efficiency of atomization. On the other hand, a decrease in flow-rate of the carrier stream brings about an increase in peak area and simultaneous decrease in peak heights. That is accompanied by an increase in time of the absorption signal duration and by a decrease of the repeatability of signal measurements at low flow-rates (Table 1).

Table 1

Relative standard deviation s_r for different flow-rates Q_C by measuring the height H or area of peaks P
 $\rho(\text{Mg}) = 1 \mu\text{g cm}^{-3}$, $V_s = 100 \text{ mm}^3$, $Q_C = 0.5\text{--}8.5 \text{ cm}^3 \text{ min}^{-1}$, 0.1 M-HCl, 10 cm burner

Q_C		$s_r/\%$		Q_C		$s_r/\%$	
$\text{cm}^3 \text{ min}^{-1}$		H	P	$\text{cm}^3 \text{ min}^{-1}$		H	P
0.5		2.8	10.0	4.8		1.5	1.1
1.0		2.6	4.8	5.6		1.9	1.6
2.0		2.5	3.7	6.2		2.3	2.2
3.1		2.1	3.1	8.5		2.9	2.5
4.4		1.8	1.5				

For keeping the optimum performance of atomizer, it is preferable from the point of view of precision and sensitivity of determination to keep more forced than sucked flow of the liquid entering the nebulizer. The flow-rate of liquid carrier medium entering the nebulizer ought to be by about 10 % higher than the inherent rate of sucking of nebulizer.

Comparison of calibration procedures

The sample volume of 100 mm^3 with concentration $\rho(\text{Mg}) = 0\text{--}2 \mu\text{g cm}^{-3}$ was injected in the acetylene—air flame (5 cm burner) through a capillary (i.d. = 0.6 mm, $L_r = 15 \text{ cm}$) while the flow-rate of carrier stream was equal to $4.8 \text{ cm}^3 \text{ min}^{-1}$. The classical calibration graph based on measuring the peak heights $A = f(\rho(\text{Mg}))$ was linear up to $\rho = 1.5 \mu\text{g cm}^{-3}$, the slope being $\Delta A/\Delta \rho(\text{Mg}) = 0.226 \text{ cm}^3 \mu\text{g}^{-1}$. If the peak area was measured, the calibration graph was linear up to $\rho = 2 \mu\text{g cm}^{-3}$. In both cases for $\rho = 1.25 \mu\text{g cm}^{-3}$ the repeatability of the determination was $s_r < 1 \%$.

If the calibration was performed by measuring the peak widths at a constant height [5] over zero line, the relationships $t' = f(\ln [c^*(\text{Mg})/(c(\text{Mg}) - 1)])$, $t' = f(\ln [A_m/(A' - 1)])$ or $t' = f(\ln [c^*(\text{Mg})])$ were used, where t' , $c^*(\text{Mg})$ or A_m , and $c(\text{Mg})$ are peak widths at a given constant height, concentration or absor-

bance at the maximum of peaks, and concentration of sample solution producing a given height (absorbance A') at the maximum of peaks, respectively.

In the course of measurements, 100 mm³ volumes of the sample solutions of concentration 1, 10, 100, and 1000 $\mu\text{g cm}^{-3}$ were injected into the flow of water functioning as carrier medium ($Q_c = 5.4 \text{ cm}^3 \text{ min}^{-1}$, $L_r = 5 \text{ cm}$, i.d. = 0.6 mm). The constant value of absorption signal was $A' = 0.080$, *i.e.* 20 mm from the baseline of recorder at the constant chart speed of 2.5 mm s^{-1} .

The calibration curves were linear over the whole range of concentrations and their slopes were 0.605, 0.589, and 0.603, respectively. The above approximations were verified for the determination of Mg(II) in samples of the concentration $\varrho(\text{Mg}) = 2.5 \mu\text{g cm}^{-3}$. The resulting relative deviations (5.6, 6.9, and 15.3 %) show that the most appropriate for Mg determination is the relationship $i' = f(\ln [c^*(\text{Mg})/(c(\text{Mg}) - 1)])$.

As the peak width can be measured with maximum precision of about 0.5 mm under given conditions, the method of calibration results in imprecision in the determination of concentration of about 5 % over the whole concentration interval. The method is less precise than other methods of calibration but it is useful for determining the concentrations of highly concentrated solutions in the first approximation. The method is especially convenient for determinations within a wide concentration range.

As far as the method of standard addition applied to the FIA—FAAS system is concerned, we used reverse arrangement by injecting 100 mm³ of the Mg(II) solutions of concentrations $\varrho'(\text{Mg}) = 0.5, 1.0, 1.5,$ and $2.0 \mu\text{g cm}^{-3}$ in 0.1 M-HCl into continuous flow of Mg(II) solution of concentration *e.g.* $\varrho(\text{Mg}) = 1.0 \mu\text{g cm}^{-3}$ in 0.1 M-HCl. The calibration graphs $A = f(\varrho'(\text{Mg}))$ were linear and intersected the concentration axis in the point corresponding to the concentration of "unknown" Mg sample. In our case, the concentration values $\varrho(\text{Mg}) = 1.05 \mu\text{g cm}^{-3}$ were obtained with $s_r = 1.86 \%$. The method is very precise and of good use for eliminating the influence of interfering substances.

Determination of magnesium in luminophores

The FIA—FAAS method was used for developing a method of determination of the content of Mg(II) in luminophores. The accuracy of the method was tested by redetermining the addition of $\varrho(\text{Mg}) = 2.5 \mu\text{g cm}^{-3}$ to individual sample solutions. The recovery varied by $R = 100.0\%$. The accuracy was also verified by continuous atomization of the corresponding solutions of Mg(II). The repeatability of Mg(II) determination in a sample with $\varrho(\text{Mg}) = 125 \mu\text{g cm}^{-3}$ corresponded to $s_r = 2.5 \%$ for ten independent measurements ($n = 10$). The calibration graph was strictly linear over the range $\varrho(\text{Mg}) \leq 15 \mu\text{g cm}^{-3}$ for 10 cm

burner. The slope of this graph was equal to $\Delta A/\Delta \rho(\text{Mg}) = 0.0246 \text{ cm}^3 \mu\text{g}^{-1}$. The content of magnesium in the original sample subjected to melting was $125 \mu\text{g cm}^{-3}$, which was in very good agreement with the results obtained by FAAS ($125 \mu\text{g cm}^{-3}$).

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