A computerized flow injection analysis manifold for interference determination in flame atomic absorption spectrometry

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Abstract. A computerized flow injection analysis (FIA) manifold was set up and its performance is described for automatic determination of the influence of interferences in flame atomic absorption (FAA) spectrometry. The manifold operates on the principle of multiple injection of the sample solution of the metal to be determined with the interference to the FAA-spectrometer. The sample is simultaneously diluted with a pure solution of the analyte, which allows covering a wide range of interference concentrations. As an example, calcium determination with phosphate as the interference and lanthanum as the interference suppressor is demonstrated. The method was applied to study calcium concentration in milk.

Key words: atomic absorption spectrometer, flow injection, interference phosphate, calcium, milk.

Chemical interference is quite common in flame atomic absorption (FAA) spectrometry. A number of different approaches have been provided to overcome this effect and possible ways are documented in official manufactual descriptions and textbooks [1, 2]. Usually evaluation of the interference influence on the determination accuracy of analyte involves tedious volumetric manipulation consisting of preparation and measurement of several standards, which takes a considerable amount of time.

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Flow injection analysis (FIA) offers FAA-spectrometer not only a means for automatic sample introduction but also techniques for automated sample management, including dilutions, addition of reagents, and calibration. Among the fundamental characteristics of FIA are the controlled dispersion of the injected sample plug in the carrier flow producing a reproducible peak-like transient FAA-spectrometer signal, which can be characterized by height, area, and width. Many successful applications of FIA–FAA-spectrometer combinations for e.g. calibration purposes are well documented in two monographs [3, 4]. Surprisingly, the determination of the effect of interferences by means of FIA in FAA-spectrometer has received much less attention. Sperling et al. [5] proposed the use of the total information contained in the transient FIA–FAA-spectrometer signal with a relevant signal processing algorithm for correcting multiplicative interferences. Kościelniak [6] used a technique of injecting the sample and the standard solution one after another into the carrier stream to correct matrix interference effects.

Although matrix interference effects can be reduced by a standard addition calibration technique, the true value of the dependence of interference on the concentrations of both the analyte and the interference itself remains frequently unclear. In this work a simple computerized manifold for the determination of the interference effect as a function of interference concentration is provided.

The manifold operates on the principle of multiple injection of an analyte solution containing a certain amount of interference into the carrier stream. The interference concentration is exponentially diluted during the measurement process, while the analyte concentration remains constant. The method was verified by the measurement of the influence of phosphate on the determination of calcium in milk products. The calcium/phosphate system was chosen because it is a textbook example of an interference effect in FAA-spectrometer.

It is well known that the content of phosphate in samples is one of the principal limiting factors of accuracy, sensitivity, and precision in the determination of calcium. Phosphate reacts in flame with calcium and forms a compound of a high melting point ($1670\,°C$), thus increasing the deficiency of free atoms and decreasing the absorption signal of calcium. The lanthanum salts used as spectroscopic buffer are known to form more stable molecules with phosphate than calcium does and indicate the releasing effect for calcium atoms.

Let us assume that multiple injections have been performed from the vessel of the sample solution where the analyte concentration is fixed and the initial concentration of interference is c_0. Injections are performed with a time interval Δt to the water flow, which is aspired to the FAA-spectrometer. Simultaneously the flow of the sample solution with a fixed concentration of the analyte but without an interference is pumped into the same vessel at a rate F (Fig. 1). In that way the initial concentration of the interfering salt in the solution in the vessel will be diluted. The concentration of the interfering salt c_k just before the kth injection can be calculated as follows:

$$c_k = \frac{c_{k-1}V_{k-1} - c_{k-1}V_{\text{inj}}}{V_{k-1} - V_{\text{inj}} + F\Delta t}, \tag{1}$$

where V_k and V_{inj} are the total volume of the sample/interference solution and the volume injected into the FAA-spectrometer, respectively. If the sample flow is adjusted in such a way that $F\Delta t = V_{\text{inj}}$, then $V_0 = V_1 ... V_k \equiv V$ and Eq. 1 simplifies as follows:

$$c_k = c_{k-1}\left(1 - \frac{V_{\text{inj}}}{V_0}\right). \tag{1'}$$

It is easy to show that Eq. 1' can be expressed through the initial interference concentration as follows:

$$c_k = c_0\left(1 - \frac{V_{\text{inj}}}{V_0}\right)^k. \tag{2}$$
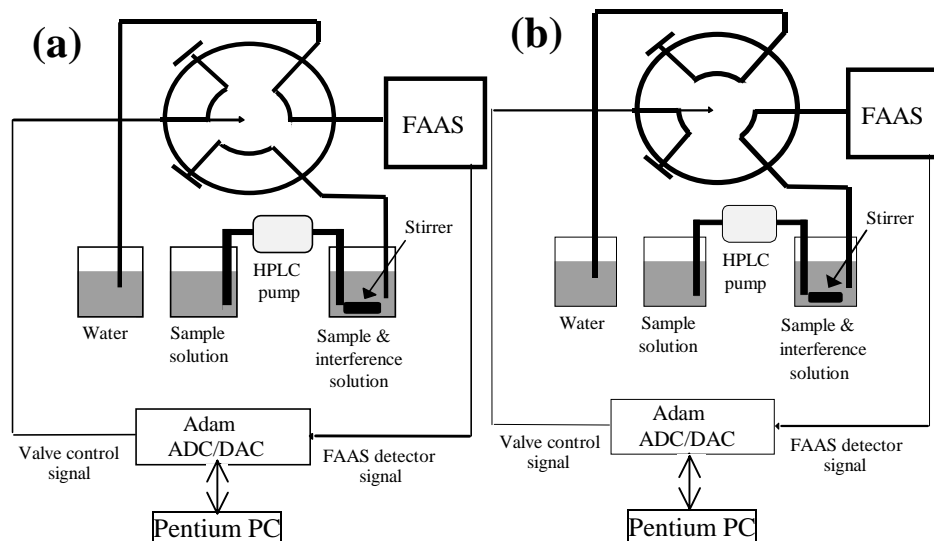
EXPERIMENTAL

Apparatus

A Carl Zeiss 30, Jena AA spectrometer (Germany) was used. The conventional parameters of acetylene–air FAA-spectrometer analyses were applied: Ca-lamp current 20 mA, bandpass 422.7 nm.

Chemicals

The Merck AAS standard stock solution of calcium nitrate 1000 mg/dm^3 was diluted until 10 mg Ca/dm^3. Lanthanum chloride (25 g La/dm^3), diammonium hydroxide phosphate (0.0125–1.25 g P/dm^3), hydrogen chloride acid (36.5%), and nitric acid (63%), all analytical grade, were used. Deionized (MilliQ^R) water was used.

Procedures

Experimental set-up is shown in Fig. 1. Carrier water is continuously aspired to the FAA-spectrometer through a six-path mechanical valve (Design Office of the Estonian Academy of Sciences). When the injection of the sample/interference solution into the carrier flow is needed, a control signal from the PC activates the valve via a digital-to-analogue converter (Advantech Ltd., Taiwan Model Adam 4060) and reverses its state. Now the sample/interference solution is aspired through the injector into the FAA-spectrometer. The water vessel is connected to the atmosphere during the injection to prevent water flow into the sample/interference flow through the injector.

Fig. 1. Experimental set-up for the manifold operation. A six-path mechanical valve is used to inject the solutions into the flame atomic absorption spectrometer: a, water injections; b, sample injections. Sampling control is performed by the Labview software.

Manifold control, data acquisition, and processing

Sampling control is performed by the Labview software (National Instruments, USA). The same program records the detector signal via the analogue-to-digital converter. Recordings of the detector signal are later transformed to the MATLAB (Mathworks, Natic, MA, USA) environment and subjected to the digital filtering by a 5th order Butterworth filter. Also the detector signal baseline was subtracted. From the edited signal peak areas were determined by numerical integration.

Preparation of analytical samples

The calcium analyte sample, 10 mg Ca/dm^3, was kept steady and the content of phosphate as interference was changed in the range from 0.0125 g P/dm^3 to 1.25 g P/dm^3. Lanthanum solution was added to the sample and interference solution to investigate its buffering ability. Per 100 cm^3 of the solution with a concentration of 10 mg Ca/dm^3, a volume of 2 cm^3 of the solution of lanthanum chloride (25 g La/dm^3) was added. All analyte solutions were acidified with concentrated nitric acid up to pH 3.

The precision and accuracy were evaluated using Certified Reference Materials: Trace Elements in Milk Powder IAEA-153. The optimum content of calcium for determination is 10 mg/dm^3.

Mineralization of milk samples

Milk (0.5 g) was mineralized as described in [7]. The mineralized sample was diluted to 50 cm³. Before dilution 1 cm³ of lanthanum salt solution was added. The molar ratio of calcium/lanthanum (solution) is the same we had in the first solution.


RESULTS AND DISCUSSION

In the first experiment the system performance was tested by multiple injection of the standard solution with a fixed calcium concentration (10 mg/dm³) buffered with lanthanum chloride (0.5 g La/dm³) into the FAA-spectrometer. The ratio of the injected volume and sample/interference volume was set so that V_{inj}/V_0 was equal to 0.1 (Eq. 1).

After the 12th injection the standard was diluted by the carrier water until the background level was received. Figure 2 shows that after the 12th injection the absorbance starts to decrease until the background level is reached after the 24th injection. The measured V_{inj}/V_0 value equal to 0.095 appears to be close to the set value of 0.1. The reproducibility of the injections can be calculated from the area of the first 11 peaks, and it is equal to 1.09% (Fig. 2).

In the next experiment (Fig. 3) the unbuffered calcium standard solutions with three different dilutions of phosphate were injected into the FAA-spectrometer to study the influence of phosphate concentration on the absorbance signal of calcium. The absorption signal of calcium fell from 10 mg/dm³ to 1.1, 2.9, and 3.6 mg/dm³. After the 10 first peaks the concentration of the phosphate was diminished by the injection of pure Ca standard. After the next 23 injections the concentration of phosphate calculated by Eq. 2 was 111, 11.1, and 1.11 mg P/dm³,
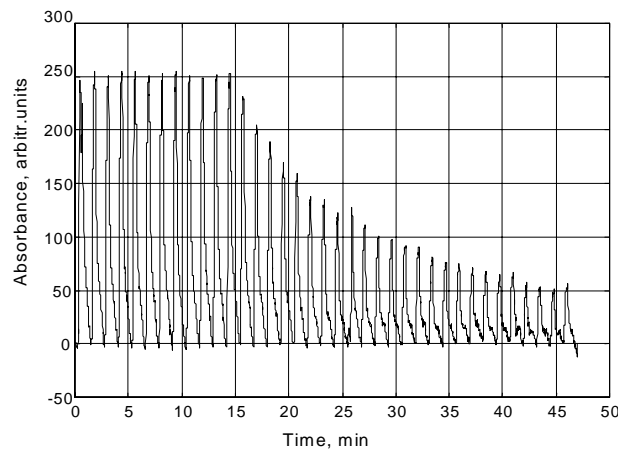

Fig. 2. The sequence of multiple injection peaks of calcium standard (10 mg/dm³) buffered with lanthanum chloride (0.5 g La/dm³). After the 10th peak the standard was diluted by carrier water until the background level was received.

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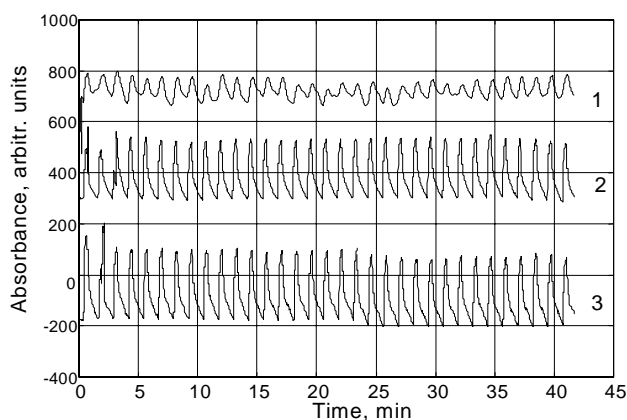
Fig. 3. Effect of interference of Ca $(10 \, \text{mg/dm}^3)$ with phosphate: $1 - 1.25$, $2 - 0.125$, and $3 - 0.0125 \, \text{g P/dm}^3$. Calcium and phosphate solutions are introduced into the FAA-spectrometer during the first ten injections and then the interference is diluted by the injection of pure Ca standard $(10 \, \text{mg/dm}^3)$.

respectively. This was still too high to suppress the signal of calcium. It can be supposed that at a higher concentration of phosphate the interference will be more complicated. The velocity of nebulization and transparency of the flame will decrease and the physical interference by a high salt content will also suppress the absorbance.

In the third experiment (Fig. 4) the effect of lanthanum as a suppressor of the calcium interference with phosphate was studied. The calcium and phosphate solutions with three different phosphate concentrations were diluted by lanthanum and calcium standard solutions. The dilution rate V_{inj}/V_0 was equal to 0.1. The
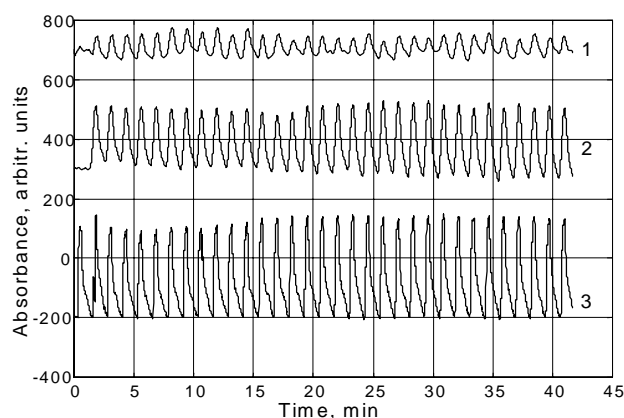
Fig. 4. Effect of lanthanum as a spectroscopic buffer by the interference of Ca $(10 \, \text{mg/dm}^3)$ with phosphate: $1 - 1.25$, $2 - 0.125$, and $3 - 0.0125 \, \text{g P/dm}^3$. Calcium and phosphate solutions are introduced into the FAA-spectrometer during the first ten injections and then the phosphate is diluted by the injection of Ca standard $(10 \, \text{mg/dm}^3)$ buffered by lanthanum salt $(0.5 \, \text{g La/dm}^3)$.

concentration of phosphate in the dilution process was calculated by Eq. 2 (Fig. 5). About 90% of the normal absorbance of calcium was received in the presence of lanthanum in the course of the dilution of the initial phosphate concentration from 0.125 to 0.02 g P/dm^3 (Fig. 5a). For the solution of the initial phosphate concentration of 0.0125 g P/dm^3 (Fig. 5b) and in the presence of lanthanum the normal absorbance was received if the concentration of phosphate was diminished down to 0.004 g P/dm^3.

Calcium determination was carried out also with a mineralized and diluted milk reference sample (10 mg Ca/dm^3) buffered by lanthanum solution. The phosphate concentration in the milk samples was supposed to be about 9.5 mg P/dm^3, as mentioned for normal milk by de Man [8], and it was not determined in this work. In our experiments with multiple diluting injection the normal absorbance of calcium was received if the content of phosphate in milk was below 2 mg P/dm^3 (calculated by Eq. 2) and the solution was buffered by lanthanum salt solution (Fig. 6). The elimination of the interference of the absorbance of calcium at a twice
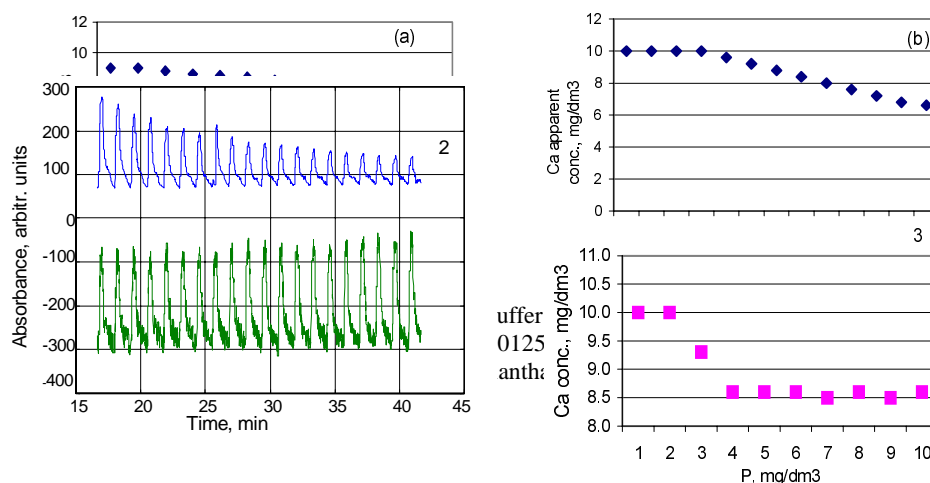
Fig. 6. The study of the interference of Ca with matrix of milk. 1 – the first five peaks belong to the buffered with La milk samples. After that the sample is diluted by injecting calcium and lanthanum salt solutions (10 mg Ca/dm^3 and 0.5 g La/dm^3). 2 – the standard Ca (10 mg/dm^3) buffered by lanthanum salt solution (0.5 g La/dm^3) was diluted by carrier water. 3 – the concentration of phosphate in the dilution process was calculated by Eq. 2.

lower content of phosphate than in the experiment with the pure salt solutions was evidently caused by the general mineralization in the milk supporting the interference with phosphate.

CONCLUSIONS

It can be concluded that the method of multiple injections performed by manifold operation and controlled by PC software is a fast and reliable way to study the effect of interference and spectroscopic buffer efficiency in FAA-spectrometer. In the analytical practice of atomic absorption spectrometry the effect of interference can occur in the analysis of all biological objects as was shown on the example of the determination of calcium in the presence of phosphate in milk. It is not always easily detectable.

It can be supposed that the interference of the FAA-spectrometer signal is influenced by chemical reasons as well as by physical phenomena. A high salt content of the solution, which is usual for real biological objects, may cause an additional interference of physical character as for example a decrease in the velocity of nebulization and flame transparency. The determination of a calcium concentration of 10 mg/cm^3 may be carried out in the presence of phosphate of a concentration of 2–4 mg P/dm^3 using solutions buffered by lanthanum salts (0.5 g La/dm^3).

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Komputeriseeritud voogsisestusmeetod interferentide mõju uurimiseks leek-aatomiabsorptsioonspektromeetrias

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On kirjeldatud komputeriseeritud voogsisestusmeetodit ja vastavat seadet, mis võimaldab interferentide mõju uurimist leek-aatomiabsorptsioonspektromeetrias oluliselt kiirendada. Meetod seisneb määratava lahuse pidevas asendamises puhta metalli lahusega, mis sisaldab muutumatus kontsentratsioonis metalli ja muutuvas kontsentratsioonis interferenti.

Näitena selgitati fosfaadi sisalduse mõju kaltsiumi kontsentratsiooni määramisele piimaproovis. Ilmnes, et lantaani kui vabastava komponendi manulus on sel puhul vajalik. Piimas kasvab interferendi mõju hüppeliselt kui fosfaadi kontsentratsiooni väärtus on alla 4 mg P/dm^3. Meetod sobib bioloogiliste proovide kaltsiumi sisalduse kindlakstegemiseks.