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Solenoid micropump-based flow system for generalized calibration strategy

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ABSTRACT

Generalized calibration strategy (GCS) is one of the innovative approaches aimed at verification and improvement of accuracy of analytical determinations. It combines in a single procedure the interpolative and the extrapolative calibration approaches along with stepwise dilution of a sample with the use of a dedicated flow system. In the paper a simple solenoid micropump-based flow system designed for implementation of GCS has been described. The manifold consists of several modules fully operated by a computer and connected with each other in a properly designed network. Its performance and usefulness were tested on determination of calcium by FAAS in synthetic and natural samples containing strong interferents. It was shown how GCS can serve for detection, examination and elimination of the interference effects. It was demonstrated that the designed manifold enabled to perform GCS procedure with very good precision, in short time and with very low standard, sample and reagent consumption.

1. Introduction

In analytical chemistry several calibration methods are known and exploited in practice. Their definitions and classifications have been presented in several papers [1–6] and some novel calibration strategies aimed at overcoming the problem of analytical inaccuracy have been developed [3,7–12]. Generalized calibration strategy (GCS) is one of the innovative approaches in the field of analytical calibration [13].

In general, GCS is conceptually based on the integrated calibration method (ICM) [14] consisting in integration of the interpolative and extrapolative calibration approaches (i.e. the set of standards method and the standard addition method) in a single procedure and, consequently, allowing the analytical result to be estimated by a set of (and not by a single – as commonly) independent values. In addition, it is assumed to perform ICM calibration in several steps with the sample and standard solutions progressively diluted. As a result, GCS has significant analytical advantages over traditional calibration approaches giving a possibility to a) diagnose an examined analytical system in terms of interferences, b) verify analytical results in terms of accuracy, and c) choose an adequate way to eliminate the interference effect, and, finally, d) obtain results with improved accuracy. In order to keep the analytical procedure fast, easy, and low-cost, it is suggested to exploit GCS in flow mode with the use of a dedicated instrumental system.

While several flow manifolds designed in our laboratory have been adapted to calibration in accordance with ICM— only two of them, namely the ones working in flow injection [14,15] and sequential injection mode [16], offer the possibility to realize GCS procedure. They were successfully tested and employed to spectrophotometric determination of iron in pharmaceuticals [14], as well as to FAAS determination of calcium in cabbage samples [15], calcium and magnesium in plants [14] and water samples [16]. However, although the flow-injection system was able to perform ICM relatively fast and to obtain very precise and accurate analytical results, it required relatively large volume of a sample. Furthermore, the signal obtained in a form of two overlapping peaks was difficult to interpret in some cases. The sequential system, in turn, gave an opportunity to consume small volumes of sample and standard; nevertheless the calibration procedure was very complex and time-consuming.

The main goal of the presented research was to overcome the above-mentioned drawbacks. For this purpose we carried out GCS procedure with the use of a simple micropump-based flow system. These kind of pumps have been successfully applied in flow analysis to delivery of sample and standard solutions to a detection system and their automatic on-line dilution [17]. Our system consisted of several modules fully operated by a computer and connected with each other in a properly designed network. The performance of the system was tested on the example of FAAS determination of calcium in synthetic and natural samples containing strong interferents.

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2. Principle of GCS

In the original version [13] GCS requires preparation of six calibration solutions according to the rule presented in Fig. 1. In the solutions, a sample and a standard are mixed with a diluent or with each other in two different degrees of *P* or *Q*, where *P* and *Q* are mutually complementary. Then, analytical signals are measured for all calibration solutions ($R_1 \div R_6$) and for a blank solution (R_0), and four two-point calibration graphs are constructed (see Fig. 2) on the basis on the measurement points.

The calibration graphs lead to estimation of analytical results by six apparent concentrations, $c_1 \div c_6$, which are calculated from simple formulas [13]. If an interference effect occurs in the analytical system the apparent concentrations, c_1 and c_2, can be suspected to be systematically different from the true analyte concentration in the sample as they are obtained in an interpolative way. Concentrations c_4 and c_5 seem to be more resistant to the interferences, as they are found in "semi-extrapolative" way (i.e. by extrapolation of the graph *c* along the graph *d* and the other way round). Two remaining values, c_5 and c_6, (initially as values c_5 and c_6, compare Fig. 1) are calculated in a typical extrapolative way and, consequently, they can be expected to be most accurate.

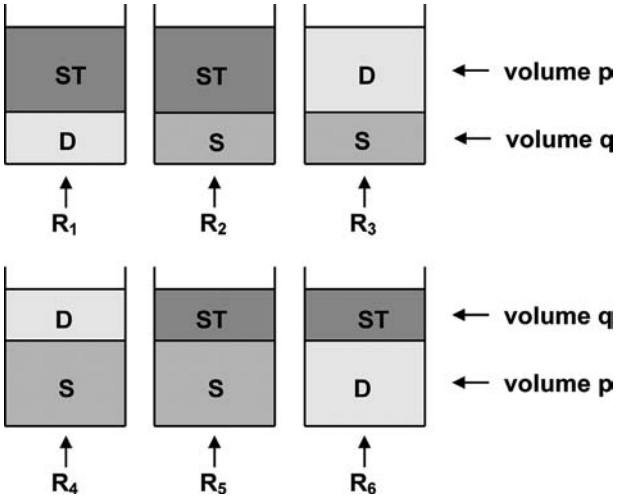

Fig. 1. Preparation of calibration solutions according to GCS procedure: standard, ST, sample, S, and diluent, D, and the corresponding analytical signals, $R_1 \div R_6$.

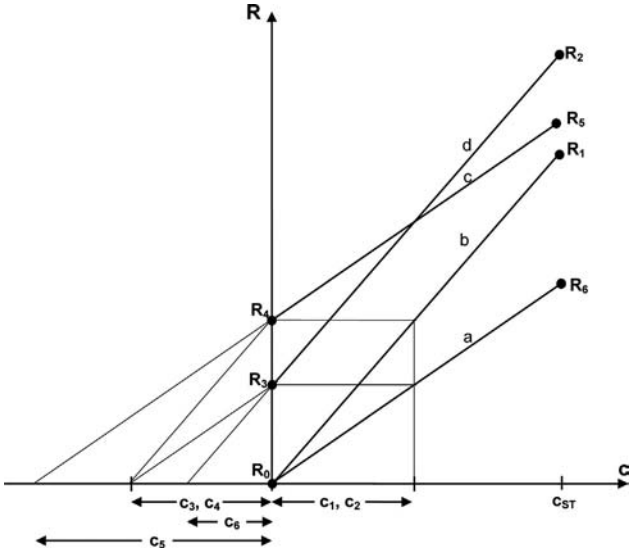

Fig. 2. Calibration graphs (*a*, *b*, *c*, *d*) constructed in accordance with GCS and analytical results estimated in interpolative (c_1, c_2), semi-extrapolative (c_3, c_4) and extrapolative (c_5, c_6) way.

Based on the experience gathered so far the following interpretation of the analytical information offered by GCS can be proposed:

(a) when all apparent concentrations, $c_1 \div c_6$, are statistically equal to each other at a pre-set confidence level, the interference effect does not occur; then the final analytical result, c_0, is calculated as the arithmetic mean of concentrations $c_1 \div c_6$;
(b) when $(c_3+c_4)/2=c_5=c_6$, the interference effect can be supposed to have multiplicative character and c_0 is calculated as the arithmetic mean of concentrations $c_3 \div c_6$;
(c) when the apparent concentrations do not fulfill conditions (a) and (b), the interference effect of non-multiplicative character is expected; then a sample and a standard solution should be progressively diluted until either condition (a) or condition (b) is fulfilled;
(d) when the apparent concentrations cannot fulfill conditions (a) and (b) during dilution process, special reagent (s) eliminating interferences need to be added to the sample and/or to the standard solution, and the results of the repeated GCS procedure should be interpreted in accordance with points (a)÷(c).

3. Experimental

3.1. Reagents, samples and solutions

Standard stock solutions containing calcium and phosphorus at concentration of 1.000 mg mL^{-1} were prepared from Titrisol standards (Merck, Germany). Standard stock solutions of lanthanum at concentration of 50 mg mL^{-1} were prepared by dissolving in water an adequate amount of $LaCl_3 \cdot 7H_2O$ (Merck, Germany). Standard solutions of calcium and lanthanum used for calibration were obtained by dilution of the stock solutions with 1.0% (v/v) HNO_3 (Merck, Germany). In the case when calibration procedure was carried out with the use of lanthanum buffer, $LaCl_3$ stock solution was added both to the sample, the standard and the carrier, before the above-mentioned solutions were introduced to the manifold. For La concentration of 1% or 0.01% every 50 mL of a standard, sample and carrier solution contained 5.00 mL or 50 µL of lanthanum stock solution, respectively.

The following natural samples were utilized: certified reference material of skim milk powder BCR® – No 063R (EC-DG JRC-IRMM, Belgium) with the certified calcium content of 13.49 mg g^{-1}, Bebilon 4® (Nutricia Poland, UE) powdered milk with the content of calcium given by the manufacturer as 6.33 mg g^{-1}, and cheese with unknown content of calcium (traditional Polish cheese from the region of the Tatra mountains made of cow's and sheep's milk).

All reagents were of analytical grade. Deionized water obtained from HLP5sp system (Hydrolab, Poland) was used throughout the work.

3.2. Instrumentation

Natural samples (ca. 0.4 g (CRM was initially dried, ground and homogenated)) were digested with 6.00 mL of concentrated HNO_3 (Merck, Germany) with the use of Multiwave 3000 microwave system (Anton Paar, Austria) in the following conditions: 600 W of max. power, 12 min of ramp time, 20 min of hold time, 0.5 bar s^{-1} rate of pressure increase and 240 °C of max. temperature. After digestion, the sample solution was cooled down in air to the

temperature of 25 °C, transferred into 100 mL volumetric flask, and diluted to the mark with 1.0% HNO_3 (v/v).

Measurements were carried out with the use of atomic absorption spectrometer PinAAcle 900 (PerkinElmer, USA). Air–acetylene flame with 10.0 L min^{-1} of air flow and 2.54 L min^{-1} of acetylene flow was used. The nebulizer free uptake rate was 8.5 mL min^{-1}. Calcium hollow cathode lamp was operated at 10 mA and the wavelength was set to 422.67 nm with a spectral slit width of 0.7 nm. Measurement data was collected for consecutive solutions with the use of a dedicated computer software as peak height was registered within 50 s.

An inductively coupled plasma optical emission spectrometer (ICP-OES) Optima 2100 (PerkinElmer, USA) was employed for reference analyses of real samples. Calcium was detected in axial plasma observation mode at 317.933 nm with nebulizer gas flow of 0.8 L min^{-1}, auxiliary gas flow 0.2 L min^{-1} and plasma gas flow 15.0 L min^{-1}.

The multipumping flow system for generalized calibration strategy based on solenoid micropumps has been schematically shown in Fig. 3. It was composed of three solenoid pumps dosing the volume of 40 μL every 0.5 s (P/N 73120-18, ColeParmer, USA), three 3-inlet solenoid valves (P/N 01540-11, ColeParmer, USA) and a peristaltic pump Minipuls 3 (Gilson, France) propelling the solution with the rate of 9.0 mL min^{-1}. All flow rates were determined experimentally. Tygon tubing was installed in the peristaltic pump and PTFE tubings (0.78 mm i.d.) were used for all connections and tubes. A special electronic adapter (KSP, Poland) was enabled to control all elements of the calibration system with the use of a computer software.

The manifold was used with the following instrumental parameters: $L_1=L_2=L_3=40$ mm, $L_4=150$ mm, $L_5=150$ mm, MC=1830 mm and $r=9.0$ mL min^{-1}. The length of the transmission line (L_1, L_2, L_3) was the same so as not to affect accuracy of volumes dispensed by pumps P_1, P_2, and P_3. The length of the mixing coil and the flow rate r were optimized in terms of accuracy and precision of analytical signal. Duration of a single peak registration was 55 s and 330 s for one full calibration cycle.

4. Operation of the calibration manifold

Each calibration cycle consists of six steps, in which six signals, $R_1 \div R_6$, are registered. Every step is performed in two stages. At stage 1 solenoid pumps P_1, P_2 and P_3 inject proper volumes (see Table 1) of a standard solution, ST, sample solution, S, and carrier solution, C, from their reservoirs to a mixing coil, MC, through a mixing unit, MU, in which all the solutions simultaneously merge with each other. In the same time peristaltic pump, PP, propels stream of a carrier, C, through direction valves V_1 and V_3 to the detector with the flow rate r and a signal for blank solution is registered. At stage 2 positions of the solenoid valves, $V_1 \div V_3$, are changed and the resulting segment of the standard, sample and carrier mixture is propelled with the use of the peristaltic pump,

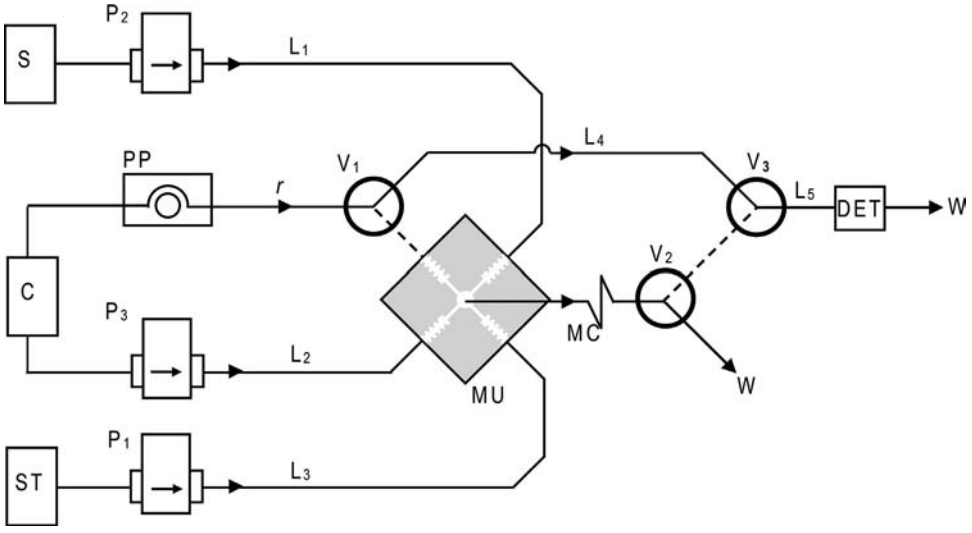

Fig. 3. Scheme of the flow-injection calibration system; C, ST, S: carrier, standard and sample reservoirs; $P_1 \div P_3$: solenoid pumps; PP: peristaltic pump; $V_1 \div V_3$: solenoid valves; $L_1 \div L_5$: transmission line; MU: mixing unit, MC: mixing coil; r: flow rate; W: waste; DET: flame atomic absorption spectrometer; active and non-active flow paths at stage 1 of each calibration cycle are marked with a solid and dotted line, respectively.

Table 1
Consumption of the standard (ST), sample (S), and carrier (C) solutions injected by micropumps P_1, P_2 and P_3, respectively, in individual stages of the GCM procedure.

Dilution degree	Volume injected (μL)															
Signal	$k=1.00$				$k=0.75$				$k=0.50$				$k=0.25$			
	P_2 (S)	P_1 (ST)	P_3 (C)	Total	P_2 (S)	P_1 (ST)	P_3 (C)	Total	P_2 (S)	P_1 (ST)	P_3 (C)	Total	P_2 (S)	P_1 (ST)	P_3 (C)	Total
R_1	0	320	160	480	0	240	240	480	0	160	320	480	0	80	400	480
R_2	160	320	0	480	120	240	120	480	80	160	240	480	40	80	360	480
R_3	160	0	320	480	120	0	360	480	80	0	400	480	40	0	440	480
R_4	320	0	160	480	240	0	240	480	160	0	320	480	80	0	400	480
R_5	320	160	0	480	240	120	120	480	160	80	240	480	80	40	360	480
R_6	0	160	320	480	0	120	360	480	0	80	400	480	0	40	440	480
Total	960	960	960	2880	720	720	1440	2880	480	480	1920	2880	240	240	2400	2880

PP, with the flow rate r from the mixing coil, MC, to the detector, and an analytical signal is registered as a single peak.

The adequate volumes of the standard, sample and carrier solutions to be injected by pumps P_1, P_2 and P_3 in each of six steps of a single calibration cycle are presented in Table 1 (complementary dilution degrees, P and Q, are equal 0.666 and 0.333, respectively). In addition, four calibration cycles can be performed (see Table 1) with the standard and sample solutions diluted with well defined dilution factors (k=0.75, 0.50 or 0.25), depending on the part of the volumes injected in the initial cycle (k=1).

5. Results and discussion

The developed manifold was assessed in terms of its analytical usefulness for calcium determination in various samples. Therefore, some most relevant analytical figures of merit were determined, namely: limit of detection (3σ) (0.71 mg L^{-1}), limit of quantification (6σ) (1.42 mg L^{-1}),, linear calibration range (0.00–7.50 mg L^{-1}), correlation coefficient R^2=0.9994. Moreover, the system is characterized with the following parameters for a single measurement cycle: time (6 min), sample/standard consumption for undiluted solutions (1.0 mL), carrier consumption (55.0 mL), and waste generation (58.0 mL).

GCS was applied to analysis of both synthetic samples and real samples of milk powder and cheese. The applied standard solutions of calcium (5.0 or 10.0 mg L^{-1}) gave signals in linear calibration range. Real samples were initially diluted to the extent enabling the analyte to be determined within linear analytical range. Each sample was analyzed five times. The mean values of the apparent concentrations were statistically compared with each other with the use of Tukey's *a posteriori* test (α=0.05). The results are shown in Tables 2 and 3.

The synthetic samples were analyzed in order to test the designed flow system. As seen in Table 2, the apparent concentrations obtained for two first samples were very close to each other and the final results (calculated as $(c_1+c_2+c_3+c_4+c_5+c_6)/6$) were also very close to the true result (|RE| < 0.5%). It was evidently so because the samples were free of interferents. In the case of the third sample all results were significantly different from each other and from the true value. Since condition $(c_3+c_4)/2=c_5=c_6$ was not fulfilled, the final result could not be calculated as $(c_3+c_4+c_5+c_6)/4$. As expected, the concentrations obtained in semi-extrapolative (c_3 and c_4) and extrapolative (c_5, c_6) way were

Table 2
Results of application of GCS to determination of Ca in synthetic samples; RSD (%) and RE (%) values are given in parenthesis.

Concentration of sample component		Dilution degree, k	Apparent concentrations (mg L^{-1})							Final result (mg L^{-1})
Ca (mg L^{-1})	P (mg L^{-1})		c_1	c_2	c_3	c_4	c_5	c_6	$\overline{c}$*	
2.5	0	1.00	2.53 (3.5; 1.0)	2.43 (3.0; −2.8)	2.52 (2.1; 0.7)	2.51 (2.3; 0.6)	2.59 (4.4; 3.5)	2.46 (7.8; −1.7)	2.51 (0.6; 0.2)	2.51 (0.6; 0.2)
5.0	0	1.00	4.97 (1.6; −0.6)	4.75 (3.3; −5.0)	5.12 (2.1; 2.4)	4.96 (2.1; −0.9)	5.02 (1.1; 0.4)	5.06 (1.4; 1.1)	4.98 (0.6; −0.4)	4.98 (0.6; −0.4)
4.0	3.3	1.00	2.06 (4.0; −49.2)	2.28 (2.6; −43.7)	2.56 (3.7; −36.7)	6.46 (3.8; 59.5)	5.63 (3.1; 39.0)	2.94 (2.5; −27.5)	*4.40 (2.73; 10.0)*	–

* Values shown in italics are the mean values calculated for the concentrations $c_3 \div c_6$

Table 3
Results of application of GCS to determination of Ca in certified reference material of slim milk powder (No 063R), in the Bebilon 4® powdered milk, and in a cheese sample; RSD (%) values are given in parenthesis.

Concentration of sample component		Dilution degree, k	Apparent concentration (mg g^{-1})							Final result (mg g^{-1})
Ca (mg g^{-1})	La (%)		c_1	c_2	c_3	c_4	c_5	c_6	$\overline{c}$*	
The certified reference material of slim milk powder (No 063R)										
13.49	0	1.00	8.23 (2.7)	10.12 (2.6)	10.30 (2.3)	17.80 (1.4)	12.85 (2.8)	14.26 (2.8)	*13.80 (0.6)*	–
		0.75	8.82 (3.9)	11.24 (3.7)	10.44 (2.2)	17.20 (3.2)	12.06 (4.2)	14.90 (4.9)	*13.65 (1.1)*	13.65 (1.1)
		0.50	9.79 (5.4)	11.90 (6.0)	10.93 (4.6)	16.61 (6.0)	12.97 (6.1)	14.01 (7.7)	*13.63 (1.5)*	13.63 (1.5)
		0.25	10.30 (5.4)	12.19 (4.5)	11.20 (3.1)	16.27 (3.3)	13.05 (7.2)	14.02 (7.1)	*13.64 (1,8)*	13.64 (1,8)
	0.01	1.00	10.81 (1.3)	11.94 (4.9)	11.99 (1.4)	15.18 (2.7)	13.32 (1.0)	13.66 (1.6)	*13.54 (1.4)*	13.54 (1.4)
		0.75	11.21 (2.8)	12.18 (4.3)	12.19 (3.9)	14.85 (4.2)	13.47 (1.7)	13.43 (1.6)	*13.49 (1.3)*	13.49 (1.3)
		0.50	11.72 (5.0)	12.49 (4.0)	12.57 (2.9)	14.45 (4.1)	13.43 (3.3)	13.52 (2.1)	13.48 (3.6)	13.48 (3.6)
		0.25	11.95 (3.9)	13.80 (11.3)	12.17 (2.4)	14.89 (2.1)	13.09 (8.2)	13.90 (6.5)	13.30 (5.7)	13.30 (5.7)
	1	1.00	13.28 (2.3)	13.16 (2.6)	13.35 (1.6)	13.58 (1.6)	13.51 (4.0)	13.43 (4.0)	13.38 (2.7)	13.38 (2.7)
Bebilon 4® powdered milk										
6.33	0	1.00	4.33 (4.4)	5.10 (9.3)	4.73 (4.3)	4.98 (9.5)	3.91 (3.6)	6.03 (9.8)	*4.90 (8.5)*	–
		0.75	4.48 (3.9)	4.80 (6.4)	4.96 (5.0)	4.68 (9.1)	4.17 (6.0)	5.57 (8.3)	*4.85 (6.5)*	4.85 (6.5)
		0.50	4.32 (5.2)	4.94 (9.5)	4.66 (6.0)	4.89 (6.4)	4.08 (9.2)	5.62 (9.2)	*4.81 (4.0)*	4.81 (4.0)
		0.25	5.01 (11.2)	4.28 (17.3)	5.06 (12.0)	4.51 (19.4)	5.13 (16.5)	4.45 (17.7)	*4.79 (14.2)*	4.79 (14.2)
	0.01	1.00	5.75 (3.7)	6.13 (1.9)	6.05 (1.2)	7.06 (2.0)	6.46 (0.5)	6.61 (2.2)	*6.55 (0.7)*	6.55 (0.7)
		0.75	5.98 (4.8)	5.90 (2.7)	6.43 (4.3)	6.65 (4.1)	6.55 (2.8)	6.52 (2.6)	*6.54 (0.5)*	6.54 (0.5)
		0.50	5.84 (4.9)	6.10 (4.1)	6.08 (4.0)	7.05 (3.8)	6.49 (2.0)	6.61 (2.2)	6.56 (0.6)	6.36 (3.5)
		0.25	5.85 (9.9)	6.34 (8.0)	6.28 (3.5)	6.81 (4.1)	6.41 (5.6)	6.68 (5.7)	6.39 (6.5)	6.39 (6.5)
	1	1.00	6.49 (7.4)	6.32 (8.1)	6.34 (8.7)	6.75 (10.9)	6.64 (7.7)	6.43 (6.9)	6.49 (4.2)	6.49 (4.2)
Cheese sample										
Unknown	0	1.00	6.37 (2.6)	7.25 (4.3)	6.93 (3,3)	7.43 (4.7)	6.14 (5.3)	8.39 (6.4)	*7.27 (3.9)*	–
		0.75	6.82 (4.6)	7.11 (8.3)	7.51 (5.2)	7.79 (7.5)	7.04 (7.0)	8.32 (9.1)	*7.68 (5.3)*	7.68 (5.3)
		0.50	7.13 (3.6)	8.24 (12.1)	7.80 (4.0)	8.83 (11.5)	7.31 (6.4)	9.44 (13.1)	*8.38 (7.1)*	8.38 (7.1)
		0.25	8.64 (5.5)	10.10 (12.5)	9.38 (5.1)	11.90 (13.5)	9.58 (8.3)	11.67 (13.3)	10.21 (9.7)	10.21 (9.7)
	1	1.00	10.28 (11.0)	10.35 (8.1)	10.52 (8.8)	11.45 (10.0)	11.38 (12.5)	10.75 (13.6)	10.79 (8.6)	10.79 (8.6)

* Values shown in italics are the mean values calculated for the concentrations $c_3 \div c_6$.

closer to the expected value than those calculated interpolatively (c_1 and c_2); however the analyte could not be determined by every single estimation with |RE| lesser than 20%. The evident reason for this fact was strong interference effect caused by phosphorus. In all cases the apparent concentrations were obtained with satisfactory repeatibility allowing the final analytical result to be evaluated with very good precision (RSD < 2%).

The presence of some interferents was also revealed in undiluted sample of the certified reference material of slim milk powder (see Table 3). This is evident because of statistically significant differences between the apparent concentrations obtained interpolatively and the remaining ones, as well as between the concentrations calculated extrapolatively and the one calculated from $(c_3+c_4)/2$. For diluted samples the condition $(c_3+c_4)/2=c_5=c_6$ was fulfilled and the analytical results (calculated as $(c_3+c_4+c_5+c_6)/4$) were very close to the expected value independent of the dilution factor. Good accuracy of these determinations was confirmed by the results obtained for the sample spiked with lanthanum at both applied concentrations (0.01 and 1.00%). Because the detected interference effect could be eliminated rather by the semi-extrapolative and extrapolative procedures but not due to sample dilution, it is supposed to have multiplicative character.

Some difficulties in interpretation of analytical data were met in the case of analysis of Bebilon 4® powdered milk (see Table 3). Similar to the previous case, the results obtained for a gradually diluted sample were similar to each other allowing us to expect that the interference effect (detected in the undiluted sample) was eliminated and that the analyte was determined with good accuracy. However, in fact these results were far from the expected value and accurate determination could be achieved only when using lanthanum. The reason for the interpretative mistake was poor repeatability of the apparent concentrations resulting from very low signals measured for calcium already in undiluted sample. Due to addition of lanthanum to the sample, calcium – now not influenced by interferents – was able to produce higher signals and, consequently, the concentrations could be obtained with much better precision.

In contrast to the previous cases, the interference effect occurring when calcium was determined in the cheese sample was progressively changed with the sample dilution (see Table 3). As the expected value was not known, the analytical result obtained for the most diluted sample ($k=0.25$) could only be expected to be accurate. This was confirmed by the analysis of undiluted cheese sample spiked with lanthanum. In this case the interference effect – which is possible to be eliminated by dilution – apparently has a more complex character than a multiplicative one. Accuracy of the analytical results obtained for the samples of Bebilon 4® powdered milk and cheese (collected in Table 3) was confirmed by ICP-OES analysis. The reference values were 6.38 and 10.01 mg g^{-1}, respectively.

Separate attention should be paid to the fact that lanthanum used during GCS procedure for elimination of interference effects did it effectively in very low concentration (0.01%), i.e. in much lower concentration than is usually recommended. As seen in Table 3, even in such small amount, when supported by dilution of a sample to an appropriate grade, it was capable of overcoming the interferences totally, i.e. to such an extent that all apparent concentrations were statistically equal to each other. The use of this reagent can be then highly recommended as a part of GCS procedure in determination of calcium by AAS.

6. Conclusions

The obtained results proved correct construction of the designed solenoid micropump flow system and its proper operation in the context of GCS procedure. The calibration strategy carried out with the use of this system gave a possibility to determine an analyte with very good accuracy and precision in a sample free of interferents, as well as to detect interference effects (when they occurred) avoiding serious analytical errors. Consequently, an attempt was made to eliminate the detected interferences by stepwise dilution of a sample and/or by using special reagents. It is worth to be stressed that the same could not be possible when using any of the common calibration methods (i.e. set of standards method or standard addition method), as they lead to only a single estimation of the analytical result.

The performed research revealed that independent of the instrumental aspects the results, offered by GCS, had to be interpreted very carefully. When the signals measured for an undiluted sample are not high enough, they can be too low when produced by diluted sample and the interferences can be assumed wrongly as being eliminated. If the results are supected to be unreliable in terms of their repeatibility, GCS procedure should be repeated in improved conditions or supported by addition of a special reagent to the sample before dilution.

The developed manifold enables us to obtain 7 measurement signals, 4 calibration graphs and 6 analytical results, just like the other flow systems dedicated to GCS [14–16]. However, the major advantage of the micropump system is the possibility to perform GCS procedure relatively fast (6 min per cycle) and with low consumption of the standard and sample solutions (1 mL both), while the flow-injection system requires 5 min and 8 mL, and the sequential injection manifold as many as 36 min and only 1 mL, respectively. Similarly to a sequential injection manifold, the proposed multipumping system enables to register six single peaks (for whom peak height or peak area are measured), whereas a flow-injection manifold requires registering two three-part peaks for whom local plateaus have to be measured.

What is also very important, the solenoid micropump-based system makes it possible to dilute the calibration solutions automatically, precisely and extremely easily. However, constructed systems so far are complementary to each other to some extent; hence they can be applied alternatively to calibration by GCS depending on the current conditions and needs (e.g. if a sample is available in relatively large volume, the flow injection system [14,15] should be preferably recommended).

It has been proven that the designed system works well in terms of verification and elimination of systematic errors in case of determination of calcium in real samples by flame atomic absorption spectrometry. It should be however emphasized that the manifold can be considered as a calibration module, which may be incorporated in other flow systems of various configurations and analytical purposes. In particular, there are no obstacles to use it in cases when a sample is required to be pretreated before measurements (by means of, e.g. dilution, reagent addition, preconcentration, hydride generation), as well as when some special flow injection techniques (e.g. merging zone or stopped-flow techniques) are needed to be applied.

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