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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 interferences. 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.

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## 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 interferences.

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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 of 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  $c_5$

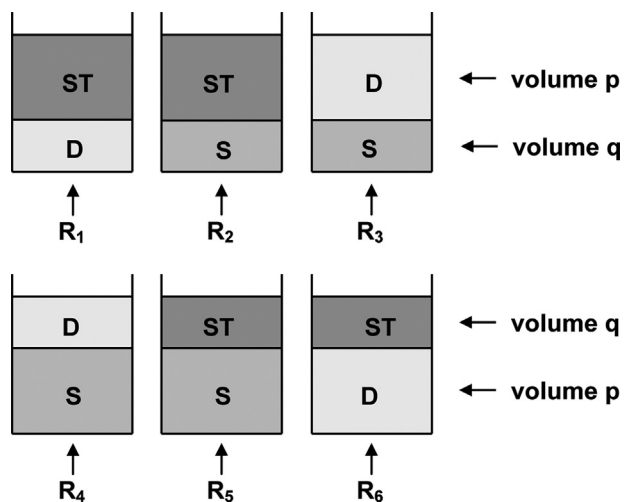


Fig. 1. Preparation of calibration solutions according to GCS procedure: standard, ST, sample, S, and diluent, D, and the corresponding analytical signals,  $R_1 \div R_6$ .

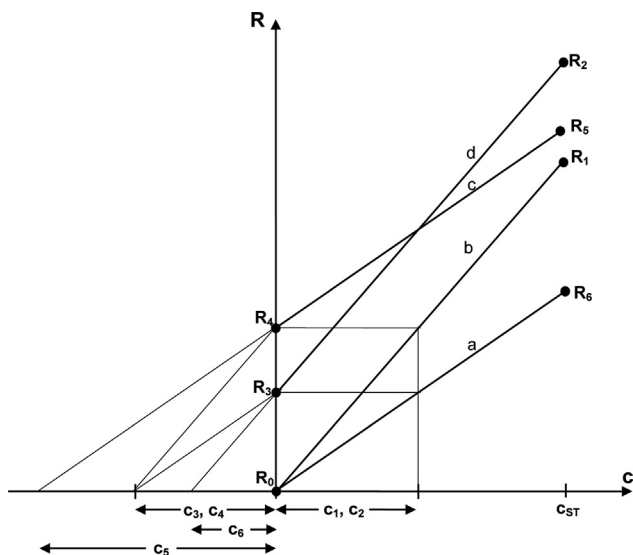


Fig. 2. Calibration graphs (a, b, c, d) constructed in accordance with GCS and analytical results estimated in interpolative ( $c_1, c_2$ ), semi-extrapolative ( $c_3, c_4$ ) and extrapolative ( $c_5, c_6$ ) way.

and  $c_6$ , compare Fig. 1) are calculated in a typical extrapolative way and, consequently, they can be expected to be most accurate.

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

- 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  $c_1 \div c_6$ ;
- 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  $c_3 \div c_6$ ;
- 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;
- 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  $1.000 \text{ mg mL}^{-1}$  were prepared from Titrisol standards (Merck, Germany). Standard stock solutions of lanthanum at concentration of  $50 \text{ mg mL}^{-1}$  were prepared by dissolving in water an adequate amount of  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  (Merck, Germany). Standard solutions of calcium and lanthanum used for calibration were obtained by dilution of the stock solutions with 1.0% (v/v)  $\text{HNO}_3$  (Merck, Germany). In the case when calibration procedure was carried out with the use of lanthanum buffer,  $\text{LaCl}_3$  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  $\mu\text{L}$  of lanthanum stock solution, respectively.

The following natural samples were utilized: certified reference material of skim milk powder BCR<sup>®</sup> – No 063R (EC-DG JRC-IRMM, Belgium) with the certified calcium content of  $13.49 \text{ mg g}^{-1}$ , Babilon 4<sup>®</sup> (Nutricia Poland, UE) powdered milk with the content of calcium given by the manufacturer as  $6.33 \text{ mg g}^{-1}$ , 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  $\text{HNO}_3$  (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  $\text{s}^{-1}$  rate of pressure increase and  $240^\circ\text{C}$  of max. temperature. After digestion, the sample solution was cooled down in air to the

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