INTEGRATED CALIBRATION METHOD IN ANALYTICAL CHEMISTRY

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Abstract

A concept of the integration of the interpolative and extrapolative calibration methods - commonly used in analytical chemistry - is presented, i.e. it is proposed to perform both methods according to a single calibration procedure. Such an approach allows one to obtain two estimations of the analyte concentration in a sample and to verify it in terms of accuracy. It is suggested to execute the integrated calibration method by the flow injection technique in accordance with two different procedures. The instrumental flow systems designed for this purpose are shown. The principle of both procedural versions is revealed and the specificity of them is discussed. The reasons are explained why the method is worth to be brought into the analytical practice.

Keywords: Analytical calibration; calibration method; flow injection analysis

1. Introduction

The most significant aspect of chemical analysis is the requirement from the analytical results to be reliable in terms of accuracy, i.e. to be so close to the true values as possible. The importance of this problem becomes more evident if it is considered from economical point of view. For example, it has been reported [1] that 10 % of ca. 250 million chemical measurements, which are made in the United States every day, have to be repeated because of suspected inaccuracy and the cost of all these repeat analyses is estimated at $15 billions every year. It

seems that such an alarming situation can be supposed to exist in other countries as well.

Along an analytical procedure performed a lot of potential sources of systematic analytical errors threatens. From among them a very common and dangerous is the interference effect. It occurs when certain substances (interferents) present in a sample together with a component determined (an analyte) contribute in such a way that the analytical signal is changed. As the signal is almost always an indirect measure of the analyte concentration in the sample, the interference effect can cause a difference between the estimated and true analytical results.

Certainly the interference effect can be corrected by isolation of interferents from a sample using some relevant technique. However, this self-evident manner is usually very strenuous and sometimes quite unreliable in fact. Therefore, the way commonly used for overcoming the interferences is to apply a proper strategy at very critical stage of an analytical procedure, namely at the stage of calibration.

2. Analytical Calibration

Analytical calibration can be considered as the reconstruction of the real dependence (calibration dependence) of the analytical signal on the analyte concentration in order to transform the signal measured for a sample assayed to the concentration of the analyte in this sample. In very most cases the calibration is realised in an empirical mode, i.e. by measuring the signals for standards (of well-known component concentrations) and for a sample in well-defined experimental conditions.

The calibration procedure is commonly performed with the use of a set of standards containing an analyte only. However, the empirical calibration can be executed according to some specific procedures, which are different from each other in terms, for instance, of a treatment of:

- standard solutions (e.g. standards are matched to a sample in terms of chemical composition),
- a sample (e.g. some special substances are introduced),
- both a sample and standards (e.g. the dilution process is applied, the internal standard is introduced),

- standard solutions in relation to a sample (standards are mixed with a sample).

In fact, all above efforts are undertaken almost exclusively in order to overcome the interference effects and, as a consequence, to avoid the systematic errors in the analytical results.

In spite of a procedure performed, the empirical calibration is always realised according to one of three general methods, which are different from each other in respect of a way of calculation of the analytical results on the basis of the calibration dependencies reconstructed [2]. They are as follows:

- the interpolative method, comprising the common calibration procedure (usually named “the set of standards method” or “the calibration curve method”) and its versions, e.g. with matching standards to a sample or using special substances;
- the extrapolative method, corresponding to so called “the standard addition method”;
- the indicative method, comprising all titration techniques.

The means of how the calibration dependencies are reconstructed and the analytical results are calculated in all above cases are schematically presented in Fig. 1.

The application of the indicative method is very limited. First of all, it can be practically used only when a sample assayed is in a liquid state. Moreover, as this method is based on a reaction between the reactive component of a standard (titrant) and an analyte, the special analytical conditions are required to execute it successfully. In such a situation the chemical analysis is performed more often with the use of either interpolative or extrapolative calibration method.

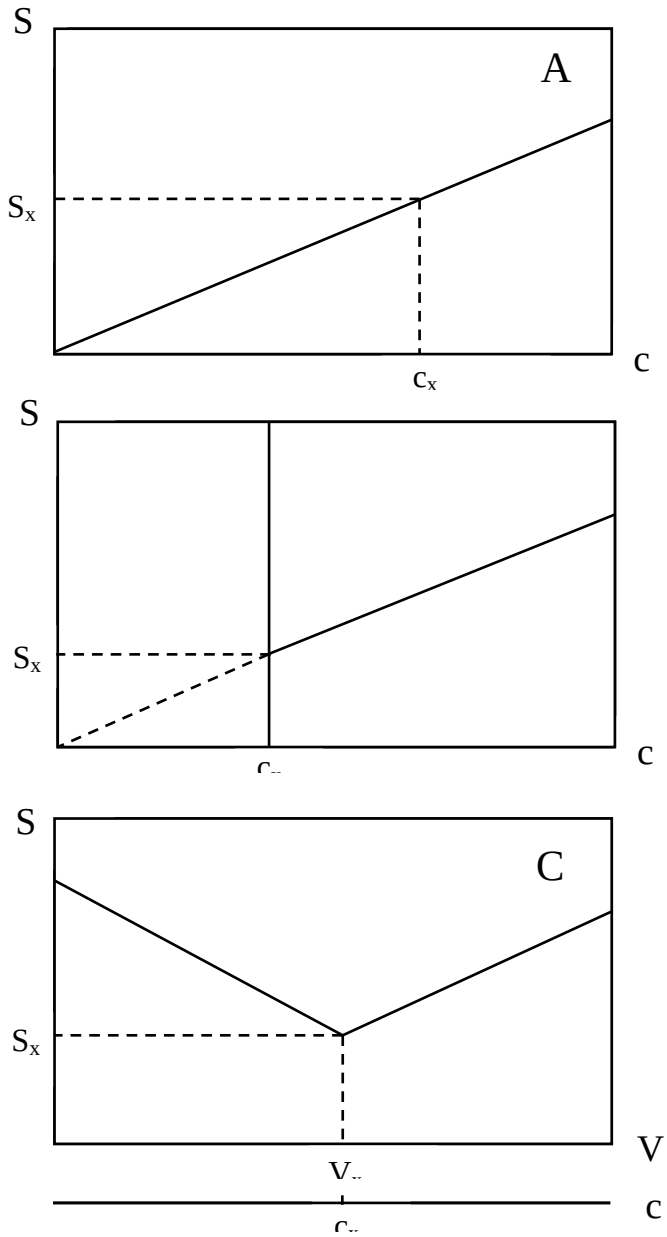

Fig. 1: Calibration by the interpolative (A), extrapolative (B) and indicative (C) methods: the analytical results, c_x, are calculated from the signals, S_x, measured for a sample in particular conditions

3. Interpolative and Extrapolative Calibration Methods

The interpolative calibration method is typified of that the standard solutions and the sample are prepared, treated and measured separately from each other. As a consequence, the calibration dependence can be reconstructed in any required concentration range (see Fig. 1) and the analytical result has a chance to be calculated in the interpolative way. In contrast, the calibration procedure of the extrapolative method comprises the addition of the standards into the same portions of the sample and measurement of the analytical signal for total amount of the analyte in each portion. By doing so, the calibration dependence is able to be reconstructed only over the original concentration of the analyte in the sample (see Fig. 1) and the analytical result has to be estimated in the extrapolative way.

If the analyte is influenced by an interferent in the sample and the sample are exposed to the measurements separately from each other, the interference effect is not able to be reduced unless some additional chemical or physicochemical treatments (mentioned above) are carried out. On the other hand, if the analyte is measured in original environment of the sample, the interferents have a chance to affect the signal proportionally to the analyte concentration and consequently the interference effect can be expected to be compensated for.

The great advantage of the extrapolative calibration method is that it can be used for overcoming of interferences when the composition of a sample is very complex or even completely unknown. In such cases the interpolative method usually fails as the procedures with matching the sample composition in standards and with using adequate reagents eliminating the interference effect require to know what components of the sample cause this effect and what is (at least approximately) their amount in the sample.

On the other hand, there are some serious limitations of the extrapolative method that are directly connected with the extrapolation process. The point is that the analytical results are generally less precise than those obtained by the interpolative method [3] and they can be also less accurate in such cases when the calibration dependence in the extrapolative region is not really following this part which is constructed experimentally [4].

However, it has been proved that those limitations can be considerably minimised under optimised analytical conditions [3,5], even when the calibration dependence is non-linear [6].

Another problem of the calibration methods considered is of economical nature. If the interference effect is required to be eliminated and the interpolative method is applied, the calibration procedure becomes quite laborious and costly because of some additional efforts needed. However, even in such a case the calibration dependence reconstructed once can usually serve for estimation of the analyte concentration in several samples of similar compositions at least. If the extrapolative method is used, no addition treatments are needed but the calibration dependence has to be reconstructed separately for each of the samples assayed what consumes a lot of work and time as well.

The conclusions from the above discussion about the interpolative and extrapolative calibration methods are as follows:

- the character either interpolative or extrapolative is then an essential feature of both methods in respect of the intereference effect,
- both methods are able to correct the interference effects and they are complementary to one another in this field,
- if both methods are used in traditional batch manner for correction of interferences they are rather not very economical from practical point of view.

4. Integrated Calibration Method

In spite of the complementary character of the interpolative and extrapolative calibration methods, a common analytical practice is to use them separately from each other for determination of an analyte in a given sample. As a consequence a single analytical result is obtained, which is believed to be accurate and particularly not affected by the interferents present in the sample. The accuracy of this result is sometimes checked in some adequate ways, including e.g. the use of the reference materials or application of the recovery method. If it is not done a doubt always appears whether the sources of systematic errors, in particular the interference effects, are properly recognised and completely overcame.

Furthermore, in routine analysis the custom is to perform determinations according to well-developed and verified analytical procedures. They are believed to be effective enough in terms of correction of the analytical errors, hence the accuracy of the analytical results is then not checked or it is done only occasionally. A great proportion of analyses which are still required to be repeated because of suspected inaccuracy is a proof that such an analytical strategy is generally not right.

In order to solve the above problems to some extent at least, a concept of the integrated calibration method (ICM) has been developed that is here presented. Two main characteristic features of this method are suggested, namely:

- the calibration is to be carried out according to a procedure integrating the interpolative and extrapolative methods,
- the procedure of the ICM is to be performed by the flow injection technique.

Owing to integration of the interpolative and extrapolative methods two independent estimations of the analytical result have a chance to be obtained in a single course of the analytical procedure. Both estimations are expected to be mutually verified in terms of accuracy providing valuable information on the reliability of the analyte determination.

The flow injection technique is characterised by specific facilities that are proved to be very useful for calibration purposes [1,7,8]. Offering an automation of chemical processing it is capable of improving the preparation of the sample and standard solutions before measurements. Moreover, it offers an analytical signal in the form of a transient peak that is a potentially rich source of information, e.g. about the interference effects occurring in the analytical system assayed. As a consequence, the flow injection calibration procedures in comparison with batch procedures are able to be not only more efficient in terms of labour, time and reagent consumption but also more resistant to interferences.

However, if the flow injection calibration approaches recommended in the literature are analysed in detail, some of their drawbacks appear, which perhaps are not so much noticeable at the stage of laboratory development but certainly create some limitations in analytical practice [1]. As a consequence any of those approaches can not still compete with those conventionally

performed if they are to be used in routine analysis. The ICM realised by means of the flow injection technique is believed to have a chance to change this situation.

The ICM is suggested below to be performed according to two different procedures. One of them is based on manipulation of the flows of calibration solutions and the other – on examination of the flow injection peaks in terms of the concentration gradient. Both procedures are the expanded and modified versions of the calibration approaches presented elsewhere [9-14]. Two dedicated flow injection instrumental systems have been designed in order to perform the ICM in both modes.

The crucial part of the designed flow system is the multifunctional fully rotary valve (FRV), shown schematically in Fig. 2. It has been already successfully used in our laboratory for calibration purposes [9-11,15,16]. The FRV is of a doubly-layer rotary design, with eight channels on both rotor and stator, uniformly positioned around the axis of the rotor and separated 45^{O} from each other. If compared with conventional design it is modified in such a way that the rotor, when actuated, is capable of not only 45^{O} but 360^{O} rotation. As a consequence, the rotor is able to be situated in eight (but not two as commonly) different positions allowing each channel to be connected with different channels on the stator.

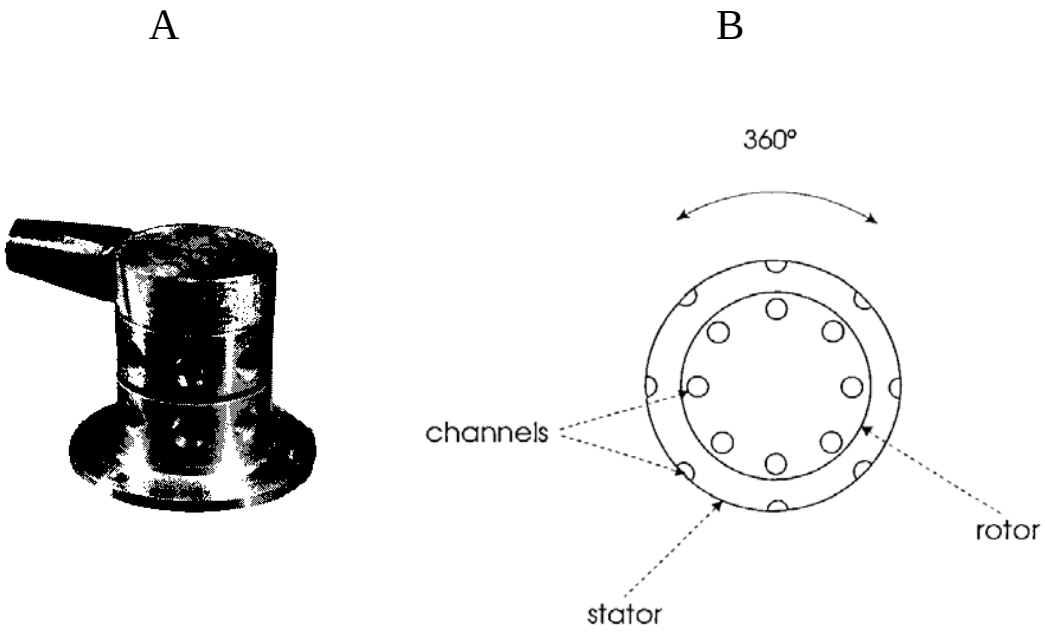

Fig. 2 : The scheme of the fully rotary valve in general (A) and top (B) views

5. Flow-Manipulation Calibration Procedure

5.1. Flow System Operation

The ICM in the version of the flow-manipulation procedure (ICM-FMP) is proposed to be executed with the use of the flow injection system presented in Fig. 3.

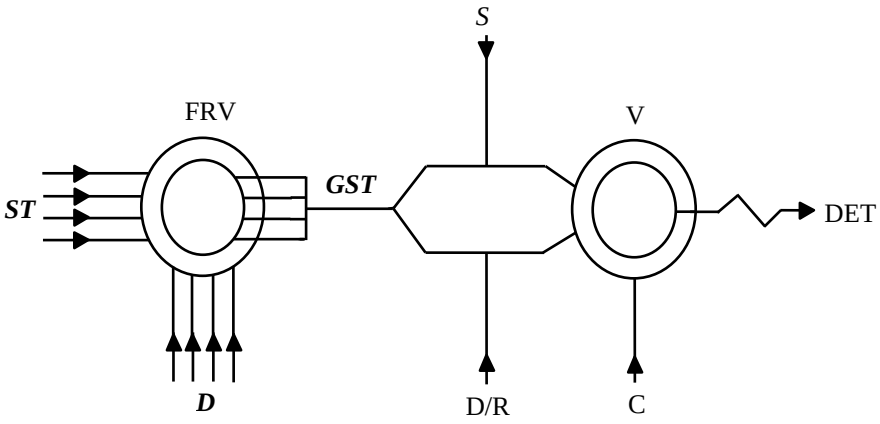

Fig. 3: Scheme of the flow system designed for the ICM-FMP calibration method; ST- standard solution, D - diluent, S - sample, R- reagent, C - carrier, GST - standard solution generated, FRV - fully rotary valve, V - two-positional valve, DET- detector

The standards are prepared with an aid of the FRV, which is configured as shown in Fig. 4. A single standard solution (ST) is propelled into the FRV's stator by four tubes and a diluent (D) is propelled by other four tubes. Eight tubes are also connected to the rotor: four of them are joined to each other allowing a part of the solutions to be merged and carried away toward the detector but other four tubes serve to deliver the remaining part of the solutions to the waste. When the FRV is in position *A (see Fig. 4) a diluent is directed to the detector but the ST solution is directed to the waste. If the FRV is rotated gradually counter-clockwise from position *B to *H, different parts of the ST solution are merged and mixed with different parts of the diluent. As a consequence, the standard solutions with various concentrations of the analyte have a chance to be generated in stream GST and directed to the detector (see Fig.3).

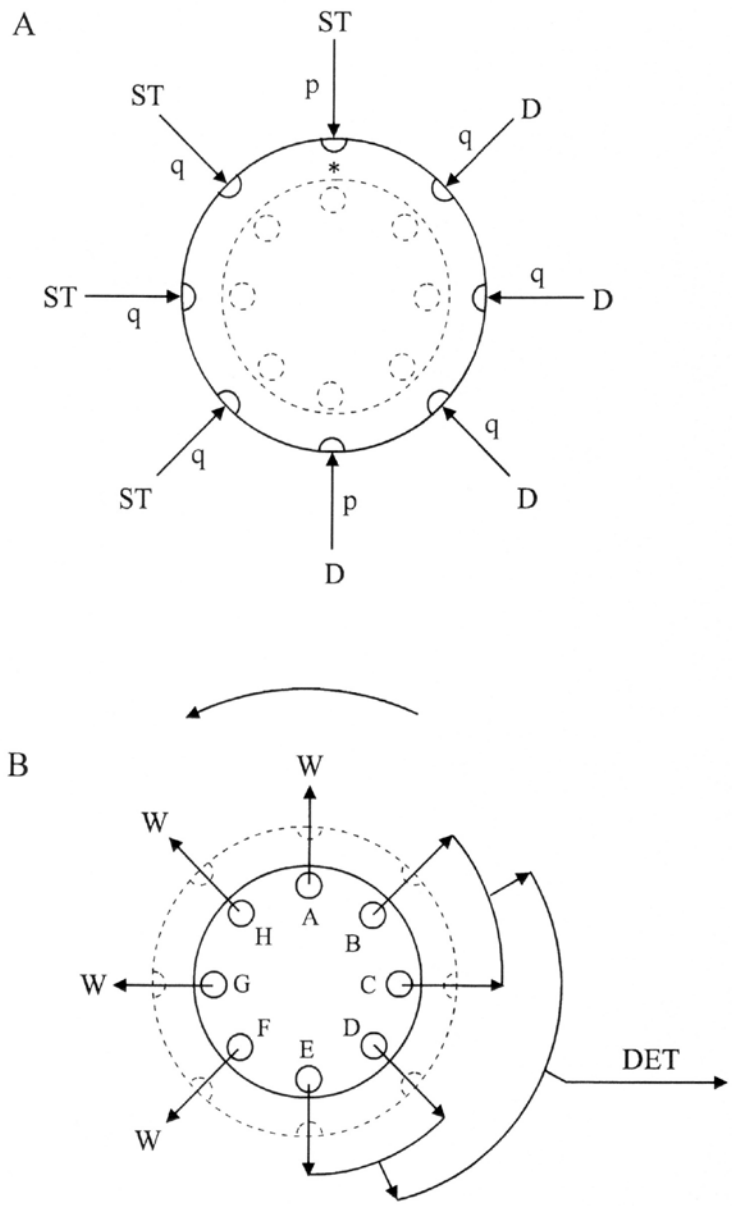

Figure 4 : The FRV configured for the ICM-FMP calibration method; ST- standard solution, Ddiluent, W - waste, DET - detector; A, B, C, D, E, F, G, H - channels changing the position in relation to channel * ; p, q - flow rates

A stream of each standard solution is then split into two streams. One of them is merged with the sample and the other with the diluent only or with any reagent R (both flowing with optional flow rates). Both streams are directed to two injection loops, which are installed in the common two-positional valve. The streams are simultaneously injected into a carrier stream and carried away towards the detector in the form of two zones. One of them contains no additional amount of the analyte and the other contains additionally that amount of the analyte (still the same), which is coming from the sample.

5.2. Processing and Handling of the Measurement Data

For each standard solution two flow injection peaks are detected as shown in Fig. 5. After the calibration procedure completed (i.e. if changing the FRV position from *A to *H) two sets of measurement data are produced (see Fig. 6). The allow one to construct two calibration lines and, consequently, to estimate the unknown analyte concentration in the sample twice, in both interpolative and extrapolative ways. Both estimations of the analytical result are then statistically compared with each other. Depending on the result of this comparison two decisions can be taken:

- if the estimations are the same, the analyte concentration in the sample is considered as evaluated accurately with a great probability and the calibration procedure is finished,
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- if the estimations are different from each other, the interference effect can be suspected to occur; in such a case the calibration procedure is recommended to be repeated with the use of, for instance, some reagent (R, see Fig. 3) eliminating interferences.

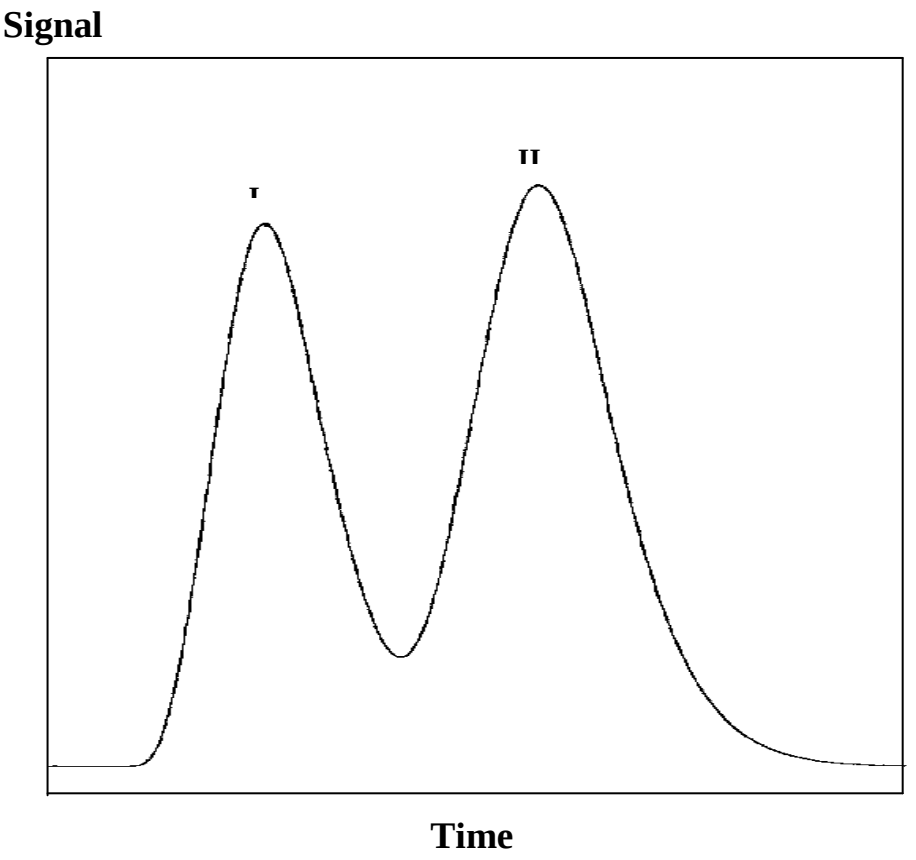

Fig. 5: Two flow injection peaks measured for the standard solution (I) and for the standard with sample (II) in the ICM-FMP calibration method

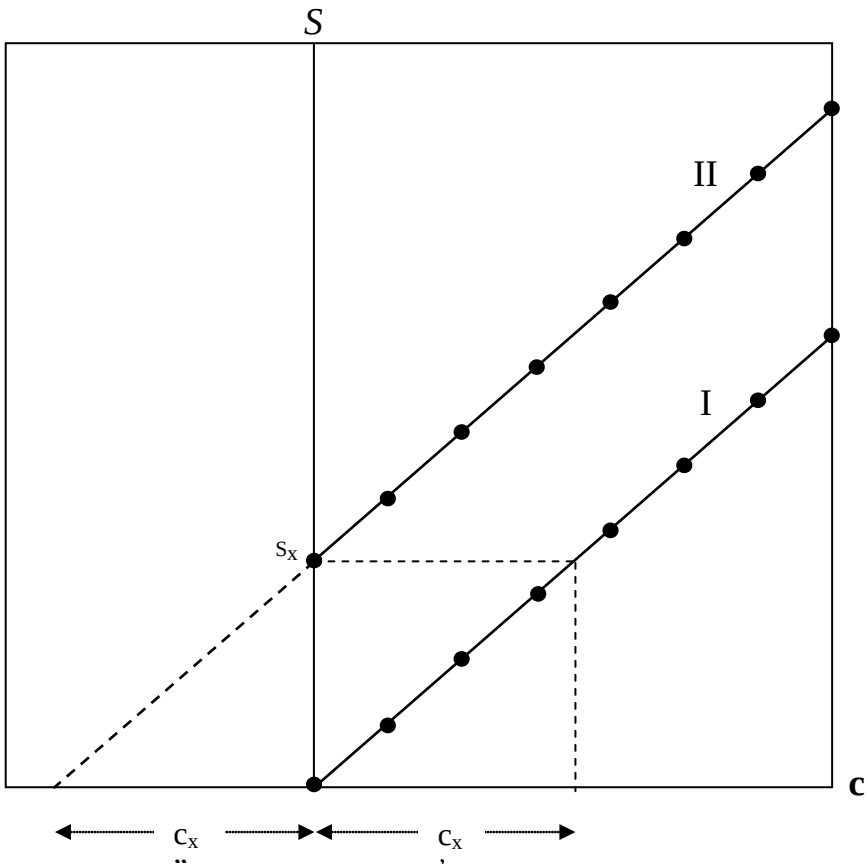

Fig.6: Two sets of measurement data produced in the ICM-FMP calibration method and two adequate calibration lines (I and 11) allowing one to estimate the unknown analyte concentration twice, c_x' and c_x", in both interpolative and extrapolative ways, respectively

5.3. Specificity of the ICM-FMP method

The characteristic feature of the ICM method in the FMP mode is the possibility to generate automatically (with the use of the FRV) an optional number of standard solutions of optional analyte concentrations.

The analyte concentration in a standard generated depends on the ratio of the total flow rate of streams of the ST solution inflowing to the FRV to the total flow rates of stream GST. As seen in Fig. 4, in the flow system proposed the ST solution is propelled with two different flow rates, p and q, in a sequence p-q-q-q, and the diluent is propelled with correspondingly the same flow rates. In such a situation the total flow rate of the ST solution inflowing to the FRV in each its position is different, as specified in Table 1. Moreover, this flow rate is complemented by the flow rates of the accompanying streams of the dilution, hence the total flow rates of stream GST is still the same ((p + 3q). For this reason the standard solutions with eight different analyte concentrations are able to be prepared and they are transported to the detector at a constant flow rate (see Table 1).

Table 1. Analyte concentrations (in normalised units) in the standard solutions generated in particular positions of the FRV

Position	Rate of the ST streams	Rate of the diluent streams	Total rate	Concentration
*A	0	p + 3q	p +3q	0
*B	p	3q	p + 3q	p / (p + 3q)
*C	p + q	2q	p + 3q	(p + q) / (p + 3q)
*D	p + 2q	q	p + 3q	(p + 2q) / (p + 3q)
*E	p + 3q	0	p + 3q	1
*F	3q	p	p + 3q	3q / (p + 3q)
*G	2q	p + q	p + 3q	2q / (p + 3q)
*H	q	p + 2q	p + 3q	q / (p + 3q)

If the FRV is activated as described above, in positions *A and *E the standard solutions are generated with the analyte concentrations which are always equal to 0 and to the maximum level (i.e. as in the ST solution), respectively. The analyte concentrations in remaining six standards (generated in positions *B, *C, *D, *F, *G, *H) depend directly on the ratio of flow rates p and q. The concentrations (in normalised scale from 0 to 1) possible to be produced when ratio p/q is changed from o to 5 are shown in Fig. 7.

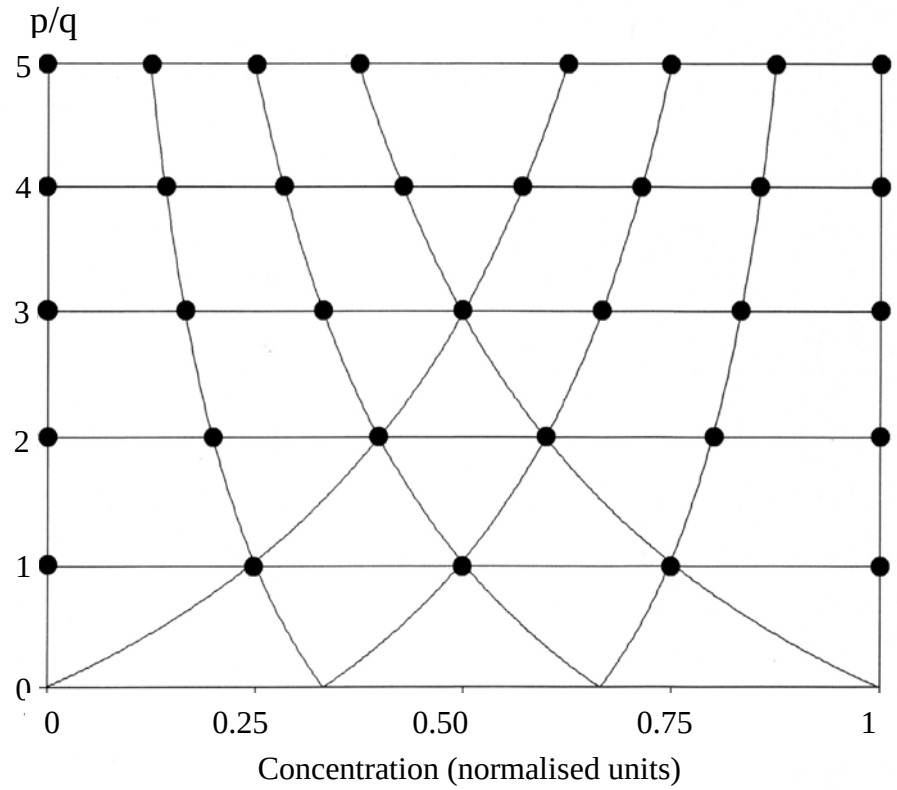

Fig. 7: The anałyte concentrations in the standard solutions generated by the FRV at ratio p/q ranged from 0 to 5

It is seen that the system designed enables to obtain maximum number, that is, eight, of the standard solutions of different concentrations, only except for p/q = 1, 2 or 3 when 5, 6, or 7 such standards are generated. It can be also generalised that the concentrations produced have a tendency to cover the whole concentration scale more or less regularly (if $1 < p/q < 5$) or regularly in pairs (if p/q is fractional).

In general, the flow rates of streams of the ST solution inflowing to the FRV can be quite different from each other. When controlling the values and sequences of the flow rates in a selected configuration of the FRV, the standards of various numbers of different analyte concentrations (from 5 to 8) are possible to be prepared [9]. Moreover, if doing the same, the optional distribution of the measurement points along the calibration lines can be achieved and chosen depending on the analytical requirements in a given case (e.g. on curvature degree of the calibration lines) [9].

6. Gradient Calibration Procedure

6.1. Flow System Operation

The ICM in the mode of the gradient procedure (ICM-GP) is proposed to be realised with the use of the flow injection system presented in Fig. 8.

The standards are prepared with an aid of the FRV, which is configured as shown in Fig. 9. Three solutions are simultaneously propelled into the FRV's stator with equal flow rates: a single standard solution (ST), a sample (S), and a diluent (D). Two of four tubes connected to the rotor are joined to each other allowing a pair of the solutions to be merged and carried away toward the detector. When the FRV is rotated gradually counter-clockwise from position *A to *D, four solutions are generated one after the other, namely: the sample solution, the sample mixed with standard solution, the standard solution, and the diluent, respectively. Finally, the solutions generated are successively injected using the common two-positional valve with a single injection loop installed.

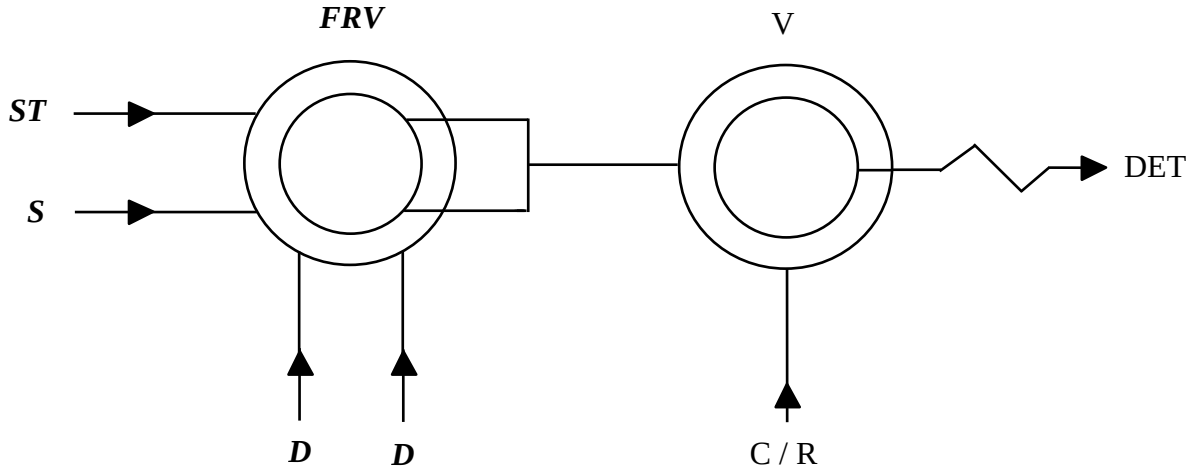

Fig. 8 : Scheme of the flow system designed for the ICM-GP calibration method; ST - standard solution, D - diluent, S - sample, R - reagent, C - carrier, FRV - fully rotary valve, V - two-positional valve, DET - detector

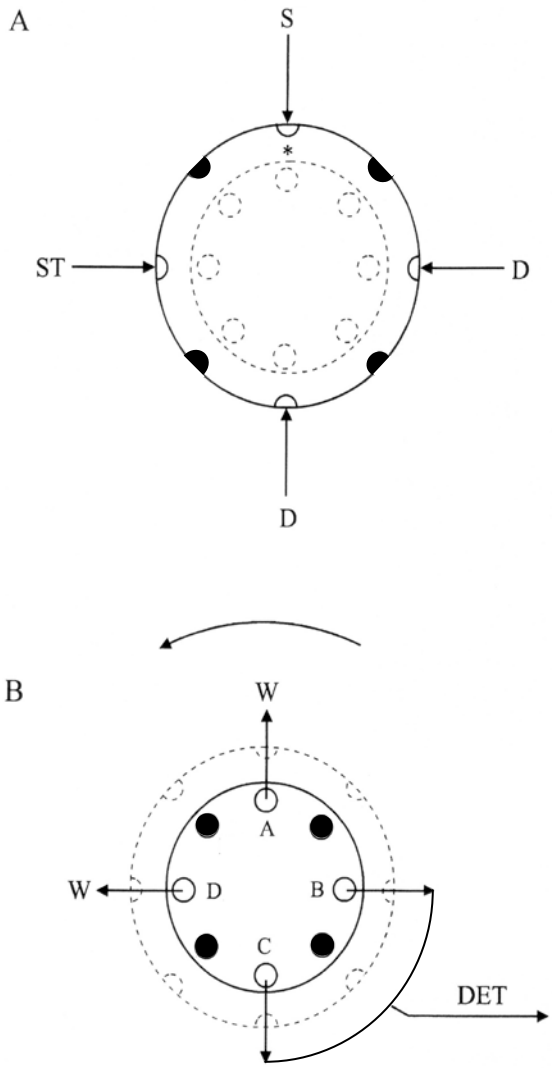

Fig. 9: The FRV configured for the ICM-GP calibration method; ST- standard solution, S sample, D - diluent, W - waste, DET - detector; A, B, C, D - channels changing the position in relation to channel *; inactive channels are denoted in black

6.2. Processing and Handling of the Measurement Data

During the calibration procedure, i.e. if rotating the FRV from position *A to *D, three flow injection peaks are successively produced (assuming that the diluent is free of the analyte): for the sample, for the sample with standard, and for the standard. With the use of dedicated software [12, 13] the peaks are adjusted to each other in a time window (t_b, t_f), which is corresponding to the region between the beginning and the end of each peak (as shown in Fig. 10). Then, the peaks are considered point by point along the concentration gradients, i.e. along the falling parts of the peaks, beginning from the maximum points (detected at time t_h) to the last points (detected at time t_f).

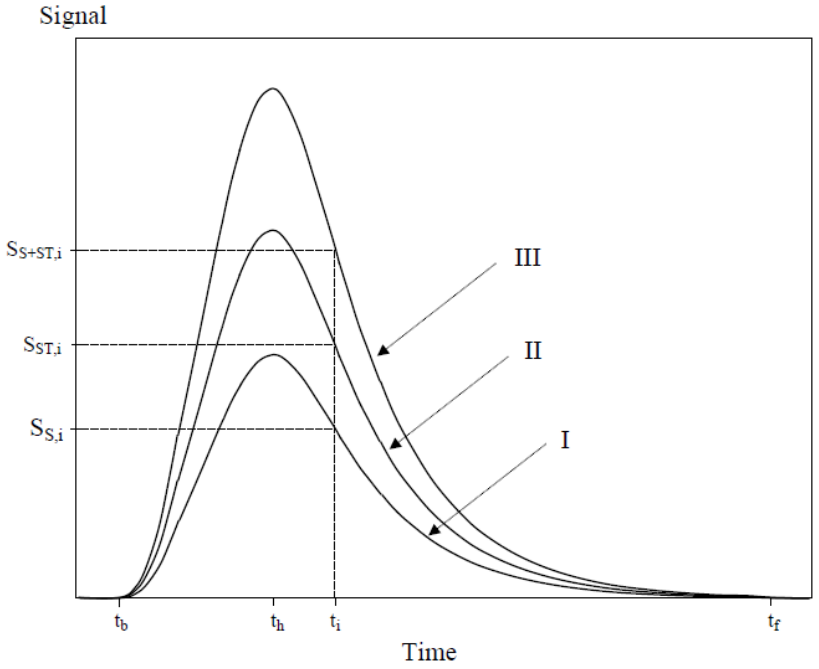

Fig. 10: The flow injection peaks produced in the ICM-GP calibration method for the standard (I), sample (II) and standard with sample (III) solutions in a time window (t_b, t_h); t_f - moment corresponding to maximum of the signals measured, t_i - a moment when transient signals $S_{ST,i}$, $S_{S,i}$, $S_{S+ST,i}$ are measured for calculation of a pair of apparent concentrations

Thus, at any moment t_i in the entire time range (t_h, t_f) considered three single signals are measured. The signals are produced by the analyte appearing just at this time in the zones of the sample ($S_{S,i}$), the standard ($S_{ST,i}$) and the sample with standard ($S_{S+ST,i}$). Taking into account all of those signals, as well as the concentration of the analyte in the standard solution injected, c_{ST}, two estimations of the analytical results, c_i' and c_i", (called "the apparent concentrations") can be calculated. As presented in Fig. 11, the estimations are obtained in the interpolative and extrapolative ways, respectively.

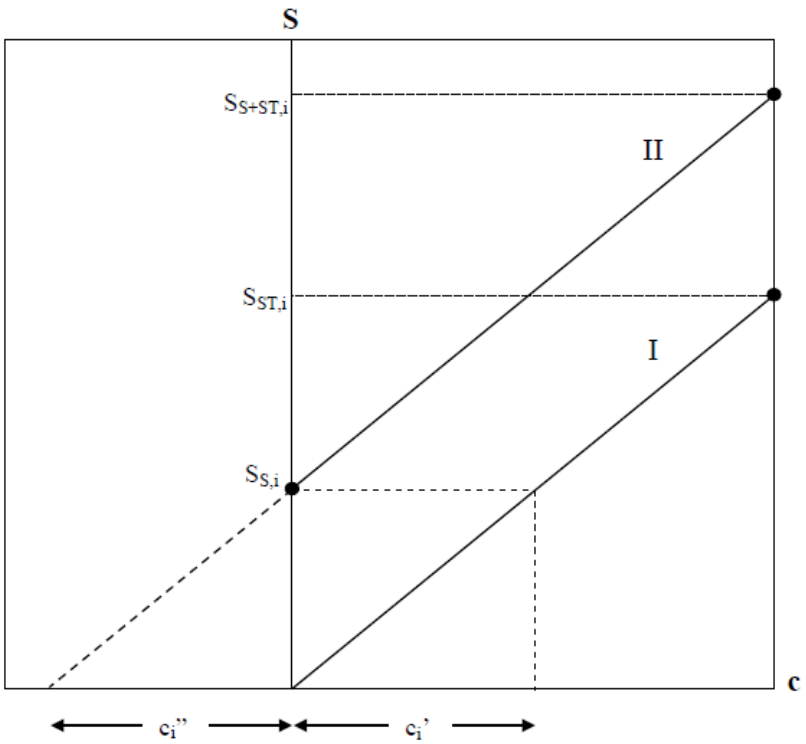

Fig. 11: Measurement data produced in the ICM-GP calibration method at moment t_i (compare Fig. 10) and two adequate calibration lines (I and II) allowing one to estimate a pair of apparent concentrations, c_x' and c_x", in both interpolative and extrapolative ways, respectively

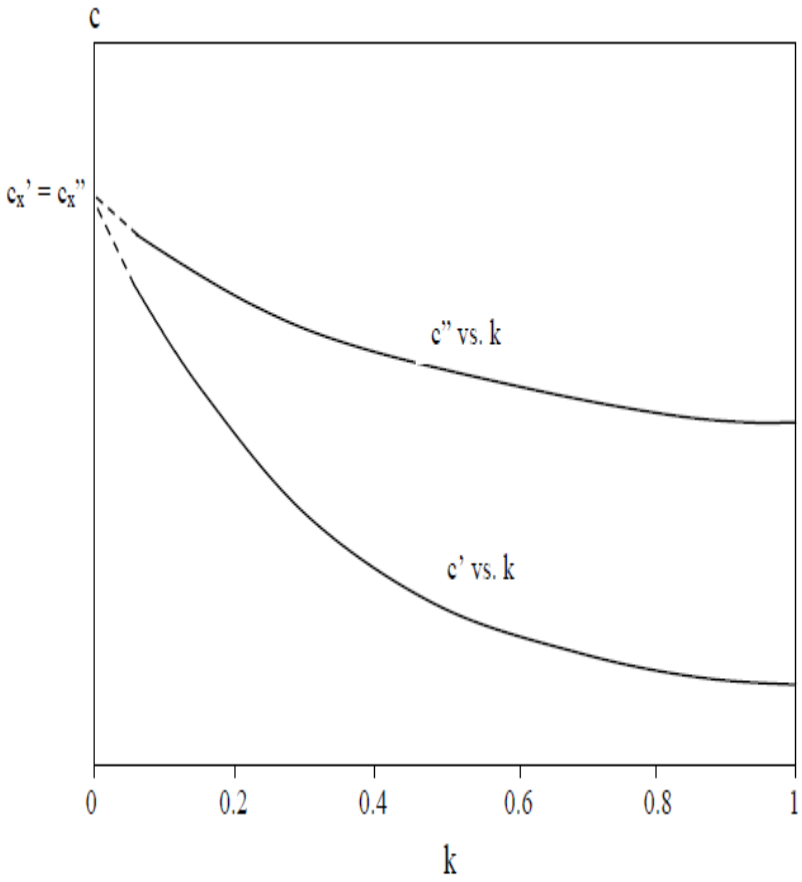

Fig. 12: An example of two relationships between apparent concentrations, c', c", and the relative dilution, k, allowing one to calculate two estimations, c_x' and c_x", of the analytical result

Within a time range (t_h, t_f) two sets of apparent concentrations, c' and c", are collected. They are related to a measure of progressively decreasing signals, e.g. to the relative dilution k, which is calculated as the ratio of a transient signal $S_{ST,i}$ and the maximum signal $S_{ST,h}$, both measured for the standard solution [13]. By doing so, two experimental relationships c' vs. k and c" vs. k are created, as shown in Fig. 11. When they are then approximated by a nonlinear function [12,13] and extrapolated to k = 0, two final estimations, c_x' and c_x", of the analytical result are able to be calculated.

As in the case of the ICM-FMP method, both estimations are statistically compared with each other. If the are the same, the analyte concentration in the sample is believed to be determined accurately and the calibration procedure is decided to be finished. If the estimations are different from each other, the calibration procedure has to be repeated. In such a situation a reagent eliminating interferences is recommended to be used by introducing it to the system through the carrier line (see Fig. 8).

6.3. Specificity of the ICM-GP method

What is characteristic for the ICM method realised in the version presented it is the possibility to obtain a great number of double estimations of the analytical result along the gradient of the analyte concentration. Since the peaks are examined with decreasing signals corresponding to decreasing concentrations of the anlalyte in the injected zones, the method allows one to investigate in fact how the apparent concentrations of the analyte are changed in the sample progressively diluted.

In general, there are two reasons of a change of either c' or c" concentration with dilution. One of them is the non-linearity of the calibration dependencies reconstructed. As two signals only are taken for calculation of a value of the apparent concentration (see Fig. 11), a true non-linear dependence can be approximated by linear function only and the result of calculation depends on that how great the effect of non-linearity is. The other evident reason of the changes considered is the interference effect. If the signals measured for the solutions of the sample and for the sample with standard, both progressively diluted, are biased by an interferent

variously, both apparent concentrations, c' and c", are calculated as also different at any stage of the dilution process.

Both effects, of the non-linearity of calibration dependencies and of the interferences, are believed to decrease with dilution of the solutions examined (i.e. with k approaching to 0) [12,13]. If so, the final values of apparent concentrations, c_x' and c_x", have a chance to be accurate estimations of the analytical results.

In linear signal-to-concentration analytical system the method allows one to investigate functions c'(k) and c"(k) with respect to interferences [14]. Namely, when comparing both lines in terms of their shape and mutual position, some conclusions dealing with the interferences can be drawn, for instance:

- if both functions appear to be linear and additionally the lines are overlapped to each other, the interferents are supposed to be absent in the sample assayed with a great probability;
- if the functions are linear but not overlapped, it has to be supposed that the interference effect exists and it is not eliminated with dilution of the sample;
- if the functions are non-linear and overlapped, it can be sure that the interference effect is eliminated;
- if the functions are non-linear and not overlapped but progressively approaching to each other, the interference effect can be considered as being not only eliminated but additionally compensated for with dilution (as concentrations c", in contrast to c', are calculated in the extrapolative way).

Thus, using the calibration method proposed it is possible to detect and examine the interference effects. The information achieved is so rich that the mechanism of interferences can be even revealed in some cases [14].

Owing to the above feature, the method offers the possibility not only to obtain two estimations of the analytical result but also to compare them with each other with respect to their "history", e.g. to the apparent concentrations changed. It helps to make proper decision about the further procedure. For instance, if both estimations are statistically the same but they are obtained after elimination of a great interference effect, it can be still reasonable to decide to repeat the calibration. On the other hand, if the estimations are different but very close to each other, it can be

sufficient to perform the procedure again with the sample solution diluted initially to some extent (instead of to use the chemical approach). The most expected case is to obtain two equal estimations on the basis of two sets of equal apparent concentrations; it is then almost sure that the analytical result found is accurate.

The other characteristic aspect of the ICM-GP method is that the reagent eliminating interferences is suggested to be introduced to the system through the carrier line and not through the separate line (see Fig. 8). A great efficiency of such procedure has been proved experimentally elsewhere [13].

7. Conclusions

The integrated calibration method in both modes proposed reveals some advantages being very important from analytical point of view; They are, for instance:

- the method is based on clear concept that can be easy brought into the practice,
- it works reliably under difficult analytical conditions, i.e. when the calibration dependencies are non-linear and the interference effects occur,
- it needs only a single standard solution initially prepared to perform completely the calibration procedure,
- owing to the natural features of the flow injection technique, the method can be fast and easy executed with the use of fully automated instrumental systems.

If taking into account all of above advantages, the method seems to be effective enough to accept it in analytical practice instead of the calibration methods commonly applied.

Two procedures recommended here for realisation of the integrated calibration method are considerably different from each other. The flow-manipulation procedure is methodologically more similar to the common batch procedure as the analytical results are calculated on the basis of multi-point calibration dependencies. The gradient procedure is perhaps more sophisticated but it provides more valuable information about the interference effect. The decision as to what of them has to be applied in a given case certainly depends to some degree on individual preferences and instrumental facilities. However, the most important question

influencing this decision seems to be how much information about the sample origin and composition in respect of interferents is available.

The greatest value of the calibration approach suggested here is the facility to obtain two independent estimations of the analytical result during a single calibration course. In spite of differences between the procedures, the integrated calibration method gives a chance to verify the reliability of a determination performed and, consequently, gives rise to be more sure that the analytical result obtained is accurate. This feature is expected to be warmly welcome in routine analysis in the light of the problems mentioned at the beginning of this paper.

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