

FLOW INJECTION SYSTEMS WITH INDUCTIVELY-COUPLED ARGON PLASMA ATOMIC EMISSION SPECTROMETRY

Part 2. The Generalized Standard Addition Method

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SUMMARY

In multicomponent analysis by inductively-coupled argon plasma emission spectrometry, the generalized standard addition method is useful in overcoming matrix and/or spectral interferences. As this method requires many standard additions, it becomes cumbersome when done manually if many elements are to be determined. By using a flow injection system, the standard addition manipulations required can be significantly simplified and completed within a shorter period of time with much less sample material. A flow injection system with merging zones is used to demonstrate the method for analyses of a Ni/Cu/Zn standard and of alloys. The reproducibility of measurements of the injected sample, with or without additions of standards is always better than 99%. The results obtained compare well with those obtained by the manual procedure and also with those obtained by atomic absorption spectrometry.

The increasing interest in flow injection analysis (f.i.a.) [1] is due to its characteristics of simplicity, versatility, cost, precision, and high sampling rate. This high sampling frequency makes f.i.a. particularly suitable for long runs of samples, e.g., in hydrological, biomedical, agronomic and geological work [1]. A successful combination of f.i.a. with inductively-coupled argon plasma emission spectrometry (i.c.p.e.s.) was described earlier [2], and, the good performance of such systems has been emphasized [3]. A main advantage is that losses in accuracy caused by variations in the sample matrix, mainly sample viscosity, can be decreased by the provision of a more constant sample flow rate to the nebulizer of the spectrometer. In i.c.p.e.s., for some types of samples, however, spectral interferences are often the limiting factor on the accuracy as well as the sensitivity of determinations [4].

Recently, the generalized standard addition method (g.s.a.m.) [5, 6] has been proposed as an expansion of the well known standard addition method. Its success in overcoming both matrix effects and spectral interferences in i.c.p.e.s. has been reported [7]. This method requires a number of additions of standard solutions to the sample in order to measure mutual interferences

and also the matrix effect, allowing accurate simultaneous determinations of several analytes. In addition, complete characterization of the instrument is attained [7]. The concepts and related calculations are described elsewhere [5, 7, 8]. The application of this method in routine large-scale analysis is cumbersome if the many standard additions required are done manually. The large number of measurements required for each sample drastically reduces the sampling rate and increases the sample volume needed.

The good performance of flow injection systems with i.c.p.e.s., and the feasibility of standard additions in these systems, make it attractive to include the g.s.a.m. for the analysis of materials where spectral interferences and/or matrix effects impair accuracy. This paper reports the development of such a flow injection system for the routine analysis of copper-nickel alloys by i.c.p.e.s.

EXPERIMENTAL

Reagents, standards and samples

Freshly distilled-deionized water was used. The acids were analytical grade and high-purity argon was employed. The stock standard solutions were prepared from spectrographically pure substances (Johnson-Matthey; Specpure). Working standards for the application of the g.s.a.m. (20.0 ppm Cu, 40.0 ppm Cu, 60.0 ppm Cu, 20.0 ppm Ni, 40.0 ppm Ni, 60.0 ppm Ni, 1.00 ppm Zn, 2.00 ppm Zn, 3.00 ppm Zn and the blank) were prepared in 4% (w/v) nitric acid. For comparison, the same synthetic sample (40.0 ppm Cu + 40.0 ppm Ni + 2.00 ppm Zn, in 4% w/v nitric acid) as used in the earlier manual procedure [7] was prepared. The blank solution, used as carrier streams and as standard, was a 4% (w/v) nitric acid solution.

The alloys (250 mg) were dissolved in 10 ml of aqua regia (3:1 hydrochloric acid and nitric acid), the final volume being completed to 100.0 ml with water. Before measurement, the samples were diluted manually 25-fold with water. This dilution, which may also be done in the flow injection system by using a smaller injected volume [1, 2], is necessary to match the mean analyte concentrations in the samples with the i.c.p. linear ranges.

Apparatus

A Jarrell-Ash model 975 ICAP AtomComp spectrometer with a cross-flow nebulizer was employed. The wavelength for nickel measurements was 243.7 nm; the other operating conditions were as specified in Part 1 [2]. The standard software furnished by the manufacturer in the PDP-8 computer was maintained with no background correction applied. The integration period was fixed at 10 s and the pre-burn time at 13 s. The calibration for the usual measurements was based on a two-point standardization, from the blank and standard concentrations of 40.0 ppm Cu, 40.0 ppm Ni and 2.00 ppm Zn. Mixed standards were not employed to avoid any effects of spectral interferences. For the g.s.a.m., no previous calibration was required

and the responses measured after each addition were those of intensities from the channel for each element ratioed to a constant current source. The intensities related to the blank were measured from time to time; very small variations relative to the analytical responses were observed. As the standard addition method requires the analytical response to be zero in the absence of the analyte [9, 10], the net intensity values were obtained by subtracting the small blank values from the measured intensities.

The proportional injector, manifold tubing and connectors were the same as used earlier [2]. Alternatively, a Technicon AAI peristaltic pump furnished with tygon pumping tubes was used. The flow injection system and the spectrometer were coupled as already described [2].

Flow system

The system used for the analysis of alloys utilizes successive injections of the sample, each one accompanied by the injection of a different standard, the additions being achieved by the merging zones approach [11]. This system therefore does the manual part of the partition generalized standard addition method [5, 7, 8], because the successive sample zones can be considered as aliquots for which the volume does not vary after the different additions.

The flow diagram of the system is shown in Fig. 1. When the proportional injector (I) rests in the sampling position, as indicated, both sample (S) and standard solution to be added (A) are pumped to fill the corresponding loops (L_S and L_A) before going to waste (W). After the sampling period, the central sliding part of the injector is moved to the alternative position so that the selected volumes of sample and standard are introduced into their corresponding carrier streams (C_S and C_A) as well defined, reproducible zones [1]. The zones merge at confluence point y , and mixing is improved inside the following mixing coil (M_C) before the processed sample zone reaches the nebulizer. After measurement, the sample zone is discarded. The standard solution pumped is replaced by another, the sample is kept and the injector

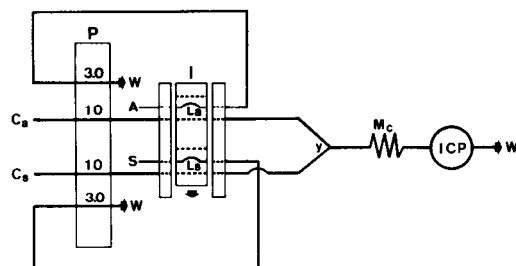


Fig. 1. Flow diagram of the proposed system. P is the peristaltic pump with indication of flow rates (ml min^{-1}); I is the proportional injector shown in the sampling position. The sample (S) and standard (A) solutions fill loops L_S and L_A which are the volumes introduced into the carrier streams (4% w/v nitric acid). M_C is the mixing coil (70 cm).

is switched back to the position specified in Fig. 1, starting a new cycle. After successive measurements involving all standards, including the blank (without addition), the g.s.a.m. data have been obtained and next sample can be processed.

Application of the generalized standard addition method

The amounts of added standards can be expressed either in quantity or concentration units, because the volume of the processed sample zone is the same regardless of the additions involved. Concentration units (ppm) are preferred here. These concentration values could be processed without correction in a perfectly symmetrical flow injection system [11], where both the sample and the standard solutions undergo the same degree of dispersion. However, the construction of a perfectly symmetrical flow injection system is very difficult.

In this study, any effect of system asymmetry can be corrected by multiplying the added concentration values (ΔC , Table 1) by the f_A/f_S ratio, where

TABLE 1

Input file for the f.i.a.—g.s.a.m. application to the synthetic sample

Input file			Comment
FIA—ICP—GSAM for Zn, Cu, Ni			Title
4 9 3 0			TDC computational method, number of additions, number of analytes, no scaling
0.	0.	1.	C Matrix of concentrations (ppm)
0.	0.	2.	
0.	0.	3.	
20.	0.	0.	
40.	0.	0.	
60.	0.	0.	
0.	20.	0.	
0.	40.	0.	
0.	60.	0.	
24477.	15759	9299.	R ₀ Matrix of the responses related to the situation without addition
24155.	15724.	13281.	R Matrix of responses related to C
24339.	15737.	17385.	
24514.	15805.	21805.	
37901.	16242.	9836.	
50954.	15859.	9877.	
62722.	15407.	9927.	
23546.	23900.	9096.	
23762.	33072.	9682.	
24725.	40639.	9978.	

f_A and f_S are the dispersion factors related to standard and sample, respectively. This is demonstrated by considering a single-analyte solution which is injected into the f.i.a.—i.c.p.e.s. system to simulate first the sample and then the standard. If linearity of the response plot can be assumed, responses R_S and R_A are related to the analyte concentration (C) by the equations $R_S = \alpha_S C$ and $R_A = \alpha_A C$. Here, α_S and α_A are the global response constants of the whole system for the analyte present in the sample and standard, respectively. Thus $R_S/R_A = \alpha_S/\alpha_A$.

The α values depend both on the flow injection system and on the i.c.p. spectrometer, being regarded as the product of the dispersion factors (f_A or f_S) and the response constant of the detection unit. For a given analyte, this constant is the same for both sample and standard, and the above equation reduces to $R_S/R_A = f_S/f_A$. In symmetrical systems, $f_S = f_A$ and no correction is needed because $R_S = R_A$. In asymmetrical systems, the added concentrations must be multiplied by f_A/f_S so that $R_S = R_A$ for a given analyte. In the g.s.a.m. calculations, these factors may be considered as a pseudo-matrix effect which alters the slope of an hypothetical calibration curve and is eliminated by the g.s.a.m.

Calculations

All calculations were done by a PDP-10 computer, the g.s.a.m. program written in Fortran IV (Infometrix, Seattle, WA) being used with small modifications. Table 1 shows one of the input data files which contains information about the sequence of additions, amounts of added standards, responses measured initially and after each addition, and dispersion factors. The final results of initial amounts of analytes are given in ppm.

The g.s.a.m. solves the overdetermined system of equations $\Delta CK = \Delta R$, where ΔC and ΔR are matrices representing changes in concentrations and analytical responses caused by the additions of the analytes. Matrix K contains the coefficients relating the contribution of each of the analytes to the different responses. The dimensions of these matrices are discussed elsewhere [5] and for this application, ΔC and ΔR are 9×3 (i.e., nine standard additions and three analytes to be determined). The 3×3 K matrix is determined from the eqn. [5]

$$K = (\Delta C^t \Delta C)^{-1} \Delta C^t \Delta R$$

and indicates the sensitivities of all sensors to all analytes for the system studied. The initial analyte concentrations C_0 are obtained [5] from

$$C_0 = [R(\Delta C^t \Delta R)^{-1} \Delta C^t - I] \Delta C$$

Here, R is the matrix of responses, related to the concentration matrix C (Table 1).

Procedures

Prior to system dimensioning, it was necessary to investigate the effect of the emergent flow rate on the Cu, Ni and Zn measurements. The solutions (blank, 10.0 ppm Cu, 10.0 ppm Ni or 10.0 ppm Zn in 4% (w/v) nitric acid) were pumped continuously at different flow rates (0.5–6.3 ml min⁻¹) and measured with a 10-s integration period. For three pumping rates (1.5, 3.0 and 4.5 ml min⁻¹), relative standard deviations of ten measurements were calculated. These tests showed that a flow rate of 2.0 ml min⁻¹ was optimal; this means 1.0 ml min⁻¹ for each of the merging carrier streams C_S and C_A (Fig. 1) in a symmetrical flow system. The effect of the length of the M_C mixing coil on reproducibility was investigated with 40, 70 or 110 cm coils. Finally, injected volumes of the sample and standard solutions, compatible with the integration period and the other system dimensions, were chosen.

The pre-burn time was then fixed by analysing the measured peak shape of the sample zone. These tests involved a ΔI scan [2], an integration period of only 1 s and the utilization of 10.0 ppm standards of Cu, Ni or Zn. Later, the dispersion factors related to sample and standards (f_S and f_A) were determined for Cu, Ni and Zn as already described [2]. The same standards as used for the i.c.p. calibration were employed.

Before the g.s.a.m. was applied, the linearities of the calibration plots for Cu and Ni were checked by measuring 0.0, 25.0, 50.0, 75.0 and 100.0 ppm standards prepared in 4% (w/v) nitric acid. This procedure was not applied for zinc because of the expected small zinc concentrations in the alloys and the low concentration levels of the zinc additions.

The flow injection system (Fig. 1) was then employed for the analysis of the synthetic sample and of the alloys by using the g.s.a.m. The standards were added in the following order: blank, 1.00 ppm Zn, 2.00 ppm Zn, 3.00 ppm Zn, 20.0 ppm Cu, 40.0 ppm Cu, 60.0 ppm Cu, 20.0 ppm Ni, 40.0 ppm Ni and 60.0 ppm Ni. For some samples, the entire procedure was applied in triplicate so that the precision of results could be assessed.

Finally, the samples were analysed by a manual procedure with the g.s.a.m. Equal volumes (15.0 ml) of the sample and the standards (the same as specified above) were mixed and measured in the i.c.p. with pneumatic sample aspiration.

RESULTS AND DISCUSSION

Changes in flow rate within the interval studied here caused small variations in the measured signal for both sample and blank solutions (Fig. 2), and the reproducibility of measurements was also affected, as was noted previously [2]. Reproducibility also deteriorated when the flow rate was 6.3 ml min⁻¹, probably because higher flow rate affected the plasma stability [2]. These results are general, and similar effects were observed for 30 other metals under different acidity conditions. All these data, useful for designing other f.i.a.-i.c.p.e.s. systems, are available on request. For the

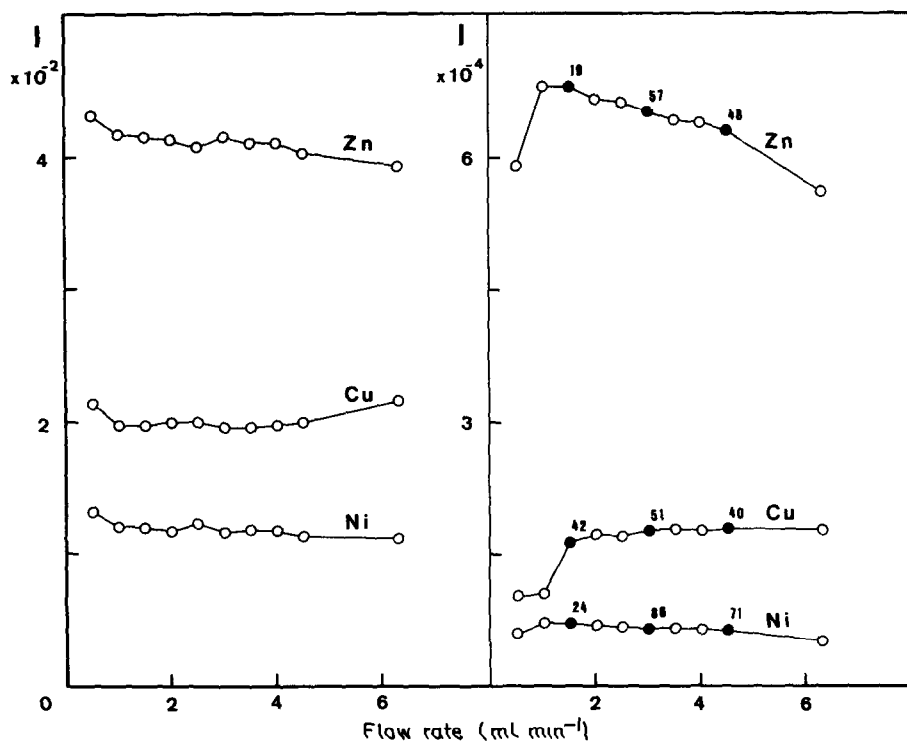


Fig. 2. Effect of the sample flow rate towards the inlet of the plasma on the signal (I). The left-hand curves refer to the blank and the right-hand curves to 10.0 ppm Zn, Cu and Ni standards. The numbers near the filled points indicate the relative standard deviations (%) of the corresponding measurements calculated after ten measurements.

present system, in which Cu, Ni and Zn concentrations were to be determined simultaneously, a 2.0 ml min⁻¹ flow rate was chosen as the best compromise between reproducibility, sampling rate and plasma stability.

The relative standard deviations of the measurements were almost unaffected by variations in the length of the M_C mixing coil (Fig. 1), which therefore does not play an important role in the precision of measurement, in contrast to most flow injection systems. As there is no chemical reaction within the mixing coil, and the signal is averaged over the integration period, the mean signal is less dependent than usual on the mixing conditions. The coil length was, therefore, kept as small as possible while still allowing some mixing as well as attachment of the Y-connector (Fig. 1) to the inlet of the i.c.p. nebulizer. The short coil also enhanced the possible sampling rates [1].

The injected volumes were 500 μ l, which corresponds to L_s and L_a loops of 100 cm. These large volumes are necessary to permit an integration period of 10 s without significant decrease in dispersion factors which leads to loss

in sensitivity. Analysis of the measured peak profiles showed that a pre-burn time of 13 s is sufficient to permit initiation of the i.c.p. operation and sample injection to be simultaneous ($\Delta I = 0$) [2]. Also, with the large peak width, the integration period can be located in the central part of the sample zone, where there is a more constant concentration than at the ends of the zone. Under such conditions, small differences in injection and measurement starting times are not significant, and the internal standard technique used earlier [2] becomes unnecessary. Parallel experiments confirmed that the precision of measurements without an internal standard was always somewhat better than the precision obtained in measurements based on ratios involving cadmium as internal standard.

After system dimensioning, the f_s and f_A dispersion factors were determined for Cu, Ni and Zn (Table 1). The differences between f_s and f_A reflect the system asymmetry. The small but significant differences observed for dispersion factors corresponding to different metals indicate that although the measured peak shape depends basically on the flow injection system [2], the i.c.p. spectrometer also has some influence on peak shape.

The linearity of the i.c.p. responses for copper and nickel were considered adequate for this application, as the linear regression coefficients were 0.99984 and 0.99988, respectively ($n = 5$). Linear responses were noticed also with regard to the other involved sensors. The relative standard deviations of measurements of the injected sample (40.0 ppm Cu + 40.0 ppm Ni + 2.00 ppm Zn, in 4% w/v nitric acid) were estimated after ten repetitions as 0.9, 0.3 and 1.4%, respectively. As the physical sample dispersion inside the flow injection system is the same for all metals, the differences in precision must be due to the i.c.p. system.

The proposed system for the application of g.s.a.m. requires about 10 min for each sample, which is significantly shorter than the time necessary to perform the equivalent manual procedure. Also the f.i.a.-g.s.a.m. combination offers the advantage of requiring only one set of standards for all samples.

After experimental measurements for all the standard additions to the synthetic sample, initial analyte concentrations of 39.2 ppm Cu, 40.3 ppm Ni and 2.23 ppm Zn were calculated by using the g.s.a.m. computer program in the TDC calculating mode [7]. The values based on the IDC computational method [7] were almost identical. The deviations from the true values are probably due to the inherent extrapolation of the standard addition method which decreases precision [9]. In fact, after a triplicate application of the g.s.a.m., relative standard deviations of 4.7, 2.5 and 9.3% were calculated for Cu, Ni and Zn, respectively.

The results obtained by applying the g.s.a.m. to the alloys are shown in Table 2 which also presents the results obtained by the manual procedure, by conventional i.c.p.e.s. based on calibration curves, and by atomic absorption spectrometry (a.a.s.) [12]. The same standards as used for the g.s.a.m. were employed for the a.a.s. calibration, after suitable manual dilutions of the samples and standards. Of particular interest are the erroneously high

TABLE 2

Results obtained by the proposed method (a), by the manual i.c.p.—g.s.a.m. procedure (b), by conventional i.c.p.e.s. (c) and by atomic absorption spectrometry (d) (The concentrations are given as ppm of the element in the diluted sample. Values related to conventional i.c.p.e.s. and a.a.s. are based on three measurements.)

Alloy	Method	[Cu]	[Ni]	[Zn]
1	a	44.1	17.1	~0.09
	b	45.3	17.3	~0.01
	c	48.4	18.4	0.26
	d	44.7	17.5	0.03
2	a	59.0	24.5	~0.12
	b	60.5	23.5	~0.04
	c	62.8	24.9	0.36
	d	62.8	23.5	0.05
3	a	33.0	60.3	~0.08
	b	32.4	59.5	~0.01
	c	32.9	61.5	0.67
	d	32.5	58.3	0.01

zinc concentrations obtained by conventional i.c.p.e.s., which can be explained by spectral interferences from copper and nickel (cf. Table 3). The g.s.a.m. results indicate that this interference is overcome as the zinc results are scattered around zero concentration, i.e., zinc measurements are limited by the noise from the zinc channel. The g.s.a.m. results for zinc are in agreement with those obtained by a.a.s., where interferences from copper and nickel are negligible [12].

The K matrix related to alloy 1 is shown in Table 3 which indicates the contribution of the three metal concentrations to the three sensors. The data related to spectral interferences between copper and nickel are characterized by uncertainties of about 20%, as was shown by successive measurements of alloy 1.

By comparing the K-matrices obtained for the other alloys, small variations in the diagonal values, in general less than 3% per 4 hours of ICP operation, were verified. This indicates the absence of both a pronounced matrix effect and instrumental drift. These variations did not affect the g.s.a.m.

TABLE 3

K matrix related to alloy 1

Element	Analytical channel		
	Cu	Ni	Zn
Cu	1360	~5	32.8
Ni	~56	878.2	21.2
Zn	—	—	4203

results but, in the conventional procedure, would require successive ICP recalibrations.

Conclusions

The feasibility of applying the generalized standard addition method in a flow injection system connected to a multielement detector has been demonstrated for a simple quasi-symmetrical flow injection system and inductively-coupled plasma emission spectrometry. The equivalent manual procedure is significantly simplified. The proposed system should, however, be regarded as only a step in the development of new technology. Present limitations include the relatively low sampling rate and the necessity of preparing a series of standards. The latter disadvantage might be overcome by using the zone-sampling approach [13], which permits controlled dilution of a given standard before its injection into the final standard carrier stream. Studies concerning this point are in progress.

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REFERENCES

- 1 J. Růžička and E. H. Hansen, *Flow Injection Analysis*, Wiley-Interscience, New York, 1981.
- 2 A. O. Jacintho, E. A. G. Zagatto, H. Bergamin F^o, F. J. Krug, B. F. Reis, R. E. Bruns and B. R. Kowalski, *Anal. Chim. Acta*, 130 (1981) 243.
- 3 S. Greenfield, *Ind. Res. Development*, August 1981, 140.
- 4 S. Greenfield, *Pure Appl. Chem.*, 52 (1980) 2509.
- 5 B. E. H. Saxberg and B. R. Kowalski, *Anal. Chem.*, 51 (1979) 1031.
- 6 C. Jochum, P. Jochum and B. R. Kowalski, *Anal. Chem.*, 53 (1981) 85.
- 7 J. H. Kalivas and B. R. Kowalski, *Anal. Chem.*, 53 (1981) 2207.
- 8 R. W. Gerlach and B. R. Kowalski, *Anal. Chim. Acta*, 134 (1982) 119.
- 9 J. Kragten, *Talanta*, 28 (1981) 901.
- 10 I. L. Larsen, N. A. Hartmann and J. J. Wagner, *Anal. Chem.*, 45 (1973) 1511.
- 11 H. Bergamin F^o, E. A. G. Zagatto, B. F. Reis and F. J. Krug, *Anal. Chim. Acta*, 101 (1978) 17.
- 12 M. Pinta, *Atomic Absorption Spectrometry*, Adam Hilger, London, 1975.
- 13 B. F. Reis, A. O. Jacintho, J. Mortatti, F. J. Krug, E. A. G. Zagatto, H. Bergamin F^o and L. C. R. Pessenda, *Anal. Chim. Acta*, 123 (1981) 221.