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Simultaneous determination of sulphide and sulphite by gas-phase molecular absorption spectrometry. Comparative study of different calculation methods

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Abstract

A method for the simultaneous determination of sulphide and sulphite is described, which involves continuous H₂S and SO₂ generation, preconcentration in a liquid nitrogen trap and measurement of the molecular absorption spectra of volatiles in the gas phase in 190–220 nm range. Under the recommended conditions (sample flow: 50 ml/min and concentrated sulphuric acid flow: 12 ml/min; generation time: 4 min) linear response ranges from 0.05 µg/ml for S²⁻ and 0.20 µg/ml for SO₃²⁻ are obtained with detection limits of 0.05 and 0.20 µg/ml respectively. Synthetic mixtures of the two components have been solved and a comparative study of different calculation methods has been made. In conclusion, multiwavelength methods offer better precision and accuracy.

1. Introduction

Classical approaches to the simultaneous determination of sulphur anions, i.e. titration [1], spectrophotometry [2,3] or polarography, typically involve differential assays, reaction of the sample with iodine, bromine compounds of many others [4,5] under different conditions. In many cases, the need for extensive manipulation of samples, subtraction of large numbers from each other, and substantial time investment per sample limit their applications. Automated or semi-automated methods offer opportunities to approach the problem. Burguera and Burguera [6] have attempted the simultaneous determination of several sulphur anions using a relatively uncommon technique, molecular emission cavity analysis (MECA); Hauge [7] and Sonne [8] have described a complicated simultaneous photometric flow injection determination of sulphide, polysulphide,

thiosulphate, sulphite and sulphate based on different chemical reactivities, differing pK_as and volatilities of the various sulphur-containing acids, and kinetic differences.

Many papers about several sulphur-containing anions determination are based on chromatographic separation and later determination. So Story [9] has indeed demonstrated the successful determination of a large number of sulphur anions with postcolumn reaction detection. Other authors that use chromatographic separation are Shpigun et al. [10] for determining sulphide, sulphite, sulphate and thiosulphate, or Steudel et al. [11] for sulphide, sulphite, thiosulphate and polysulphide.

Although previous methods offer good results, they all show different problems; for example, instrumental complexity (as MECA), sensitivity (as Sonne's method) or the excessive manipulation of samples (as methods with post-column deviation). Furthermore, the methods described are in fact sequential, not simultaneous, which leads to more complex

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procedures. The introduction of diode-array detection systems in UV-visible spectrophotometers allows new developments in GPMAS (Gas Phase Molecular Absorption Spectrometry) by Sanz et al. for single [12–15] and multi-component simultaneous determinations [16–18]. The first papers on this technique were published by Cresser and Syty, independently. Both of them used a mono-channel detection system (an atomic absorption spectrometer with hollow cathode or deuterium lamps as radiation sources) so they were not able to perform simultaneous determination; Syty reported only single sulphide (by H_2S generation) [19] or sulphite (by SO_2 generation) [20] determination.

From this period on, few works have been published on sulphite or sulphide [21] single determination of GPMAS. Simultaneous determination has only recently been proposed by Jin et al [22]. Using a similar approach to Syty, they perform simultaneous determination by measuring sequentially from two different radiation sources (magnesium and tellurium hollow cathode lamps) emitting at 202.6 and 214.3 nm; these wavelengths are far from the maximum molecular absorption of SO_2 and H_2S (198 and 196 nm, respectively) and two problems could arise: low sensitivity (which can be avoided by using a more expensive long path cell) and low precision (reproducibility values are not indicated by the authors). In addition, owing to the high overlap of the molecular absorption spectra of both volatiles, the use of the two-wavelength method for simultaneous determination is prone to inaccuracy.

In this paper generation of sulphur volatiles in a continuous mode, coupled to a retention in liquid nitrogen, permits the use of GPMAS with diode-array detection for the simultaneous determination of sulphide and sulphite at low concentration levels. Different mathematical data treatments for binary determinations of these compounds have been compared; the multiwavelength method give more accuracy and precision than the two wavelength methods.

2. Experimental

2.1. Apparatus

All measurements were performed using a Hewlett-Packard model HP 8451A diode-array

spectrophotometer furnished with a quartz flow cell of 1 cm path length (Hellma 174 QS) and equipped with a Keyboard HP98155A (Hewlett-Packard), a floppy disk drive for bulk data storage (Hewlett-Packard HP9121) and a graphics plotter (HP7475A). For mathematical treatment a Hewlett-Packard Vectra microprocessor with Eureka[®] software was used. Masterflex models 7518-10 and 7016-20 peristaltic pumps (Cole Parmer Instrument Co. Chicago, Illinois 60648), were employed throughout.

2.2. Reagents

All reagents used were of analytical-grade quality. Doubly distilled water was used.

Standard sulphide solution was prepared by dissolving $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (0.75 g) in 100 ml water, and then titration with ferricyanide. This and working standard solutions (prepared by serial dilution of the stock solution), were prepared daily.

Standard sulphite solution was prepared by dissolving $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ in a 5% glycerin water solution as stabilizer. Working standards were prepared by serial dilution of the stock solution, immediately before use.

Concentrated perchloric (70%, 1.67 g/ml) and sulphuric (96%, 1.84 g/ml) acids were also used.

2.3. System description. Procedure

Volatiles generation and cold trap systems are shown in Fig. 1. Two peristaltic pumps were used for mixing analytes solution (50 ml/min) and concentrated sulphuric acid (12 ml/min). H_2S and SO_2 generated into the mixing coil (in which an additional 600 ml/min nitrogen gas-auxiliary carrier flow, AF, was flowing) were separated in a first gas-liquid separator where there was a nitrogen flow (transport flow, TF, 100 ml/min) and the remaining liquid phase reached a second gas-liquid separator. The volatiles were swept through a water trap (a flask full of Raschig rings and immersed in an ice and salt bath at -10°C) and were finally condensed in the U-tube immersed in liquid nitrogen which contained a small quantity of glass spheres (2 mm diameter). The Raschig rings and the small glass spheres were both silanized.

After generation and trapping of volatile compounds for 4 min, the U-tube was closed, removed from the liquid nitrogen and left at

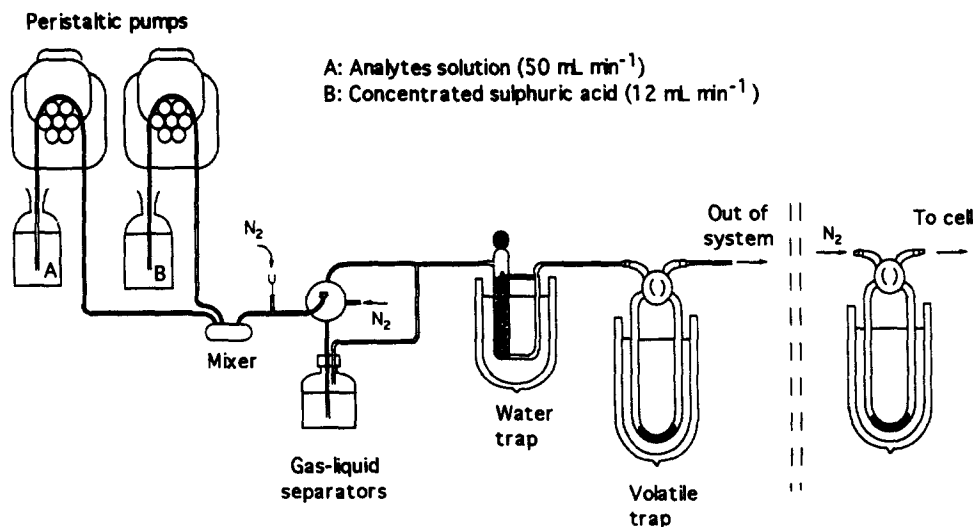


Fig. 1. Schematic diagram of the system (see explanation in the text).

room temperature. After 10 min the volatiles were transported to the continuous flow cell, placed in the spectrophotometer, with a nitrogen flow (measuring flow, MF) of 2000 ml/min.

To measure the transient signal, the spectrophotometer was programmed with a BASIC program that permitted us to obtain and store molecular absorption spectra in the 190–250 nm range, with a time interval of 0.2 s. All determinations of mixtures and standards were made at least in triplicate.

To determine S^{2-} and SO_3^{2-} contents in a mixture, the maximum absorbance values for every wavelength between 190 and 220 nm were obtained (the spectral bandwidth of the spectrophotometer was 2 nm, so 16 absorbance values were used).

3. Results and discussion

3.1. Optimization of parameters

Generation and preconcentration of volatiles were performed using a system which is based on another described in a previous paper [18]. This system had been used for hydride generation so many parameters had to be reoptimized because the nature of the compounds to be generated is quite different.

Although other mixers have been employed, the results obtained using that shown in Fig. 1 were the best. With respect to the glass reaction coil, different lengths were studied (3, 10 and 40 cm), and almost no influence on the absorbance or signal shape was observed, so a

reaction coil length of 3 cm (the minimum possible) was chosen. Using 40 cm instead of 3 cm gives a slight decrease in absorbance (about 10%) observed.

In most manifolds used in continuous flow determinations involving a gas–liquid separation process, a single gas–liquid separation step is used. In this work we observed that two serial gas–liquid separators produce signal increases of 35% compared to the use of only one separator. This increase is explained if one considers that the temperature of the solution to be separated is higher than ambient (owing to the heat liberated during the mix of aqueous analyte solution and concentrated sulphuric acid) so the separation process continues in the second gas–liquid separator; in addition, the shape of this second gas–liquid separator favours the process further.

Nitrogen TF is one of the parameters which most affects the analytical signal. As has been described for hydride generation [18], the TF must be the lowest possible to obtain the maximum retention yield in the liquid nitrogen trap. This is logical considering that the larger the flow, the less the residence time of the volatiles in the trap. However, when we employed low flows (as hydride) for sulphur volatiles, a retention of the nitrogen in the cryogenic trap was observed; when the trap was later brought to room temperature, the nitrogen suddenly escaped from the valve and allowed the volatiles to escape. In order to avoid this problem, three alternatives were tested.

Table 1
Variation of SO₂ signal with AF/TF ratio (total flow = 1200 ml/min)

AF (ml/min)	TF (ml/min)	AF/TF (ml/min)	Signal
1100	100	11	0.036
1030	170	6	0.040
600	600	1	0.030
100	1100	0.1	0.025

AF = Auxiliary flow, TF = transport flow.

(a) Changing the cryogenic trap to another at a higher temperature, so that nitrogen gas could not be held. A liquid nitrogen-ethanol bath (ca. -117 °C) was used, but a large decrease in absorbance values was observed which indicated a low retention yield for sulphur volatiles.

(b) Addition to the analyte solution of a substance capable of forming a gas in an acidic environment; this gas could act as an internal carrier gas [21]. NaBH₄ can not be used because it is a reducing agent and would transform sulphite into sulphide. Low carbonate concentrations were employed, but CO₂ causes the same problem as nitrogen.

(c) Increasing the nitrogen flow. To do this an AF was bubbled through the reaction coil (between mixer and first gas-liquid separator). This alternative gives successful results.

Nitrogen TF and AF were studied in a wide range of possible flow-rate combinations. H₂S and SO₂ were optimized separately. Table 1 shows SO₂ absorbance for different AF/TF ratios (maintaining a total flow of 1200 ml/min). The optimum value was for a ratio equal to 6. Table 2 shows the SO₂ absorbance variation with total flow (maintaining an AF/TF of 6). The best results were obtained using 700 ml/min total flow. A total flow of nitrogen of less than 400 ml/min produced the retention of N₂ in the cryogenic trap. Contrary to what happened with SO₂ absorbance, the H₂S optimiza-

Table 2
Variation of SO₂ signal with total flow (AF/TF ratio = 6)

AF (ml/min)	TF (ml/min)	Total flow (ml/min)	Signal
1800	300	2100	0.027
1030	170	1200	0.040
600	100	700	0.063
430	70	500	0.044

AF = Auxiliary flow, TF = transport flow.

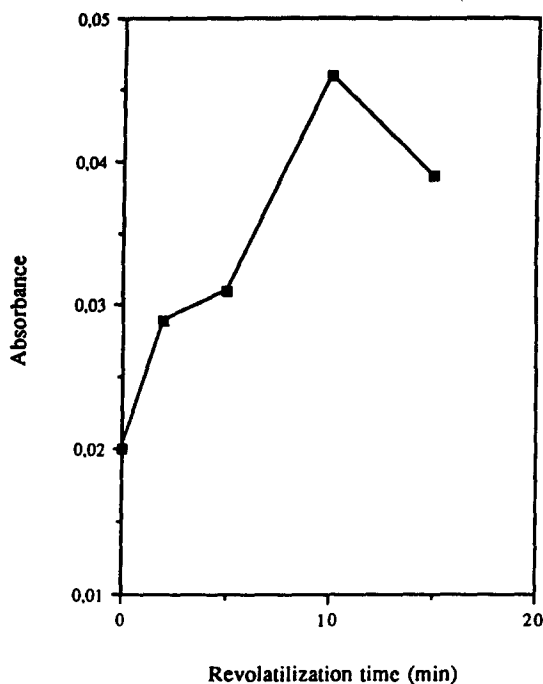


Fig. 2. Variation of absorbance with revolatilization time.

tion showed the best results using a total flow of 2000 ml/min. Finally, 700 ml/min total flow (AF = 600 ml/min and TF = 100 ml/min) was used because sulphite sensitivity was poorer than sulphide. With respect to the nitrogen MS, 2000 ml/min was found to be the optimum for different reasons, as discussed previously [18].

An exhaustive study was also performed of the time necessary for volatiles revolatilization at room temperature from the nitrogen trap; Fig. 2 shows peak height variation with this time (from 0 to 15 min). Other assays were performed by heating the U-tube after this time, but no improvements in the analytical signal were observed.

Sulphuric and perchloric acids at various concentrations were used both to achieve optimum acidity of the medium and to obtain quantitative generation of H₂S and SO₂. These acids were selected because they are used for batch generation of H₂S and SO₂, respectively. A first comparison for both acids in a 50% (v/v) solution, indicated better results by using 50% H₂SO₄; the reason was, perhaps, the high temperature of the acid solution that favours the volatilization of H₂S and SO₂. In a second series of assays, the absorbance values obtained using different concentrations of sulphuric acid indicated that concentrated acid gives much higher results than any other acid concentra-

Table 3
Optimization of analyte flow/acid flow ratio

Analyte flow (ml/min)	Acid flow (ml/min)	H ₂ S signal	SO ₂ signal	Analyte/acid
50	2	0.022	0.027	24:1
50	6	0.021	0.035	8:1
50	12	0.023	0.048	4:1

tion, which confirms the positive heating effect obtained with this acid.

Another optimized chemical parameter was the acid flow/analytes flow ratio. Ratios ranging from 24:1 and 4:1 did not produce variations in absorbance for H₂S, whereas the best results for SO₂ appeared when a 4:1 ratio or lower is used (Table 3). On the other hand, maintaining the 4:1 ratio and decreasing flow (acid flow = 3 ml/min and analyte flow = 12 ml/min, for example) gave a slight enhancement in signal (about 15%) but the analysis time increased.

The best conditions for the simultaneous determination of sulphide and sulphite by GP-MAS are given in Table 4.

3.2. Analytical characteristics

Under the compromise conditions found for S²⁻ and SO₃²⁻, individual calibration studies were performed by measuring the absorbance at the corresponding wavelengths of maximum absorbance (196 and 198 nm for S²⁻ and SO₃²⁻, respectively). The equations of the calibration graphs obtained by the method of least squares were:

$$Y = 1.46 \times 10^{-3} + 5.03 \times 10^{-2}[S^{2-}]$$

$$r = 0.998$$

$$Y = 1.65 \times 10^{-3} + 1.57 \times 10^{-2}[SO_3^{2-}]$$

$$r = 0.998$$

A linear response from 0.05 µg/ml to at least

Table 4
Optimum conditions for simultaneous determination of sulphide and sulphite

Analyses solution	50 ml/min
H ₂ SO ₄	12 ml/min
N ₂ Auxiliary flow	600 ml/min
N ₂ Transport flow	100 ml/min
N ₂ Measurement flow	2000 ml/min
Generation time	4 min
Revolatilization time	10 min

Table 5
Results obtained for simultaneous determination of sulphide and sulphite by MLRA and MLRA-TA

Mixtures ^a		MLRA		MLRA-TA	
Mixture 1	[S ²⁻] = 0.50 [SO ₃ ²⁻] = 2.0	0.43	0.43	0.51	0.52
		1.7	1.8	1.7	1.5
Mixture 2	[S ²⁻] = 0.50 [SO ₃ ²⁻] = 15.0	0.62	1.2	0.62	0.78
		15.7	15.5	16.0	15.1
Mixture 3	[S ²⁻] = 1.5 [SO ₃ ²⁻] = 3.0	1.7	1.6	1.4	1.5
		2.6	2.7	2.3	2.5

^aConcentrations in µg/ml.

5 µg/ml for sulphide and from 0.2 µg/ml to at least 20 µg/ml for sulphite was obtained; reproducibility values (expressed as RSD) were 2.9% (for 0.2 µg/ml S²⁻) and 3.1% (for 0.8 µg/ml SO₃²⁻). Detection limits calculated from a signal three times the height of the background of the blank measurement were 0.05 µg/ml for sulphide and 0.2 µg/ml for sulphite.

In conclusion, the sensitivity of this method (expressed as specific absorptivity, in ml µg⁻¹ cm⁻¹) is 10 times higher than we obtained by batch model [21]. With regards to the results obtained by other authors, it is very difficult to make comparisons; as we have used a 1 cm optical path length cell while other authors have used larger cells (normally, 15 cm optical path length). Using specific absorptivity as the comparison parameter, the values obtained by this method are about 15 times higher than obtained by other authors [22].

3.3. Simultaneous determination

In this work several mathematical procedures for the resolution of three synthetic samples of sulphite and sulphide have been tested, involving different versions of the two-wavelength method and multiwavelength methods.

3.4. Two-wavelength methods

In these methods, absorbance is measured at two appropriate wavelengths; the concentrations of both components were determined by resolving the following equations system:

$$Abs_{s(\lambda_1)} = a_{(\lambda_1)^s}^{Sulphide} [S^{2-}] + a_{(\lambda_1)^s}^{Sulphite} [SO_3^{2-}] - Abs_{s(\lambda_1)}^{blank}$$

$$Abs_{s(\lambda_2)} = a_{(\lambda_2)^s}^{Sulphide} [S^{2-}] + a_{(\lambda_2)^s}^{Sulphite} [SO_3^{2-}] - Abs_{s(\lambda_2)}^{blank}$$

(1)

where Abs_{s(λ₁)} and Abs_{s(λ₂)} are the absorbance

Table 6
Results obtained for simultaneous determination of sulphide and sulphite by CMM

Range (nm)	Mixture 1		Mixture 2		Mixture 3	
	[S ²⁻]	[SO ₃ ²⁻]	[S ²⁻]	[SO ₃ ²⁻]	[S ²⁻]	[SO ₃ ²⁻]
	0.50 µg/ml	2.0 µg/ml	0.50 µg/ml	15.0 µg/ml	1.5 µg/ml	3.0 µg/ml
190–220	0.42	1.8	0.43	17.8	1.4	3.5
190–210	0.51	1.5	0.42	18.0	1.3	3.7
190–214	0.50	1.6	0.40	18.2	1.4	3.5
190–216	0.44	1.8	0.39	17.7	1.4	3.5
198–208	0.26	2.1	0.21	18.3	1.3	3.6
198–210	0.05	2.3	0.25	18.0	1.3	3.6
198–212	0.05	2.5	0.17	17.6	1.2	3.7
198–214	0.05	2.5	0.05	19.3	1.2	3.6
198–216	0.05	2.6	0.05	19.0	1.2	3.7
204–220	0.07	2.5	0.13	18.8	1.3	3.5
198–220	0.05	2.6	0.10	18.6	1.6	2.7
210–220	0.51	1.6	0.93	17.3	2.1	1.7
212–220	0.53	1.6	0.80	16.8	1.9	2.5

of the mixture at each of the two wavelengths; $a_{(\lambda_1)}^{\text{Sulphite}}$, $a_{(\lambda_1)}^{\text{Sulphide}}$, $a_{(\lambda_2)}^{\text{Sulphite}}$, $a_{(\lambda_2)}^{\text{Sulphide}}$, $a_{(\lambda_1)}^{\text{Sulphite}}$ are the specific absorptivity (slope of calibration graph) of the individual compounds at the wavelength specified. The selection of λ_1 and λ_2 were performed on the basis of two analytical parameters as follows.

(i) Optimum sensitivity. This is the more used criteria for wavelength selection and corresponds to the maximum absorbance value of each of the two volatiles, i.e. 196 and 198 nm.

(ii) Optimum precision. The two wavelengths were calculated by applying a procedure described by DiTusa et al. [23], resulting in 196 and 212 nm for this case.

By using both methods, the results were very unsatisfactory (negative concentration values were obtained in some cases), so new alternatives were tested.

(i) Wavelength average. In this method each of the absorbance values is obtained as the average of the absorbance at three close wavelengths; firstly, the average at 192, 196 and 200 nm and secondly the average at 194, 198 and 202 nm. By this method the wavelength inaccuracy of the spectrophotometer is partially avoided.

(ii) Time average. As has been indicated above, we obtained a sequence of 50 spectra in each measurement and we used the maximum absorbance spectrum for obtaining the absorbance values at the selected wavelength. In many cases the maximum absorbance values spectrum appears close to other spectra of a similar area. This method, therefore, uses the

average absorbance values at similar times (taking the two spectra before the maximum and the two after the maximum), in order to correct the time inaccuracy.

(iii) Wavelength and time averages. This method is a combination of the previous two.

The results obtained using these alternatives were unsatisfactory too, so multiwavelength methods were applied.

3.5. Multiwavelength methods

In this method absorbance values obtained in a wavelength range is employed. Blanco et al. [24] demonstrated that the best results in the resolution of mixtures of species with overlapped spectra are obtained when the widest possible wavelength range is used. Such a range was 190–220 nm throughout this work. Two different methods has been tested:

(i) Multiwavelength Linear Regression Analysis (MLRA), proposed by Blanco et al. [25]. Table 5 shows the results obtained. Concentrations found agreed reasonably with known values. This method was also applied after performing a time average of absorbance values, but no better results were observed.

(ii) Complete Multiwavelength Method (CMM). This method basically consists of solving a set of equations similar to Eq. (1); the number of the equations is selected empirically but normally corresponds [24] to the wavelength range in which a higher overlapping of the spectra is observed. In order to solve the equations, mathematical program (Eureka®)

using an iterative procedure was employed. Different wavelength intervals were assessed and the best results were obtained using all wavelengths between 190 and 220 nm (which means a set of 16 equations, because the spectral bandwidth of the spectrophotometer is 2 nm). The results obtained for several ranges are shown in Table 6. All results are the average of three determinations and the RSD values were, in all cases, lower than 4%. The time average of the absorbance values did not give better results either.

It can be concluded that two-wavelength methods produce imprecise and inaccurate results; using either MLRA or CMM the results are satisfactory.

4. Conclusions

This procedure shows some advantages against previous GPMAS determination, such as higher sensitivity and the possibility of using the whole molecular absorption spectrum, allowing better reproducibility and accuracy in the results. Also it is possible to forecast the spectral interferences present. As opposed to other methods, sensitivity values are similar, neither complex nor specific instrumental is required and it is easy to apply.

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References

- [1] C.M. Das, *Talanta*, 38 (1991) 347.
- [2] T. Koh and Y. Okabe, *Anal. Sci.*, 3 (1992) 285.
- [3] T. Koh, Y. Okabe and Y. Miura, *Analyst*, 118 (1993) 669.
- [4] J.F. Verchere and A.M. Don, *Analisis*, 20(1992) 437.
- [5] M. García-Vargas, M. Milla and J.A. Pérez Bustamante, *Analyst*, 108 (1986) 1417.
- [6] J.L. Burguera and M. Burguera, *Anal. Chim. Acta*, 157 (1984) 177.
- [7] S. Hauge, K. Maroy and A. Thorlacius, *Anal. Chim. Acta*, 251 (1991) 197.
- [8] K. Sonne and P.K. Dasgupta, *Anal. Chem.*, 63 (1991) 427.
- [9] J.N. Story, *J. Chromatogr. Sci.*, 21 (1983) 277.
- [10] D.A. Shpigun, D.N. Obrezkov, J. Funk and G. Werner, *Vestn. Mosk. Univ. Ser. 2: Khim.*, 30 (1989) 273.
- [11] R. Steudel, G. Holdt and T. Goebel, *J. Chromatogr.*, 475 (1989) 442.
- [12] J. Sanz, F. Gallarta, J. Galbán and J. R. Castillo, *Fresenius'Z. Anal. Chem.*, 330 (1988) 510.
- [13] J. Sanz, F. Gallarta, J. Galbán and J.R. Castillo, *Analyst*, 113 (1988) 1387.
- [14] J. Sanz, L.A. Ortega, J. Galbán and J.R. Castillo, *Microchem. J.*, 41 (1990) 29.
- [15] J. Sanz, S. de Marcos, O. Muro and J. Galbán, *Microchim. Acta*, 110 (1993) 193.
- [16] J. Sanz, F. Gallarta and J. Galbán, *Anal. Chim. Acta*, 225 (1991) 113.
- [17] J. Sanz, S. de Marcos, J. Galbán and F. Gallarta, *Analisis*, 21 (1993) 27.
- [18] S. Cabredo, J. Sanz and J. Galbán, *Anal. Chim. Acta.*, in press.
- [19] A. Syty, *Anal. Chem.*, 51 (1979) 911.
- [20] A. Syty, *Anal. Chem.*, 45 (1973) 1744.
- [21] J. Sanz, S. Cabredo and J. Galbán, *Anal. Lett.*, 25 (1992) 2095.
- [22] Q. Jin, H. Zhang, Y. Duan, A. Yu, X. Liu and L. Wang, *Talanta* 39 (1992) 967.
- [23] M.R. DiTusa and A.A. Schilt, *J. Chem. Educ.*, 62 (1985) 541.
- [24] M. Blanco, J. Gené, H. Iturriaga and S. Maspoch, *Analyst*, 112 (1987) 619.
- [25] M. Blanco, H. Iturriaga, S. Maspoch and P. Tarin, *J. Chem. Educ.*, 66 (1989) 179.