

Optimization of experimental parameters for the determination of mercury by MIP/AES

Miguel Murillo *, Nereida Carrión, José Chirinos, Alexis Gammiero, Edmondo Fassano

Centro de Química Analítica, Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, Apartado de Correos 47102, Caracas 1041A, Venezuela

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Abstract

A system using a microwave induced plasma, as an emission source was optimized for total mercury determinations. The system contains a flow injection section in which mercury is reduced and deposited on a gold/platinum collector, and carried to the emission source. The microwave was generated in a Surfatron cavity. An experimental design was applied to optimize parameters concerning plasma conditions, amalgamation, desorption and mercury vapor generation. The limit of detection of the method was 14 pg ml^{-1} of mercury, using peak area mode while LDs was 1.3 pg ml^{-1} using peak height mode, with a 2% RSD and a linear dynamic range of almost three orders of magnitude. The accuracy was assessed using a certified reference material of atmospheric particulate National Institute of Standards and Technology (NIST) 2704. No significant difference at 95% confidence level was observed between the certified value and our result. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Due to the high toxicity of mercury and its compounds, it is necessary to determine them at very low levels and in a large variety of samples, especially environmental and biological samples [1].

A variety of analytical methods have been used to determine mercury [1,2]. Among them cold vapor (CV-AAS) [3], and electrothermal atomiza-

tion atomic absorption spectrometry (ETA-AAS) [1,2,4], atomic fluorescence spectrometry (AFS) [1,2,5,6], and inductively coupled plasma mass spectrometry (ICP-MS) [1,2,7,8] have been the most applied in recent years. A review published on the determination of total mercury in environmental and biological samples [1,2,9] concluded that the technique most used for these determinations was CV-AAS. In conjunction with a preconcentration step based amalgamation of the generated mercury vapor on gold trap, detection limits in the low ng l^{-1} range can be obtained [10,11]. Microwave induced plasma atomic emis-

* Corresponding author. Fax: + 58-2-6934977.

E-mail address: mmurillo@strix.ciens.ucv.ve (M. Murillo).

sion spectrometry (MIP-AES) has been used to detect mercury in the range of the low ng l^{-1} [1,2]. Lichte and Skogerboe [12] describe a method based on a argon MIP emission spectrometry with CV technique where mercury reduced by tin (II) chloride was passed, after drying, into a plasma source and the emission signal recorded. Tanabe et al. [13] were the first to apply the atmospheric pressure He-MIP to determine Hg at the ng g^{-1} range. Watling [14] and Nojiri et al. [15] described an Ar MIP-AES system combined with a CV and collection amalgamation on Ag-trap [14] and Au-trap [15], respectively. Duan et al. [16] compared two microwave cavities for the determination of mercury with aqueous sample introduction by an ultrasonic nebulizer. The LD for mercury by Surfatron and Microwave Plasma Torch (MPT) are 0.9 and 1.3 ng ml^{-1} , respectively. Bulska et al. [17] used a similar arrangement but generated mercury vapor and used two cavities, Beenakker (TM010) and the Surfatron. The LDs using the Surfatron was 1.6–2.2 times better than with those determined with the Beenakker cavity. Camuña-Aguilar et al. [18] compared three resonance cavities, Surfatron, Beenakker, and MPT. They found that the signal was larger when helium was used as the carrier gas instead of argon. In addition, water vapor, molecular gases and high concentrations of samples (larger than 0.1 mg) affected the Surfatron cavity. However, it showed better sensitivity and limits of detection (10 pg ml^{-1} of Hg^{2+}). Costa-Fernández et al. [19] studied the effect of the pressure on Ar and He MIPs sustained in a Surfatron. They found a better LDs at low-pressure discharges in comparison with atmospheric-pressure operation of MIPs. The LDs reported were 0.7 pg ml^{-1} for a 40 Torr argon discharge and 8 pg ml^{-1} at atmospheric pressure and 3 and 4 pg ml^{-1} using Helium. Okumura et al. [20] compared AAS, AES and AFS techniques in the determination of Hg. An identical vapor generation and amalgamation procedure was used so that these techniques could be directly compared. Concluding that all have similar limit of detection. In the CV-AFS method the use of NaBH_4 as a reducing agent is not as good as the use of tin(II) chloride, because it generates H_2 during the

course of mercury reduction. Which could be interference in the determination of mercury, due the quenching of mercury fluorescence [5] In the microwave-induced plasma, the cavity of the plasma is one of the fundamental parts [21]. The most commonly used are the Beenakker cavity [22] and the Surfatron. The Surfatron [23] propagates electromagnetic surface waves along the plasma tube through the wall-plasma interface. The Surfatron can form a very stable plasma, with an annular shape and only one wave propagation mode. They do not need a waveguide or resonant structure since the plasma acts as the only wave propagation media, making their tuning more stable when compared with other cavities [24]. They are very stable and show high reproducibility.

The aim of this study was to develop a method to determine mercury taking advantage of a higher reaction velocity of sodium borohydride as a reductor [10,25] and preconcentration based amalgamation of the generated mercury vapor on gold trap as a sample introduction method to MIPs using He in a Surfatron at atmospheric pressure [26,27]. The working parameters of flow injection and gold/platinum collector coupled to MIP-AES were optimized for determination of Hg.

2. Experimental

2.1. Instrumentation

A schematic diagram of the instrumentation used is shown in Fig. 1. The MIP-AES system used was assembled using commercial parts and some constructed in our laboratory. The microwave plasma was generated in a laboratory-built Surfatron cavity, which consisted of two parts, the entrance and coupling sections and the coaxial structure where the waves are generated [26,27]. The waves are generated in a coaxial cavity filled with air that ends with an adjustable short-circuit on one side and with thin brass film on the other. The Surfatron is fed by an Electromedical Supplies model Microtron 200 Mark III ($0\text{--}200 \text{ W}$, $2450 \pm 24 \text{ MHz}$) microwave genera-

tor. Helium gas is used to induce and support the discharge. A Brook model 5878 flowmeter was used for plasma gas flow rate controlled.

The radiation emitted from the plasma was focused on the entrance slit of the Spex model 1269 monochromator with holographic grating, 3600 lines mm^{-1} . The spectral resolution was about 0.004 nm. The control and data acquisition software were developed in our laboratory and controlled by a microprocessor (processor 486, with 4 MB RAM). The computer program allowed the Pt/Au collector temperature control, data acquisition, and the data storage and editing. The software was developed in a Windows[®] environment.

The sample introduction system consists of a flow injection system (FIS) and a Pt/Au collector. The FIS consists of a Cole–Palmer model Masterflex multichannel peristaltic pump that introduced the NaBH_4 , HNO_3 , and sample solutions into the spiral reactor. The gas mixture produced was carried by argon (amalgamation gas) into a gas liquid separator (built in the lab), a water trap and then to the collector. The Pt/Au collector

consisted of a Pt gold-plated gauze introduced into the small quartz oven (internal diameter 4 mm, outer diameter 6 mm, and length 4 cm) surrounded by a thermal resistance that allowed temperature control (built in the lab). A fan was used to cool the collector.

2.2. Reagents

All reagents used were of analytical grade. HNO_3 , H_3PO_4 (Baker Analyzed), HCl (Merck) and NaBH_4 (Sigma) were used without further treatment. The standard solutions were prepared by convenient dilutions of a 100 $\mu\text{g ml}^{-1}$ stock solution (Tritisol[™] Merck). The standards were prepared in a 5% (w/v) HNO_3 solution. Ultra-pure water (MilliQ, Millipore) was used. The Au/Pt collector was platinum gauze with 0.25 mm diameter holes, electroplated with gold. High purity Helium and Argon (99.99%) were used. Certified standard National Institute of Standards and Technology (NIST) SRM 2704 atmospheric particles was used to evaluate accuracy of the method.

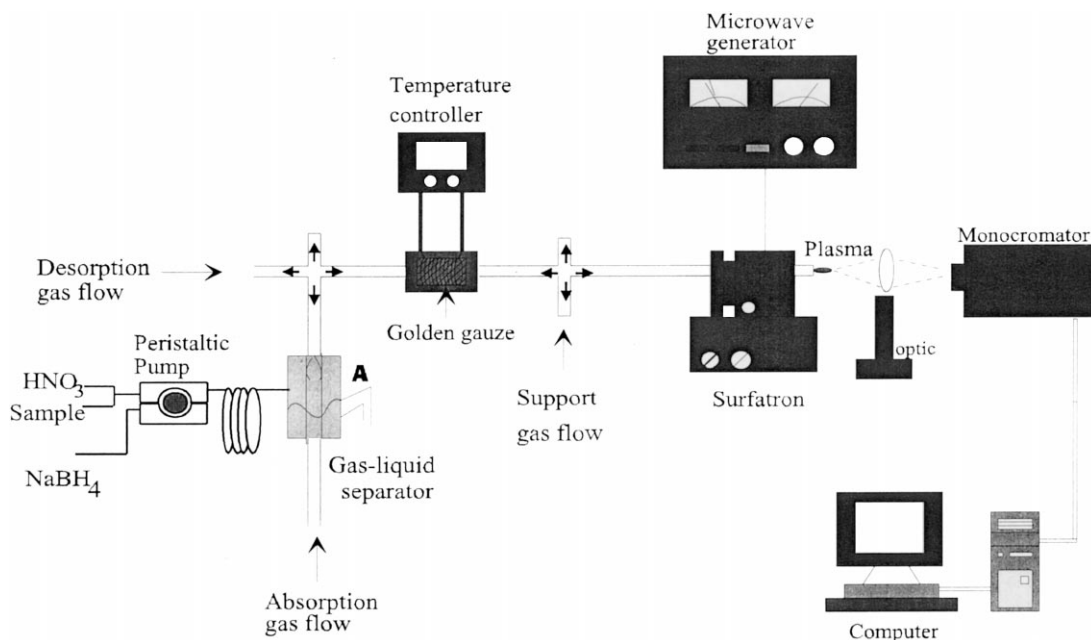


Fig. 1. Schematic diagram of the MIP-AES system.

Table 1
Microwave plasma initial operational conditions

Release gas flow rate (ml min ⁻¹)	75
Amalgamation gas flow rate (ml min ⁻¹)	370
Amalgamation temperature collector Au/Pt (°C)	90
Release temperature collector Au/Pt (°C)	350
Sodium borohydride flow rate (ml min ⁻¹)	2.4
HNO ₃ flow rate (ml min ⁻¹)	3.2
HNO ₃ concentration (% m/v)	3
Sodium borohydride concentration (% m/v)	0.2
Sample introduction flow (ml min ⁻¹)	2.0
Wavelength (nm)	253.65

2.3. Procedure

Mercury determination was done as follows. Standards or samples, HNO₃ 5% solution and NaBH₄ 0.2% solution were carried to the reactor spiral with a peristaltic pump, for 2 min (initial conditions Table 1). The gas mixture produced was carried with argon (adsorption gas) to a sulphuric acid trap, to eliminate water excess that would affect the MIP performance. The dried gas mixture was carried to the gold grid where mercury was amalgamated and the excess of gases is carried away to a mercury trap (safety feature to trap excess of reactive and any mercury that did not react) and then to the atmosphere. The collector was kept at an 80°C temperature at which gold amalgamating occurs, and the plasma was on using helium as plasma gas. After 1 min, argon carrier gas was switched to helium (release gas), and the collector was heated to 350°C to liberate all the amalgamated mercury. The helium carrier gas was allowed to flow to the MIP to introduce the mercury released, and the emission signal recorded. When mercury has been completely vaporized the collector remains at 350°C during 1 min to clean it.

2.4. Reference material treatment

Approximately 0.2 g of standard reference material SRM 2704, was weighed and digested with a mixture of 3.5 ml of HNO₃–HCl (1:3), in a ultra-

sonic-vibrating bath at 60°C for 1 h, then a 2 ml of KMnO₄ 5% (w/v) solution was added and heated for 10 min, followed by the addition of H₂O₂ (1–2 ml). This mixture was diluted with a final volume of 25 ml deionized water.

2.5. Experimental design

A two level full and fractional factorial design was applied to determine the magnitude of the main effect and their interactions. Due to the large number of variables in the whole system (Fig. 1) these were grouped in the different steps of the procedure, plasma conditions (power and plasma gas flow rate), Hg collection and trap (purge gas flow, amalgamation temperature and Hg release temperature) and vapor Hg generation conditions (HNO₃ solution flow rate, NaBH₄ solutions flow rate, HNO₃ concentration, NaBH₄ concentration and reaction carrier gas flow rate).

The signal to background ratio (SBR) was used as a response for the optimization of instrumental parameter of the plasma. This figure of merit is easily obtained and can be correlated to detection limits. SBR used throughout this work was calculated using the following equations. SBR is (Total signal – background)/background. Optimization was accomplished by using a solution containing 12.5 ng ml⁻¹ of Hg. The study was started using the conditions presented in Table 1, and changes were made to the optimized conditions along the work. Estimation of the main effects and their significance were evaluated applying the ANOVA procedure. The optimization was carried out by using the univariate and simplex methods [28].

3. Results and discussion

The initial trials were performed without using the Au/Pt collector, that is feeding the plasma with the vapor mercury generated. However, the excess of hydrogen generated in the reaction produced a very unstable plasma or even extinguished it. The use of Au/Pt collector avoided the presence of hydrogen and water vapor in the plasma.

3.1. Plasma conditions study

A two-level factorial design was applied to study plasma conditions. The effect of the power and plasma gas flow rate on the SBR was carried out to the levels, 140 and 100 W, and 60 and 30 ml min⁻¹ respectively. The analysis of variance showed that both factors were significant on the SBR while their interaction was not significant, both within 99% confidence level.

The estimated effects show that the power has a positive effect on the SBR, which would be expected since the increase of the power increases the energy to excite the analyte. On the other hand, the plasma gas flow rate has a negative effect on the SBR, since it affects the residence time of the analyte in the plasma. A lower flow rate implies longer residence times in the plasma, increasing interactions of the analyte in the plasma and the excitation efficiency. The background was 0.18 mV with a relative S.D of 5% and remained constant during the experiments.

Optimization of the plasma conditions was carried out by using a simplex optimization with a fixed step, starting with the same conditions used for the analysis of variances. The results are shown in Fig. 2. It can be appreciated that a real maximum point was not found. The use of the simplex was limited by the largest power applicable in our generator. Thus, the optimal conditions that can be selected were 170 W and 25.5 ml min⁻¹ of plasma gas flow, but the plasma under these conditions was not stable and led to poorer precision. The next set of conditions was 154.5 W

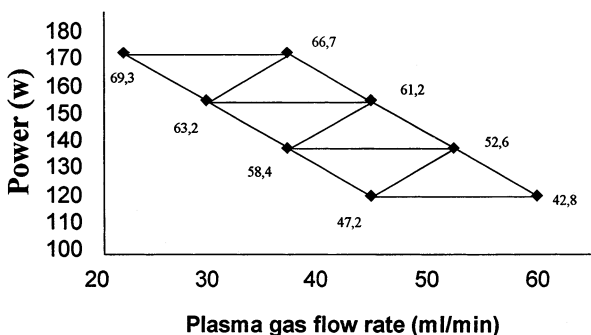


Fig. 2. Simplex optimization of MIP-AES parameters.

and 30 ml min⁻¹ helium flow and was used in the rest of the work.

3.2. Gold collector conditions optimization

The factors that could affect the SBR were the amalgamation temperature, the release temperature, and the plasma gas flow rate. To study of these factors, a two levels factorial design was applied. Interactions of more than two factors were used to evaluate the error. The levels studied for each factor were 100 and 80°C for the amalgamation temperature, 350 and 300°C for the release temperature, 54 and 30 ml min⁻¹ for the plasma gas flow rate. The results of this study showed that the release temperature and second and third order interactions were not significant within the level range used, while amalgamation temperature and carrier gas flow rate were important, within a 99% confidence level. An increase in the carrier gas flow rate produces an enhancement of the SBR. An increase in the amalgamation temperature decreased the SBR. The optimum of the amalgamation temperature was fixed to 80°C, since it considerably decreased the analysis time and interaction factors were not significant. In this case, only the purge gas flow was optimized, therefore, a study of the purge gas flow was carried out between 25 and 85 ml min⁻¹. An increase in the SBR is found when the purge gas flow rate increases up to 55 ml min⁻¹, after which decreases due to the reduction of the residence time of the analyte in the plasma. These results agree with the positive effect that the flow rate found in the factorial design, within the levels used.

3.3. Mercury vapor generation optimization

The experimental design used for this section had five variables, NaBH₄ concentration, HNO₃ concentration, reaction carrier gas flow rate, NaBH₄ solution flow rate, and HNO₃ solution flow rate. A fractionated factorial design was chosen due to the large amount of factors a regular design will involve, a total of 32 experiments. The levels selected were, 1 and 3% v/v for HNO₃ concentration, 0.05 and 0.15% w/v for

NaBH_4 concentration, 300 and 428 ml min^{-1} for reaction carrier gas flow rate, 2.1 and 3.5 for NaBH_4 solution flow rate, and 3.5 and 6.3 for HNO_3 solution flow rate. The estimated effects of individual factors and their interactions shown that the HNO_3 flow rate, adsorption carrier gas flow rate, and the concentration of NaBH_4 were statistically significant within at 99% confidence level. The HNO_3 flow rate had the largest effect and is negative, i.e. the SBR increases when the flow of acid decreases. This effect was expected since the increase in flow of acid increases the rate of the reaction and, therefore, the amount of hydrogen produced. The excess of gas carries away analyte, decreasing the contact of the mercury with the gold collector and decreasing the efficiency of the amalgamating step. The reaction carrier gas flow rate has a positive effect on the signal to SBR. Low flow rates were not sufficient to carry the mercury to the collector.

The NaBH_4 concentration was also a very important factor, with a positive effect in the vapor mercury production. Interaction effects were not significant; therefore, univariate optimization was used for the three main factors.

In order to determine the optimum reaction gas flow rate, the SBR was observed within 300 and 500 ml min^{-1} . The results of this study revealed that the SBR increases with the reaction gas flow rate, reaching a maximum of around 375 ml min^{-1} and then it decreases. This behavior is related to the amalgamating process. When the flow rate is too small, there is an incomplete transport of the vapor produced to the gold collector, while the flow is too large there is not enough contact of the mercury with the collector.

The effect of the nitric acid flow rate was studied between 2.7 and 6.3 ml min^{-1} . The acid amount into reaction loop was an important factor for the mercury reduction; the hydrogen produced from the reaction between the NaBH_4 and the nitric acid reduced the mercury. When large acid flow rates were used an important decrease in the SBR was observed. This may be due to the large amount of hydrogen that was produced in the reaction. The optimum value obtained was 4.4 ml min^{-1} .

The change of the SBR ratio with the NaBH_4 concentration was studied for a range between 0.05 and 0.3% (w/v) reaching a plateau by 0.25% w/v solution, which was used as optimum. After the value, the SBR remained constant, probably because all the mercury was reduced.

3.4. Figures of merit and characteristics of the system

The signal of 20 ng of mercury was recorded during 3 h. The signal remained constant up to 150 min of work. The coefficient of variation for seven determinations was 3%. Then, an important reduction of the signal that was even more dramatic after 3 h of continued use was observed. The continued heating of the gold grid could decrease the efficiency of the amalgamating process, and that could explain the decrease of the signal. Important changes of the plasma characteristics could also be a reason for the loss of sensitivity with time of continued use. Memory effect was found in the system. After each sample or standard an additional step to clean the grid was added to avoid the memory effect. This step consisted in a full run without sample.

The data acquisition system was also prepared in the laboratory. Therefore, the evaluation of the data integration was also performed. The results obtained when 25 ng of mercury was determined, using either peak height or integrated area were 24.8 ± 0.4 and 23.4 ± 0.7 ng, respectively. Results showed no significant differences between both methods of quantification. However, when the peak height was used better precision was obtained. The linear dynamic range obtained is about three orders of magnitude.

The limit of detection was calculated according to Kaiser's definition. It was 56 pg absolute of mercury, using peak area mode while LDs was 5 pg using peak height mode. Considering the use of 4 ml of aqueous samples and 2 min of reaction. The LDs give 14 and 1.3 pg ml^{-1} , respectively. It was possible to determine samples of minor concentration by increasing the reaction time.

Accuracy was also evaluated. A certified standard NIST 2704, atmospheric particulate matter was analyzed. There was obtained a mean concen-

tration of $1.7 \pm 0.2 \mu\text{g g}^{-1}$ (three replicates). The certified values was $1.47 \pm 0.07 \mu\text{g g}^{-1}$. No significant differences at 95% confidence level were found between the certified value and that obtained by using our system.

4. Conclusions

The application of an experimental design permits the optimization of the MIP-AES system with a number of reasonable experiments.

The evaluation of the statistical significance of the main effects and interactions for the case studied allows the best working conditions to be chosen for the determination of mercury by the MIP-AES system proposed.

The combination of a FIS, the NaBH_4 as a reducing agent and a microwave plasma detector showed as a promising tool for the determination of total mercury. Optimization of the system indicated that the SBR was affected by factors in each section of the system, that is the plasma, the amalgamating step and the reduction reaction conditions. The power and the plasma gas flow rate were the most important factors. The increase of the power one and the decrease of the plasma gas flow rate improved the SBR. The NaBH_4 showed as a satisfactory reducing agent. The optimized system showed an important memory effect, that was easily minimized with a NaBH_4 and acid reflux before each sample was run. A linear dynamic range of almost three orders of magnitude was found with a good precision and accuracy. The limit of detection of the method was 14 pg ml^{-1} of mercury, using peak area mode while LDs was 1.3 pg ml^{-1} using peak height mode.

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References

- [1] M. Morita, J. Yoshinaga, J.S. Edmonds, *Pure Appl. Chem.* 70 (1998) 1585.
- [2] W.L. Clevenger, B.W. Smith, J.D. Winefordner, *Crit. Rev. Anal. Chem.* 27 (1997) 1.
- [3] W.R. Hatch, W.L. Ott, *Anal. Chem.* 40 (1968) 2085.
- [4] Z. De-qiang, Y. Li-li, S. Jian-min, S. Han-wen, *Fresenius J. Anal. Chem.* 363 (1999) 359.
- [5] H. Morita, H. Tanaka, S. Smimomura, *Spectrochim. Acta.* 50B (1995) 69.
- [6] A. Shafawi, L. Ebdon, M. Foulkes, P. Stockwell, W. Corns, *Analyst* 124 (1999) 185.
- [7] D.E. Nixon, M.F. Burritt, T.P. Moyer, *Spectrochim. Acta.* 54B (1999) 1141.
- [8] J. Allibone, E. Fatermian, P.J. Walker, *J. Anal. Atom. Spectrom.* 14 (1999) 235.
- [9] S.J. Hill, J.B. Dawson, W.J. Price, I.L. Shuttler, C.M.M. Smith, J.F. Tyson, *J. Anal. Atom. Spectrom.* 13 (1998) 131R.
- [10] B. Welz, M. Schubert-Jacobs, *Fresenius J. Anal. Chem.* 331 (1998) 324.
- [11] B. Welz, M. Melcher, *Atom. Spectrosc.* 5 (1984) 59.
- [12] F.E. Lichte, R.K. Skogerboe, *Anal. Chem.* 44 (1972) 1321.
- [13] R.J. Watling, *Anal. Chim. Acta.* 75 (1975) 281.
- [14] Y. Nojiri, A. Otsuki, K. Fuwa, *Anal. Chem.* 58 (1986) 544.
- [15] Yi X. Duan, X. Du, Q. Jin, *J. Anal. Atom. Spectrom.* 9 (1994) 629.
- [16] E. Bulska, J.A.C. Broekaert, P.T. Schopel, G. Tolg, *Anal. Chim. Acta.* 276 (1993) 377.
- [17] J.F. Camuña-Aguilar, R. Pereira-García, J.E. Sánchez-Uría, A. Sanz-Medel, *Spectrochim. Acta.* 49B (1994) 475.
- [18] J.M. Costa Fernández, R. Pereiro-García, A. Sanz-Medel, N. Bordel-García, *J. Anal. Atom. Spectrom.* 10 (1995) 649.
- [19] M. Okumura, K. Fukushi, S.N. Willie, R.E. Sturgeon, *Fresenius J. Anal. Chem.* 345 (1993) 570.
- [20] A.E. Croslyn, B.W. Smith, J.D. Winefordner, *Crit. Rev. Anal. Chem.* 27 (1997) 199.
- [21] C.I.M. Beenakker, *Spectrochim. Acta.* 31B (1976) 483.
- [22] J. Hubert, M. Moisan, A. Richard, *Spectrochim. Acta.* 33B (1979) 1.
- [23] B. Riviere, J.M. Mermet, D. Deruaz, *J. Anal. Atom. Spectrom.* 3 (1998) 551.
- [24] J. Taffaletti, Y. Savoy, *J. Anal. Chem.* 47 (1975) 2091.
- [25] R. Selby, G.R. Hieftye, *Spectrochim. Acta.* 42B (1979) 285.
- [26] M. Caetano, R. Golding, E. Key, *J. Anal. Atom. Spectrom.* 7 (1992) 1007.
- [27] C. Bayne, I. Rubin, *Practical Experimental Design and Optimization Methods for Chemist*, VCM, Weinheim, 1986.
- [28] C. Linteanu, I. Rica, *Statistical Theory and Methodology of Trace Analysis*, Wiley, New York, 1980.