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STUDY OF ARSENIC DETERMINATION IN SOIL BY SPECTROMETRIC METHODS WITH AND WITHOUT HYDRIDE GENERATION

TIBERIU FRENTIU[1], MICHAELA PONTA[1], NADIA ALEXA[1], GEORGIANA MECULESCU[1], MARIN SENILA[2], BELA ABRAHAM[2], EMIL CORDOS[1]

[1] Babes-Bolyai University, Department of Analytical Chemistry,
Str. Arany Janos 11, 400028 Cluj-Napoca, Romania
[2] Research Institute for Analytical Instrumentation, Str. Donath 67,
400293 Cluj-Napoca, Romania

ABSTRACT. Arsenic determination in soil from residential and industrial area by inductively coupled plasma atomic emission spectrometry (ICP-AES) with and without hydride generation (HG) and hydride generation quartz furnace atomic absorption spectrometry (HG-QF-AAS) was investigated. The used HG device was manufactured at the Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania. ICP-AES with direct liquid sample nebulization (limit of quantitation, LOQ 25 mg Kg^{-1}) was suitable for As determination in contaminated soil, while HG-ICP-AES, five times more sensitive, allowed As determination in soil from both contaminated and non-contaminated area. According to the t-Test, ICP-AES and HG-ICP-AES gave similar As contents only in contaminated soils, while HG-ICP-AES and HG-QF-AAS gave similar As contents for all the analyzed samples. HG-ICP-AES and HG-QF-AAS furnished the same LOQ for As (5 mg Kg^{-1}). The determination of As in a reference soil sample (5 replicates) proved both in HG-ICP-AES and HG-QF-AAS good precision (RSD 11.6%; 11.0%) and recovery degree (102.5±11.9 %; 101.2±11.2 %).

INTRODUCTION

Arsenic is an ubiquitous natural element in environment and is known to be carcinogenic for humans [1]. Natural causes such as land erosion, volcanism, or anthropogenic activities as mining, smelting, glass manufacturing, pharmaceutical industry, electronics, pesticides favor high inputs of As in each of the environmental compartments [2]. Arsenic is present in almost all soils but when its concentration exceeds 5 mg Kg^{-1} it represents a human health risk [2,3]. As the arsenic species have different properties that influence bioavailability, the speciation of As in soil samples is necessary for toxicological and environmental assessment. The determination of the total As is always necessary and offers useful primary information about the As level in soil.

The most common methods for the determination of As in soil are atomic absorption spectroscopy (AAS) [4], atomic fluorescence spectroscopy (AFS) [5, 6], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [7] or inductively coupled plasma mass spectrometry (ICP- MS) [3]. Coupling these techniques with a hydride generation system (HG) to generate volatile arsine is the common step to improve sensitivity of As determination [8] at very low concentration.

The aim of this paper was to study the possibility to determine As in soil in industrial and residential area by ICP-AES, HG-ICP-AES and HG-QF-AAS and to investigate the suitability to use the hydride generator manufactured at the *Research*

Institute for Analytical Instrumentation, Cluj- Napoca, Romania, in the derivatisation step. Data for As obtained by HG-ICP-AES were compared with those resulted in ICP-AES and hydride generation quartz furnace atomic absorption spectrometry (HG-QF-AAS), respectively.

The accuracy of the total arsenic determination was tested by analyzing a House Reference Material of soil (HRM2, Imperial College, UK).

Samples were collected in the town of Baia-Mare, North Romania, known as having a significant pollution with heavy metals such as Cu, Pb and Zn as well as traces of Cd and As [9, 10]. The town of Baia-Mare is the site of two major companies (Romplumb Co. and Phoenix Co.) to process ores containing Fe, Cu, Pb and Zn supplied by mining companies in the area. Ores contain also sulfoarsenides, which are converted by roasting into As_2O_3. Although the resulted sulphurous gases are purified during the chemical process using electrical filters and washing with H_2SO_4, the residual gases still contain both traces of heavy metals and arsenic species soluble or insoluble in water. Thus airborne particulate matter deposits and consequently contaminates the soil with heavy metals and arsenic compounds.

EXPERIMENTAL

Apparatus

A SPECTROFLAME (SPECTRO, Germany) atomic emission spectrometer coupled or not with a hydride generator manufactured at the *Research Institute for Analytical Instrumentation* (ICIA)*, Cluj-Napoca, Romania,* and a Perkin-Elmer model 5000 atomic absorption spectrometer coupled with the same hydride generator were employed.

The SPECTROFLAME (SPECTRO, Germany) atomic emission spectrometer consists of a free-running plasma generator (27.12 MHz, 1200 W), a plasma torch viewed in radial direction and a double scanning monochromator for UV (160 – 336 nm) and Vis (335 – 800 nm) ranges, respectively. The monochromator used in the UV range is filled with high purity nitrogen quality. The sample is aspirated into the plasma by a two-channel peristaltic pump and nebulized using a Meinhardt nebulizer type and double pass Scott type chamber mounted in thermostated room. The emission signal is detected by a Thorn EMI 9781 R photomultiplier. Experimental data are processed using the *Smart Analyzer* soft. Details about characteristics and operating conditions for the SPECTROFLAME scanning spectrometer are given in Table 1.

The atomic absorption spectrometer (Perkin-Elmer-5000) was equipped with a quartz atomizer cell (170 mm length, 12 mm i.d.) built at the *Research Institute for Analytical Instrumentation*, Cluj-Napoca, Romania. The atomizer was heated at controlled temperature ($900\pm10^{o}C$) by a 700 W power supply using a Nichrome resistance heater. An arsenic hollow cathode lamp (S.&J. Juniper, Harlow, UK) operated at 12 mA was used as radiation source in AAS. The operating conditions for the Perkin-Elmer 5000 Spectrometer are shown in Table 2.

The AsH_3 generated in the HG device is separated in a gas-liquid separator and carried out by an Ar flow into the plasma or quartz atomizer cell where the atomization takes place. The absorbance of As is measured 60 s after the sample introduction in the hydride generator.

Table 1

Instrumentation and operating conditions for the SPECTROFLAME ICP-AES.

Equipment	Characteristics
Generator	Free – running 27.12 MHz, manually controlled power between 750 – 1400 W, operating power 1200 W.
Plasma torch	Water-cooled copper induction coil inductively coupled plasma. The torch is viewed in radial direction. Argon flow rates: - Outer gas 12 L min^{-1}. - Intermediate gas 1 L min^{-1}. - Nebulizer gas 1 L min^{-1}.
Torch cooler system	Recirculation of cooling water without automated control of the temperature.
Sample introduction system	2 channel peristaltic pump, 2 mL min^{-1} solution intake, concentric nebulizer Meinhardt type K (TR-30-K3), double pass Scott type spray chamber mounted in a thermo stated room controlled by the computer.
Optics	Scanning spectrometer with a double monochromator. UV range 160 – 336 nm filled with high purity nitrogen quality, grating with 3600 lines mm^{-1}, focal length 750 mm, thermostated at 15 ± 0.5 ^{0}C, entrance slit width 15 µm. Vis range 335 – 800 nm, grating with 2400 lines mm^{-1}, focal length 750 mm, thermostated at 15 ± 0.5 ^{0}C, 8 entrance slits, one for each optic fiber with a width of 10 µm. Plasma viewing through an optical fiber for the UV range and 8 optical fibers for the Vis range, respectively. Optical detector: 9781 R photomultiplier powered at 1000 V (Thorn EMI, Ruislip, Middlesex, Great Britain). Wavelength: As 193.7 nm
Data processing	Soft: Smart Analyzer, Pentium III CPU 450 MHz (SPECTRO, Kleve, Germany).

Table 2

Operating conditions for Perkin-Elmer 5000 atomic absorption spectrometer

Parameter	Conditions
Hollow cathode lamp current	12 mA
Calibration type	peak height
Measurement time	10 s
Wavelength	As 193.7 nm
Spectral band width	0.5 nm
Background correction	No

The hydride generator is equipped with a three-channel peristaltic pump, tygon tubing and a reaction coil connected to a gas-liquid separator.

The operating conditions for the HG both in HG-ICP- AES and HG-QF-AAS are summarized in the Table 3.

Table 3.

Operating conditions for the hydride generator

Parameter	Conditions
Sample flow rate/ mL min^{-1}	8
HCl carrier flow rate/ mL min^{-1}	1
$NaBH_4$ carrier flow rate/ mL min^{-1}	1
Ar carrier flow rate/ mL min^{-1}	100

The flow-rates of the reagents and sample can be adjusted either by changing the inner diameter of the tygon tubes or the rotation speed of the peristaltic pump. Thus, to achieve flow-rates of 8 mL min^{-1} for the sample and 1 mL min^{-1} for the reagents tygon tubes with inner diameters of 2.29 mm and 0.76 mm respectively, were used. The working principle of the gas-liquid separator for QF-AAS and ICP-AES are presented in fig. 1. In the QF-AAS technique, after separation of the residual liquid, the Ar stream containing arsine was introduced in the quartz furnace at a flow-rate of 100 mL min^{-1}. In ICP-AES technique, the gas flow leaving the gas-liquid separator was mixed with an additional Ar stream of 1 mL min^{-1} and introduced into the plasma.

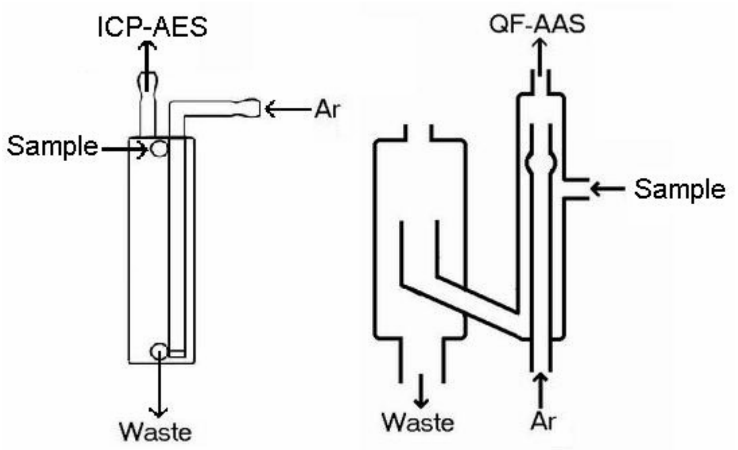

Fig.1 *The gas-liquid separators*

The experimental set-up of the HG-ICP-AES and HG-QF-AAS is shown in fig. 2.

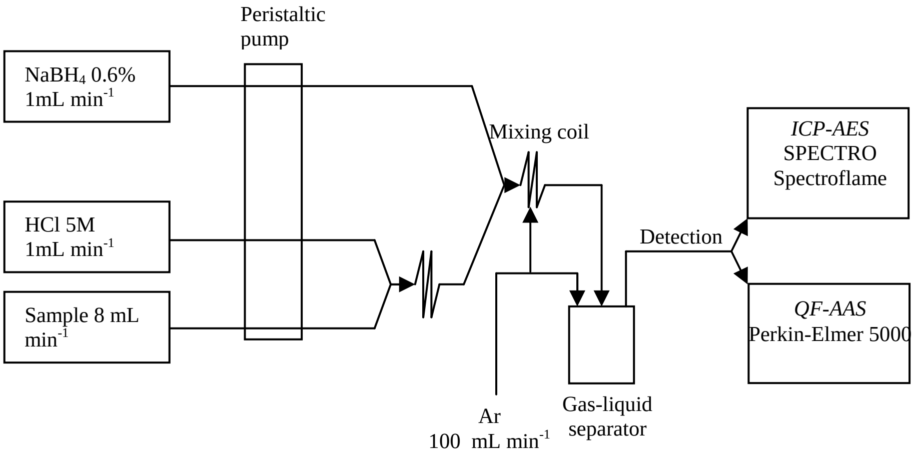

Fig. 2. *Experimental set-up of HG-ICP-AES and HG-QF-AAS for As determination*

Reagents and standard solutions

All solutions were prepared using analytical-reagent grade chemicals (Fluka-Germany) and distilled water.

A 1000 mg L^{-1} stock solution of As^{3+} was prepared by dissolving 0.1320 g of As_2O_3 in 2.5 mL 20% NaOH, followed by neutralization with 32% HCl using phenolphthalein as indicator. The final volume of 100 mL was adjusted with 1M HCl. This stock solution was used to prepare stock solution of 100 mg L^{-1} As^{3+} and of 1 mg L^{-1} As^{3+}.

A 5M stock solution of HCl was prepared by dilution of 32% HCl at appropriate volume with distilled water. This solution was used as carrier fluid to the hydride generator.

A 0.6% stock solution of $NaBH_4$ was prepared by dissolving 0.6 g of $NaBH_4$ and 0.5 g of NaOH in 100 mL of water. This solution was used for hydride generation as reducing agent.

A 10% stock solution of KI was prepared by dissolving 10 g of KI in 100 mL of distilled water and was used to pre-reduce As^{5+} to As^{3+} in 1M HCl medium.

A saturated solution of $Mg(NO_3)_2$ was prepared to extract As from soil samples.

Calibration curves for As determination were plotted in the ranges of 0-10 mg L^{-1} (ICP-AES), 0-50 μg L^{-1} (HG-ICP-AES) and 0-10 μg L^{-1} (HG-QF-AAS). The pre-reduction of As^{5+} to As^{3+} was carried out using 10 % KI and 10 M HCl, then the reduction to arsine occurred in the operating conditions shown in Table 3.

Methodology for the determination of arsenic in soil

Soil samples from both industrial and residential zones in the Baia-Mare town were collected from 5 cm depth. The samples were dried slowly at room temperature, then in an oven at 60^oC for 12 hours. The soil was milled and sieved and the fraction less than 200 μm was kept in brown bottles with stoppers till analysis.

Amounts of 0.25 g of soil were weighed in beakers and volumes of 1 mL of saturated $Mg(NO_3)_2$ solution were added. Beakers were gently shaken and heated for 12 hours in a furnace at maximum 400^oC. After 12 hours the beakers were cooled at room temperature and volumes of 5 mL of 10M HCl were added. The beakers were shaken overnight, then the contents were diluted to 100 mL with distilled water and filtered. The solutions were kept in plastic bottles before analysis.

By ICP-AES, As was determined after direct nebulization of the sample solutions into the plasma. To determine As by HG-ICP-AES or HG-QF-AAS, a pre-reduction step of As^{5+} to As^{3+} was necessary prior to hydride generation. Thus, an appropriate aliquot volume of the previous solution was transferred in a volumetric flask and followed the pre-reduction treatment with 10 mL of 10M HCl and 10 mL of 10% KI, then was put in a boiling water bath (80 ^oC) for 1 hour. The solution was cooled down to room temperature and diluted with distilled water to 50 mL. The aliquot volume of the sample to be pre-reduced and diluted was chosen so that the final As content to fall within the calibration range of the HG method. The reduction to arsine occurred in the operating conditions presented in Table 3.

RESULTS AND DISCUSSIONS

Calibration characteristics. The characteristics of the calibration curves for As in ICP-AES with direct nebulization, HG- ICP-AES and HG-QF-AAS are presented in Table 4.

Table 4

Characteristics of calibration curves for As determination by ICP-AES, HG-ICP-AES and HG-QF-AAS

Technique	Calibration range	Slope (m)	RSD of slope (%)	Correlation coefficient (R)
ICP-AES	0 – 10 mg L^{-1}	4406 a.u.*/ mg L^{-1}	11.50	1
HG-ICP-AES	0 – 50 μg L^{-1}	45164 a.u.*/ mg L^{-1}	3.30	1
HG-QF-AAS	0 – 10 μg L^{-1}	0.026 A^{**}/ mg L^{-1}	5.20	0.9999

* *arbitrary units* ** *absorbance units*

According to data in Table 4, the slope of the calibration curve in HG-ICP-AES is one order of magnitude higher than that in ICP-AES, which means a better sensitivity when a reducing stage is present. No comparison is possible between calibration characteristics of AES and AAS because the calculated parameters have different relative values. As the standard deviations of slopes show, the techniques based on hydride derivatisation are more precise (lower RSDs) compared to ICP-AES with direct introduction of the liquid sample into the plasma and offer a better stability of the signal in As determination. On the other hand, RSDs of the calibration slopes in HG-ICP-AES and HG-QF-AAS (3.3 % ; 5.2 %) are close and provide good precision. The values of 1 or almost 1 for the correlation coefficients of all three calibration curves proved good linear dynamic range and good precision in all three techniques.

Limit of detection (LOD) and limit of quantitation (LOQ) for As in soil samples

LOD and LOQ for As determination by ICP-AES, HG-ICP-AES and HG-QF-AAS are presented in Table 5. The LODs for HG-ICP-AES and HG-QF-AAS expressed as mg Kg^{-1} soil were calculated taking into account the dilution factor and the weight of soil sample. The LOQ was considered to be five times the LOD.

Table 5

Limit of detection and quantitation for As in soil

Technique	LOD/ μg L^{-1}	LOD/ mg Kg^{-1}	LOQ/ mg Kg^{-1}
ICP-AES	12*	5	25
HG-ICP-AES	0.2*	1	5
HG-QF-AAS	0.2**	1	5

* *calculated as 3 σ_b (standard deviation of background)/m (slope of calibration) [11]*
** *mass characteristic calculated as 0.004343/m*

According to data in Table 5, the detection limit of As in ICP-AES with direct liquid sample nebulization (5 mg Kg^{-1}) is five times higher than that when a hydride generation device is coupled with either ICP-AES or AAS (1 mg Kg^{-1}). The improvement of LOD by applying the derivatization to arsine is the result of both excellent sample introduction efficiency and matrix removal. Thus, considering the 100% sample introduction efficiency and the sample flow rate of 8 mL min^{-1} in the HG technique compared to cca. 5 % and 2 mL min^{-1} respectively, in the direct nebulisation, the amount of analyte reaching the plasma in the derivatisation procedure is higher at least two orders of magnitude. On the other hand, the matrix separation when HG is used eliminates interference in plasma.

Corroborating the LOQs with the recommended maximum As contents in different types of soil (Table 6), one can say that ICP-AES (LOQ 25 mg Kg^{-1}) is not appropriate to determine As in non-contaminated soil (≤ 5 mg Kg^{-1}), but only in contaminated soil containing more than 25 mg Kg^{-1}. For this kind of samples ICP-AES seems to be sensitive enough to quantitate As with at least 10 % precision.

The determination of As is soil in the range 5 mg Kg^{-1} (normal value) – 25 mg Kg^{-1} (alert value, insensitive soil; action trigger value, sensitive soil) can be carried out only if As is reduced to arsine prior the detection by ICP-AES or AAS (LOQ 5 mg Kg^{-1}).

Arsenic determination in soil

Six soil samples collected in the town of Baia-Mare from industrial (S1, S2) and residential area (S3-S6) were prepared according to the methodology described above and As was determined by ICP-AES with direct nebulisation, HG-ICP-AES and HG-QF-AAS, respectively. The mean results (3 successive measurements) are shown in Table 7. In order to compare the results the *t* Test was used and a confidence level of 95% was considered [11].

Table 6

Recommended maximum As level in different type of soils according to Romanian Guideline [12]

mg Kg^{-1}	Normal value	Alert values		Action trigger values	
		Sensitive soil*	Insensitive soil**	Sensitive soil*	Insensitive soil**
	5	15	25	25	50

* *residential and agricultural zones*
** *industrial and commercial zones*

Table 7

Comparative results for As determination in soil with and without hydride generation (n=3)

Sample	ICP-AES	HG-ICP-AES	HG-QF-AAS	t_{calc}	t_{calc}	t_{tab}
	mg Kg^{-1} (mean±s*)			ICP-AES/ HG-ICP-AES	HG-ICP-AES/ HG-AAS	(P=0.05 ν=4)
S1	1578±28	1653±39	1740±72	2.70	1.84	2.78
S2	1631±10	1578±53	1723±69	1.70	2.72	
S3	--	10.0±.0.9	11.8±0.8	-	2.59	
S4	8.0±7.0	35.0±2.7	33.0±2.0	**6.23**	0.98	
S5	93±11	109±7	110±7	2.12	0.17	
S6	44.0±3.0	110±6	98.0±5.0	**17.04**	2.66	

* *standard deviation*

Comparison of results for As determination in soil by ICP-AES and HG-ICP-AES

Adopting the null hypothesis there is no significant difference between the As mean content determined by the two methods for a confidence level of 95% when t_{calc}(ICP-AES/HG-ICP-AES) is lower than t_{tab} for the corresponding number of degrees of freedom. As seen in Table 7, the null hypothesis is retained in three cases out of six (S1, S2, S5) and is rejected in two cases (S4, S6), as there is a significant difference between As contents found by ICP-AES and by HG-ICP-AES. In addition, in the case of two samples (S3, S4) with As levels below or slightly above the LOQ in ICP-AES (25 mg Kg^{-1}), As could not be determined (S3) or the error was almost 100% (S4). Results obtained by HG-ICP-AES were always higher compared to those obtained by direct nebulisation (systematic negative error) due probably to the depressive effect of the high Mg content in the sample on As emission. Thus, in accordance with the previous findings, As can be determined by ICP-AES with good precision only in contaminated soils.

Comparison of results for As determination in soil by HG-QF-AAS and HG-ICP-AES

The *t*-Test shows that there is no significant difference for a 95% confidence level between HG-ICP-AES and HG-AAS in the As determination in six soil samples encompassing a wide concentration range, as $t_{calc} < t_{tab}$ (Table 7). LOD of As in soil is 5 mg Kg^{-1} in both techniques and, consequently, the alert value for sensitive zones (15 mg Kg^{-1}) can be detected by HG-ICP-AES/HG-AAS using the hydride generator.

Accuracy of HG-ICP-AES and HG-QF-AAS

The accuracy of arsenic determination by HG-ICP-AES and HG-QF-AAS was tested by determining the total arsenic content in a soil House Reference Material (HRM2, Imperial College, UK). The average values found for the total arsenic content and their 1s uncertainties (5 replicates) compared to the certified value are shown in Table 8.

The good recovery of As in the reference material proves that the used methodology in sampling preparation and the analysis techniques are proper to determine As in soil with good performance.

Table 8

Analysis of soil reference material

Reference material	Certified		Found			
			HG-QF-AAS		HG-ICP-AES	
	Mean ± s μg g^{-1}	n*	Mean ± s μg g^{-1}	n*	Mean ± s μg g^{-1}	n*
HRM2	153.3± 14.9	151	155.2±17.1	5	157.1 ± 18.3	5

** number of measurements*

RSD/ %	11.0	11.6
Recovery/ %	101.2±11.2	102.5±11.9

CONCLUSIONS

The comparison of ICP-AES, HG-ICP-AES and HQ-QF-AAS performance for As determination in soil has shown that ICP-AES allows an accurate As determination only in contaminated soils according to Romanian Guideline. For the analysis of polluted soils no hydride generation is necessary. When a derivatization stage using HG is introduced prior to detection by either AES or AAS, As could be determined in both non-contaminated and contaminated soils as the limit of quantitation improves five times compared to the non-derivatised ICP-AES. The tested hydride generator has good analytical performance that allows the determination of As in soil with good precision and accuracy.

REFERENCES

1. V. Cappuyns, S. Van Herreweghe, R. Swennen, R. Ottenburgs, J. Deckers; *The Science of the total Environment*, 2002, **295**, 217-240
2. D.Lievremont, M.-A. N'negue, Ph. Behra, M.,-C. Lett, *Chemosphere*, 2003, **51**, 419-428
3. R. Pongratz, *The Science of the Total Environment*, 1998, **224**, 133-141
4. A. Marin, A. Lopez-Gonzalvez, C. Barbas, *Analytica Chimica Acta*, 2001, **442**, 305-318
5. S. Garcia-Manyes, G. Jimenez, A. Padro, R. Rubio, G. Rauret, *Talanta*, 2002, **58**, 97-109
6. M. Vergara Gallardo, Y. Bohari, A. Astruc, M. Potin-Gautier, M. Astruc, *Analytica Chimica Acta*, 2001, **441**, 257-268
7. C.F. Balasoiu, G. J. Zagury, L. Deschenes, *The Science of the Total Environment*, 2001, **280**, 239-255
8. L. Cifuentes, G. Crisostomo, J. P. Ibanez, J. M. Casas, F. Alvarez, G. Cifuentes, *Journal of Membrane Science*, 2002, **207**, 1-16
9. E.A. Cordos, T. Frentiu, A.M. Rusu, G. Vatca, *Analyst*, 1995, **120**, 725.
10. T. Frentiu, M. Ponta, A. Rusu, S.D. Anghel, A. Simon, E.A. Cordos, *Anaytical. Letters*, 2000, **33**, 323.
11. J.C. Miller, J.N. Miller, Statistics for Analytical Chemistry. Ellis Horwood Limited, Chichester, 2 nd edn., 1988, p. 53-62 and 120-124.
12. Monitorul Oficial, 303/bis/06.11.1997