ARSENIC DISTRIBUTION IN ARSENIC RICH AUSTRIAN SOILS

Dejene A. Tessema[1] and Walter Kosmus[2]

[1]Institute of Chemistry, Analytical Chemistry,
Karl-Franzens-University,Universitatplatz 1,
A-8010 Graz, Austria
e-mail: dejeneayele@hotmail.com

[2]Institute of Chemistry, Analytical Chemistry,
Karl-Franzens-University,Universitatplatz 1,
A-8010 Graz, Austria
e-mail: walter.kosmus@kfunigraz.ac.at

Abstract

Arsenic rich soil was collected from Gasen, a village in south eastern Austria which lies along the Strassegg electrum-arsenopyrite vein-type mineralization, and a portion of this soil was flooded in a small lysimeter. Sequential leach experiment has been conducted on the two month flooded soil (FLS) and on the `field received´ soil (FRS) in order to investigate the variation in the distribution of arsenic among the various soil fractions with a change in the soil Eh and pH. The uptake of arsenic by plants grown on the soil (*Dactylis glomerata, Anthoxantum odoratum, Plantago lanceolata* and *Tataxacum officinale*) has also been evaluated by collecting samples from various spots and determining the total arsenic content .

The data indicated that in spite of the high level (~ 3000 ppm) of arsenic in Gasen it was tightly bound to the soil and not amenable to dissolution as evidenced by the necessity of stronger extractants to remove the greater proportion of the element. At the end of a two month flooding period, the Eh of the soil was observed to decrease to -14 mV from an initial value of 313 mV and the pH increased from 5.01 to 6.40. This lowering in the Eh and the increase in the pH caused an increase in the level of arsenic in the soil water of the FLS about 45 fold than in the soil water collected from the FRS. The water soluble and exchangeable forms in the FRS, generally considered to be the most mobile and immediately bio-available, accounted for only about 0.5% of the total arsenic.

The total arsenic level in the plant samples was observed to be comparatively low. The mean value was 1.7 mg kg^{-1} and the highest values were in the 3 mg kg^{-1} range; where this accounted for 9% of the overall determinations. The level of arsenic in samples collected along the mineralization vein, where the soil arsenic content is high, was relatively lower than in samples collected away from the vein. Moreover, there was no observable toxic effect on the plants grown in the area.

Introduction

Arsenic is a commonly occurring toxic metal in natural ecosystems. It presents potentially serious environmental problems throughout the world (1,2). Natural levels of arsenic in soils generally averages less than 10 mg/kg of the element, but soils close to or derived from sulfide ore deposits may contain up to 8000 mg of As/kg (3). Arsenic in soil may originate from the parent materials that form the soil and from industrial waste discharges or agricultural use of arsenical pesticides.

Gasen, a village in south eastern Austria, lies along the Strassegg electrum-arsenopyrite vein-type mineralization. It is located 50 km north-east of Graz. Arsenopyrite is the most common mineral in the veins. The soil in the area has high soil arsenic level ranging 2000 – 4000 mg/kg. Inspite of the high arsenic level in the soil, the concentration in the soil-water is not high (~ 150 ppb). It was also observed that the level of arsenic in the soil water is relatively higher in spring than in the other seasons of the year. The observed low level of arsenic in the soil water indicates that it is strongly bound to the soil and is less amenable to dissolution. Arsenic retention in soils is related to the content of Fe and Al oxides, exchangeable Ca, and the type and content of clay in the soil (4). To understand the reasons for the high arsenic retention, evaluation of the level of As bound to different bonding modes in the soil matrix is required.

Selective dissolution techniques are currently of renewed interest in environmental studies to understand species distribution patterns of various toxic metals (5). The identification of the main binding sites of trace metals in surfacial media allows one to predict the potential for remobilization, to determine the bioavailability of an element and to discriminate between sources (*e.g.*, atmospheric deposition *versus* hydromorphic transport *versus* clastic dispersion). Probably the most significant work in speciation of arsenic in a soil has been done by Takamatsu *et al* (6). By use of high performance liquid chromatography anion exchange and an extraction process using 1 *M* hydrochloric acid, the so-called bio-available portion of the arsenic was speciated. Published scheme, for the sequential extraction of elements associated with different phases, which is applied mostly in environmental studies is that of Tessier *et al.* (7).

The method of sequential extraction has been applied in this study to compare the distribution of arsenic between the various fractions in the FLS and the FRS with a change in Eh and pH and give a possible explanation for the strong arsenic retention and the rise in the level of arsenic in the soil water during spring. To confirm the accuracy of results, the same procedure was applied with SRM 2709, 2710, and 2711. A mixture of the grass samples was collected from the area and total arsenic level has also been investigated in order to assess the availability of arsenic.

Experimental

***Reagents and solutions*:** Ultrapure water purified by Milli Q+ system was used throughout. Standard solutions each having a concentration of 1000 mg L^{-1}: Titrisol®, Merck, for As, Titrisol®, Merck, Art. 9972 for Fe; Merck, Art. 19770 for Al; and Titrisol®, Merck, Art. 9988 for Mn were used to prepare working standard solutions. All the leaches were performed in 50 mL centrifuge tubes with a double seal cap (IWAKI, Japan).

Chemicals used for the sequential leach were: Ammonium acetate, CH_3COONH_4, (Fluka, p.a., 09690) Sodium acetate, $CH_3COONa.3H_2O$, (Merck, p.a., 494867); Acetic acid, CH_3COOH, (Merck, 81958); Hydroxylamine hydrochloride, $HONH_3Cl$ (Merck, p.a., 4616); Ammonium oxalate, $(COONH_4)_2.2H_2O$, (Fluka, p.a., 270389); Oxalic acid, $C_2H_2O_4.2H_2O$, (Merck, Suprapur®, 489)

Hydrogen peroxide, H_2O_2, 30% (w/w) (Merck, suprapur), Hydrofluoric acid, HF, 40% (w/w) (Merck, suprapur, 862935), and concentrated (65% (w/w)) nitric acid, HNO_3, (Merck, p.a., 23662256) which was purified in a duoPUR sub-boiling quartz distillation unit (Millstone Laboratory Systems, Leutkirch, Germany) were used for the digestion of soil and plant samples.

***Instrumentation and operating conditions*:** A Zeeman-effect simultaneous multi-element GF-AAS (Hitachi Z-9000) was utilized for the determination of total aluminum, iron, and manganese, in the soil extracts. Argon gas (99.999%, Messer Griesheim, Austria), was used as a carrier and sheath gas. Uncoated graphite cuvette of highest purity (Hitachi Ltd. Tokyo Japan) was used for atomization. The light sources were Hollow Cathod Lamps from Cathodeon Ltd. (Cambridge, UK). The signals for Al, Fe, and Mn were monitored at 309.4, 248.3 and 279.5 nm wavelengths respectively. For all the elements a 20 µL portion of sample solution was injected into the graphite cup. Operating temperature programs were optimized for all the elements before measurement.

A Hitachi Z-6100 Polarized Zeeman AAS fitted with an electrically heated quartz cell (at 800^{o}C) for atomization was used for the determination of As at 193.7 nm wavelength by the HG-quartz tube AAS (HG-QTAAS) technique. A computer controlled Perkin-Elmer FIAS 400 Flow Injection system coupled with a Perkin-Elmer AS-90 Autosampler was employed for the continuous supply of carrier acid and borohydride solution and, for the injection of sample solutions. Arsenic Hollow Cathod Lamp (type 3QNY) Cathodeon Ltd. (Cambridge, UK), was used as the monochromatic light source. A conventional gas-liquid separator was employed. The specific operating parameters for the HG-QTAAS determination of arsenic are given in Table 1.

Table 1 Instrumental parameters for the analysis of As using HG-AAS

Parameter	Value
Wavelength	193.7 nm
Lamp type	Cathodeon Ltd. Cambridge, UK, max. current 12 mA
Lamp current	9 mA
Sample loop	500 µL
Measurement mode	Peak-area
FIAS fill time	10 sec.
FIAS injection time	15 sec
Reductant concentration	0.08 M $NaBH_4$ in 0.04 M NaOH
Carrier HCl concentration	2 M
Cell temperature	800 ^{o}C
Carrier flow rate	10 mL/min
Reductant flow rate	5 mL/min.
Slit width	1.3 nm
Argon flow rate	16 mL/min

***Soil Flooding** :* A portion of the arsenic rich soil collected from Gasen was flooded in a small lysimeter having 450 cm^2 surface area and 15 cm depth. After a two month flooding period an aliquot from the FLS and about the same quantity from the FRS were transferred into separate clean watch glasses. The samples were freeze dried on a Christ, Alpha 1-4, type 100400, GmbH freeze drier. The dry soil samples were ground mildly in a mortar and passed through a 2 mm mesh sieve. One gram aliquot of each sample was transferred into a centrifuge tube for the sequential extraction analysis. All extraction steps were conducted in triplicates.

***Soil pH and Redox derermination**:* The pH and redox status of the FRS was determined before the leaching procedure. The pH ($CaCl_2$) and pH (H_2O) measurements were conducted according the procedures given by Hendershot W. H, Duquette M (8, 9) respectively by using an Orion pH electrode and meter (Orion Model SA 720). The redox potential measurement was conducted directly (1:1 soil/water) on the same meter by using a platinum electrode in combination with a calomel reference electrode. The pH and redox potential changes of the flooded soil were monitored in one week interval until the time of sampling.

Sequential leach procedure

***Water soluble phase**:* To 1g of each sample in a 50 mL screw-cup centrifuge tube, 10 mL of ultrapure water was added and shaken overnight (~ 14 h) on an end-over-end shaker. The resulting mixture

was centrifuged on a Jouan B3.11 centrifuge at 3000 rpm for 15 min. The supernatant solution was decanted and filtered through a Black-ribon S&S filter paper.

Exchangeable:To the residue from above 20 mL of 1M ammonium acetate, pH 7, was added and shaken for 5 h at 20 ^{0}C. The resulting mixture was centrifuged and filtered.

Bound to carbonates: To the residue from above 20 mL of 1 M sodium acetate was added and the pH was adjusted to 5 by using conc. acetic acid. The mixture was shaken for 5 h, centrifuged and filtered.

Amorphous Fe-oxide phase: To the residue from above, 20 mL of 0.25 *M* hydroxylamine hydrochloride in 0.05 *M* HCl, was added. The tube was cupped and vortexed for about 10 s. The contents were then placed in a water-bath at 60^{o}C for 2 h with the cup loosened. Every 30 min the cup was tightened and the contents were vortexed. The resulting mixture was centrifuged at 3000 rpm for 10 min and the supernatant liquid was decanted into a labeled test-tube. The residue was rinsed with 5 mL of water, vortexed, centrifuged and the supernatant rinse added to the test-tube. This step was repeated twice and the volume was made to 30 mL.

Crystalline Fe-oxide phase: To the residue from above, 30 mL of 1.0 *M* hydroxylamine hydrochloride solution in 25% acetic acid was added. The tube was cupped and vortexed for about 10 s. The contents of the tube were placed in a water bath at 90 ^{o}C for 3 h with the cup on tightly. The hot mixture was vortexed for 20 min on an end-over-end shaker and then centrifuged for 10 min at 3000 rpm, the supernatant decanted into a labeled test-tube. The residue was rinsed with 10 mL of 25 % acetic acid , vortexed and centrifuged. This step was repeated twice and the supernatant rinses were added to the test-tube. The volume of the extract was finally made to 50 mL.

A second leach of the residue was conducted by heating for 1.5 h instead of 3.

Organics and sulfides phase: To the residue from above, 750 mg of $KClO_3$ and 5 mL of 12 *M* HCl was added. The tube was cupped and vortexed with care as frothing can occur. A further 10 mL of HCl was added, vortexed for 10 s and allowed to stand for 30 min. Then 15 mL of water was added, the tube cuped, the solution vortexed for 10 s, centrifuged for 10 min, the supernatant decanted into a labeled test-tube.

To the residue, 10 mL of 4 *M* HNO_3 was added, cuped and vortexed. The resulting mixture was placed in a water-bath at 90 ^{o}C for 20 min. After digestion, the contents were transferred to a Teflon pressure tube, vortexed and centrifuged for 10 min. The resulting mixture was decanted and the supernatant liquid into the previous test-tube (*i.e.*, mix the KClO3 -HCl extractant with the present HNO3 leachate).

The residue was further rinsed with 5 mL of water, vortexed and centrifuged. This was done twice and the supernatant rinses were added to the test-tube. The final solution was made to 50 mL volume and made ready for analysis.

Silicates and residual oxides phase: To the residue from above, 2 mL of 16 *M* HNO_3 was added and placed on a hot-plate at 200 ^{o}C until the volume reduced to about 0.5 mL. The resulting digest was allowed to cool and heated for 20 min in a water bath at 90 ^{o}C after the addition of 2 mL of 12 *M* HCl. This was cooled, 10 mL of the acid mixture (all concentrated) [HF (5 mL), $HClO_4$ (3 mL), and HNO_3 (3 mL)] added, the cup tightly cuped and heated for 1 h at 90 ^{o}C in a water-bath. The contents were then transferred to a Teflon beaker, rinsing with water for complete transfer and evaporated at about 70 ^{o}C overnight and then raising the temperature to 120 ^{o}C to achieve incipient dryness. Finally 1 mL of 12 M HCl and 3 mL of 16 M HNO3 was added , the solution swirled and 3 mL of water added and warmed gently for about 10 min. The contents were then transferred to a calibrated test-tube with rinsing and the final solution made to 20 mL.

Plant sample collection and analysis: A mixture of grass samples *(Dactylis glomerata, Anthoxantum odoratum, Plantago lanceolata* and *Tataxacum officinale*) was collected from various spots in a 360 m^2 (12m x 30m) area of land; the mineralization vein in the center. The samples were freeze dried, milled and wet ashed by using a mixture of conc. HNO_3 and 9.8 M H_2O_2

The resulting digest was diluted and As determination was conducted by using HG-AAS.

Results and discussion

For the sequential leach procedures of the water soluble, exchangeable, and the carbonate bound phases the protocol given by Bombach G. *et al*. (10) was used. We presumed that the contact time required for a certain leach step would vary depending on the soil characteristics. Therefore, leachates were collected at different hours of shaking time for the three fractions and the minimum contact hour to get a constant concentration of As in the leachates was established Table 2. For the exchangeable and the carbonate bound fractions the 5 h contact time was not sufficient under our experimental conditions. A constant concentration of As in the leachates was obtained after a minimum of 12 h. For the more recalcitrant phases the protocol suggested by Hall G.E.M *et al*., was applied and results obtained were excellently reproducible.

Table 2. Concentration of arsenic as a function shaking time in the water soluble, exchangeable and carbonate bound fractionsof the FRS

	Concentration mg/kg of soil		
Shaking time (h)	Water soluble	Exchangeable	Carb. bound
1	0.05±0.03	5.3±0.2	25.7±2.8
4	0.25±0.03	6.8±0.3	39.5±1.6
8	0.38±0.02	9.6±0.2	45.0±3.7
12	0.54±0.01	10.4±0.5	76.0±2.9
16	0.63±0.03	13.8±0.3	93.5±4.5
20	0.78±0.02	15.3±0.3	95.0±3.8
24	0.80±0.02	15.2±0.5	95.2±2.5
28	0.79±0.01	15.2±0.8	96.3±4.2
32	0.78±0.01	15.8±0.2	95.8±2.7
36	0.80±0.02	15.4±0.5	95.4±2.3

Arsenic distribution in the FRS and FLS: After a 2 month incubation period some properties of the FLS were determined and compared with the respective properties of the FRS. The arsenic concentration in the soil solution increased from about 150 ppb in the FRS to about 7000 ppb in the FLS, which is around 45 fold. The soil potential of the FLS decreased substantially to –14 mV from an initial value of 313 mV and the pH increased from 5.01 to 6.40.

Table 3. presents the arsenic concentrations in the leachates of the various phases. The water soluble and exchangeable forms are generally considered as the most mobile and immediately bio-available forms in soils (11).

Table 3. Results of the sequential leach (mean ± s in mg/kg) for arsenic in the FRS and FLS Gasen soils and in SRMs 2709-2711. Values in bracket indicate the wt % of As relative to the sum.

Phase	Concentration (mg/kg)				
	FRS	FLS	SRM 2709	SRM 2710	SRM 2711
Water soluble	0.8±0.01 (0.03)	0.35±0.01 (0.01)	0.35±0.01 (1.96)	0.8±0.05 (0.13)	0.5±0.03 (0.5)
Exchangeable	15.2±0.8 (0.5)	13.9±0.4 (0.45)	0.41±0.01 (2.3)	8.5±0.5 (1.4)	6.7±0.6 (7.1)
Carbonate b.	95.4±2.3 (3.2)	97.4±2.3 (3.3)	0.63±0.03 (3.5)	45.3±1.2 (7.4)	19.5±0.8 (20.6)
Amorph. Fe ox.	561.6±8 (18.9)	544.6±11 (18.4)	1.08±0.02 (6.0)	413±15 (67.3)	34.5±0.78 (36.4)
Cryst. Fe ox.	1279±18 (43)	1278±18 (43)	9.54±0.04 (53.4)	113±3.5 (18.4)	24.1±0.55 (25.4)
Org – Sulfide	890±15 (29.9)	897±15 (13.9)	4.23±0.09 (23.7)	18.8±0.5 (3.1)	6.02±0.09 (6.4)
Residual	128±2.5 (4.3)	127.6±3.1 (4.3)	1.63±0.06 (9.1)	14.3±0.56 (2.3)	3.35±0.01 (3.5)
Sum	2970±58	2961±45	17.87±0.3	613.7±25	94.7±2.5
Certified value			17.7±0.8	626±38	105±8

In the FRS Gasen soil these fractions account for only about 0.5 % of the total arsenic. The prevalence of arsenic in the more recalcitrant phases could be a good indication for the geogenic origin of the As in the Gasen soil. Metals deposited in soils from antropogenic sources become immobilized and less available with time because of slow diffusion of trace metals into minerals under natural conditions (12).The decrease in the concentration of arsenic in the water soluble and in the exchangeable fractions of the FLS as compared to the FRS seems to be reasonable since much of the arsenic leached into the soil water is from these fractions. However, the dissolved arsenic may not necessarily be from these fractions only. The decrease in the redox potential can cause the reduction of arsenate to arsenite (a more mobile form) from other fractions too and get arsenic solubilized.

From the recalcitrant fractions, the concentration of As is significantly lower in the Amorphous iron oxide phase of the FLS than its corresponding concentration in the FRS. Arsenic combined with Fe and Al oxides may be liberated upon hydrolysis with the reduction of soil potential. As the soil potential decreases Fe(III) will be reduced to Fe(II) resulting in the subsequent dissolution of ferric arsenate which is the insoluble form of arsenic frequently found in acidic soils. The data indicates that arsenic adsorbed to the amorphous iron and aluminum oxide phases is more susceptible to dissolution upon the reduction of the soil potential relative to that adsorbed to the crystalline fractions or the other recalcitrant fractions.

The slight increase in the arsenic concentration of the carbonate bound fraction of As in the FLS from that of the FRS can be attributed to the fact that the observed increase in pH and the corresponding lowering of the Eh might have created a thermodynamically favorable condition for the resorption of part of the arsenic released from other fractions.

The values obtained for the NIST soils, SRM 2709-2711, are in close agreement with the results reported by Hall G.E.M *et al* (13).

Plant analysis: Results of the plant analysis (Fig.1) showed that the phytoavailability of arsenic remained comparably low in spite of the considerably high level of arsenic in the soil. The mean value was 1.7 mg kg^{-1} and the highest values were in the 3 mg kg^{-1} range; where this accounted for 9% of the overall determinations.

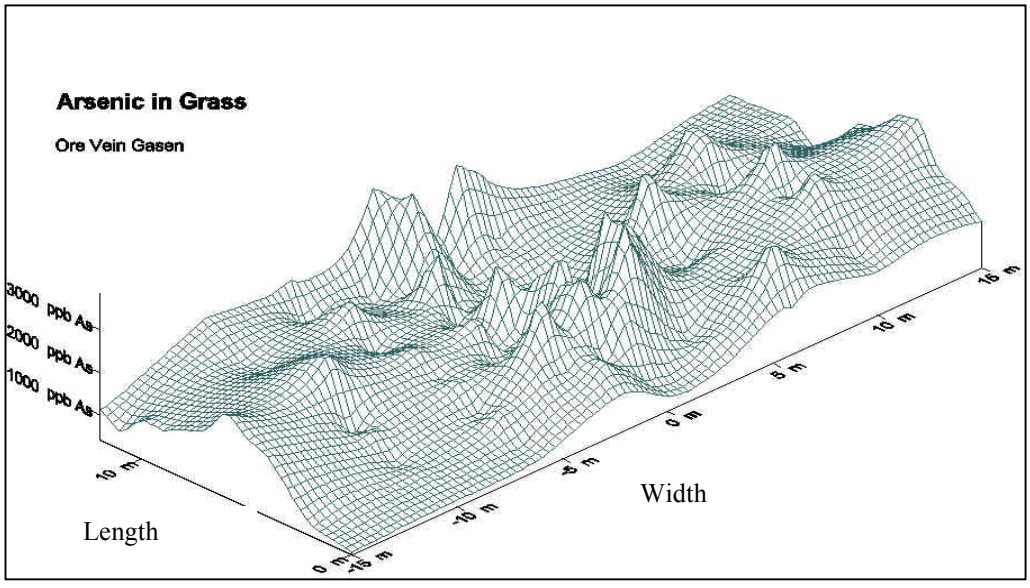

Fig.1 Arsenic content of grass samples collected from various spots at Gasen. The mineralization vein is taken to be the center of the width (0 m)

The most striking point was that, the level of arsenic in samples collected along the mineralization vein, where the soil arsenic content is high, was relatively lower than in samples collected away from the vein. This indicates that Arsenic uptake by the plants considered in our study seems to be influenced by factors other than total soil arsenic level. Moreover, there was no observable toxic effect on the plants grown in the area. The actual reason for the observed low arsenic level along the vein however, requires further investigation.

Conclusion

The existence of more than 90% of the As in the recalcitrant fractions could account for the strong retention of arsenic in the Gasen soil.

The gradual decrease in the soil potential with an increase in the flooding duration and the subsequent increase in the release of arsenic could be related with the relatively higher concentration of arsenic in the soil-water during spring. The reduced oxygen circulation during winter could possibly cause a decrease in the soil potential and an increase in the pH. As a result pentavalent arsenic may gradually be reduced to the more mobile trivalent form during winter and this may result in an increase in the level of arsenic in the soil water during spring.

The lower level of As in the grass samples collected from hot spots indicates that arsenic uptake is not influenced by total As level in the soil. The actual reason requires further investigation.

References

1. J. A. McKEAGUE, M. V. CHESHIRE, F. ANDREAUX, J. BERTHELIN, "Organo-mineral complexes in relation to pedogenesis", In: M.P. HUANG, M. SCHNITZER (Eds), Interactions of Soil Minerals with Natural Organics and Microbes, Soil Science Society of America, Madison, (1986)
2. G.S.P. RITCHIE, and G. SPOSITO, "Speciation in soils", In: A.M. URE, C.M. DAVIDSON (Eds), Chemical speciation in the environment, Chapman & Hall, UK, pp.201-233. (1995)
3. D.K . BHUMBLA, and R.F. KEEFER "Arsenic mobilization and bio-availability in soils", In: J.O. NRIAGU (Ed) Arsenic in the environment, part I: Cycling and characterization, John Wiley & Sons Inc., pp.51 – 75 (1994)
4. B.M. ONKEN and D.C. ADRIANO, Soil Sci. Soc. Am. J, **61**, 746 – 752 (1997)
5. W.F. PICKERING; Ore Geol. Rev., **1**, 83 – 146(1986)
6. T. TAKAMATSU, H. AOKI, T. YOSHIDA, Soil Science, **133**, 239 – 246 (1982)
7. A. TESSIER, P.G.C. CAMPBELL and M. BISSON, Anal. Chem., **51**, 844 – 851 (1979)
8. W. H. HENDERSHOT, M. DUQUETTE; Soil Sci. Soc. Am. J., **50**, 605-608 (1986)
9. W. H. HENDERSHOT, M. DUQUETTE, "Soil reaction and exchangeable acidity", In: M.R. CARTER (Ed), Soil Sampling and Methods of Analysis, Lewis publishers, U.S.A, pp. 141-145(1993)
10. G. BOMBACH, A. PIERRA, and W. KLEMM, Fresenius J. Anal. Chem., **350**, 49 – 53 (1994)
11. F. LI, X. SHAN, T. ZHANG, and S. ZHANG, Environ. Pollut., **102**, 269 – 277 (1998)
12. A.V. HIRNER; Intern. J. Environ. Anal. Chem., **46**, 77-85 (1992)
13. G.E.M. HALL, G. GAUTHIER, J. PELCHAT, P. PELCHAT, J.E. VAIVE, J. Anal. At. Spectrom., **11**, 787 – 796(1996)