

Effects of Various Chemical Modifiers on the Determination of Arsenic by Electrothermal Atomic Absorption Spectrometry and Application to the Solid Samples

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Various chemical matrix modifiers were studied for arsenic determination by platform atomization-ETAAS. The studied matrix modifiers include the nitrate salts of palladium, iron, molybdenum and nickel and the mixture of Ni + triton X-100. Palladium modifier was found the best reagent in comparison with other studied modifiers. The optimized methods were applied to the determination of arsenic in solid samples such as soil, coal, coal-bottom ashing and coal fly ashing, the slag of copper mining and cement raw materials such as clay, gypsum and calcareous samples taken from east of Turkey. Very high concentration of arsenic was found in copper slag as high as 10500 mg kg⁻¹.

Key Words: Chemical modifier, GFAAS, Arsenic, Solid samples, Fly ashing.

INTRODUCTION

Inorganic arsenic and arsenic compounds are classified as a human carcinogen by The International Agency for Research on Cancer (IARC) and the United States-Environmental Protection Agency (US-EPA)^{1,2}. Arsenic is present in over 200 naturally occurring minerals and may accumulate in environmental matrices due to human activities such as waste discharges of metal processing plants, burning of fossil fuels, mining of ores containing arsenic, wood preservation and agricultural use of arsenical pesticides. Arsenic concentrations in uncontaminated soils are generally in the range of 0.2–40 mg kg⁻¹. However, levels of 100–2500 mg kg⁻¹ have been reported in the vicinity of copper smelter³. A large amount of arsenic is consumed in the manufacture of herbicides and animal feed additives for agricultural purposes⁴. A significantly higher content of arsenic in the fly ash compared with the bottom ash was found both experimentally and by calculation⁵. It is known that the toxicity of toxic metals depends on their physicochemical properties such as solid, liquid or gas. The inhalation of particulates containing 0.5 mg As kg⁻¹ causes the cancer of lungs, liver and skin, teratogenic and poisonous in large doses⁶. In Turkey, the factories of cement are generally near the cities and large amounts of cement dusts are emitted from these factories, in spite of banning. On the other hand, US-EPA has decided to reduce the current maximum contamination level (MCL) of 50 ng/mL As in drinking water to 10 ng/mL arsenic⁷ because long-term exposure to concentration of arsenic at 50 ng mL⁻¹ level in drinking water can lead to skin, bladder, lung and prostate cancer⁸.

Due to all these reasons and owing to its extremely low concentration limitations in environmental and food matrices, accurate, very sensitive and reliable techniques were necessary for arsenic determinations being at very low concentrations in these matrices. For this purpose, different techniques such as electrothermal or hydride generation-atomic absorption spectrometry (ETAAS or HG-AAS) and inductively coupled plasma-mass spectrometry (ICP-MS) were generally used⁹⁻¹¹. Although ETAAS and HG-AAS are many times the techniques of choice for this purpose, nonetheless, the problems exist in the determination of arsenic by ETAAS derived from losses by vaporization at temperatures prior to atomization and from chemical interferences¹². Therefore, chemical matrix modifiers are often used in ETAAS in order to achieve better separation of analyte and matrix prior to atomization. The modifiers either reduce the volatility of the analyte or increase the volatility of the matrix. Arsenic is a volatile element that may be lost from the graphite atomizer, in absence of chemical modifier, at temperatures higher than 200°C. Moreover, in the presence of organic matrix, losses of arsenic may also be due to the formation of volatile compounds during the pyrolysis stage. In order to minimize these undesirable effects, the use of a chemical modifier is required, so it allows the application of significantly higher pyrolysis temperatures¹³⁻¹⁵. This leads to considerable simplification of the sample matrix and consequently to a lowering of the background absorbance signals and a reduction of non-spectral interferences.

Although palladium is by far the most frequently used modifier in ET-AAS, but also Pd-Zr, Pd-Ir and Pd-Mg mixtures have been used^{9, 10, 13}. The choice of modifier depends on both the analyte and the matrix. On the other hand, the pertinent literature is full of very different and often contradictory proposals for mechanisms of action of modifiers and coatings¹⁶.

In this study, various chemical matrix modifiers were studied for arsenic determination by platform atomization-ETAAS. The studied matrix modifiers include the nitrate salts of palladium, iron, molybdenum and nickel and Ni-Triton-X mixture. The optimized method was applied to the determination of As in solid samples such as soil, coal, coal-bottom ashing and coal fly ashing of Elbistan power plant, slag of copper mining and the cement raw materials such as clay, gypsum and calker taken from Elazig city in east of Turkey.

EXPERIMENTAL

A Shimadzu AA-6701 model graphite furnace atomic absorption spectrophotometer (GFAAS) equipped with hollow cathode lamp was used for the determinations. The optimum conditions for GF-AAS are given in Table-1.

Unless stated otherwise, all chemicals used were of analytical reagent grade and doubly distilled water was used throughout. The standard arsenic solution (1000 mg L^{-1}) was prepared by dissolving As_2O_3 (Merck) in 6 M NaOH solution, neutralizing with 6 M HCl and diluting it to suitable volume with distilled water. In the digestion procedures, concentrated nitric acid (65%, Merck, Germany) and hydrochloric acid (Merck) were used.

TABLE-1
 INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF As BY ETAAS
 (GRAPHITE FURNACE PROGRAM)

Step	Temp. (°C)	Ramp (°C/s)	Hold time (s)
Dry	120	0	10
2	130	2	30
3	700	50	20
4	1200	0	3.0
5	2400	0	4.0

Wavelength, nm: 193.7;
 Lamp current, mA: 12
 Measurement: Absorbance

Slit width, nm: 0.5
 Lighting mode: BGC-D₂
 Cuvette type: Coated

The solutions used as chemical modifier were prepared as 1000 mg/L from their nitrate salts so as to be 10 mg/L Pd(NO₃)₂ or 50 mg/L Ni(NO₃)₂ or 50 mg/L Ni(NO₃)₂ + 0.5% triton X-100 or 50 mg/L Fe(NO₃)₃ + 0.5% triton X-100 and 0.75 M HCl.

Preparation of Samples

Four sites were selected from major industrial areas in the east of Turkey. These areas are Elbistan thermoelectric power plant, plant of Maden copper mining at 70 km distance from Elazig (in the south-east), plant of ferrochrome at 40 km distance from Elazig (in the east) and surrounding of Hazar lake in Elazig in the east of Turkey as to be seen in Fig. 1.

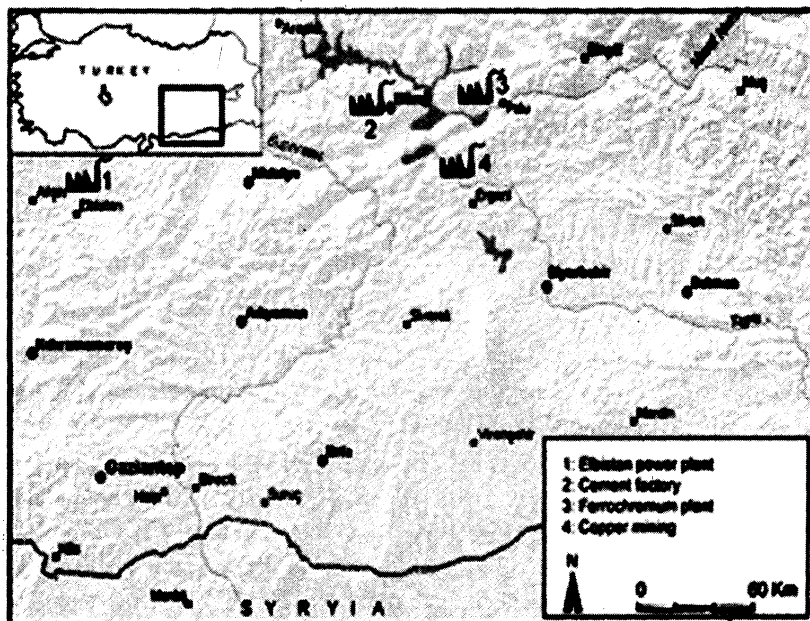


Fig. 1. The map of area east of Turkey from which the samples were taken

A soil sample (0.2 g) was placed into a flask and 2 mL of aqua regia were added. The mixture was heated until a little solvent had remained. Then, 50 mL of HCl (0.75 M) were added to the residue and centrifuged. The clear solution was diluted by adding the matrix modifier so as to become 10 mg/L Pd(NO₃)₂. The absorbance of this solution was measured by GF-AAS.

RESULTS AND DISCUSSION

Due to high volatility of arsenic, the pyrolysis step has to be conducted at relatively low temperatures resulting in severe matrix effects observed during the atomization. The addition of some chemical modifiers allows overcoming this problem because significantly higher temperatures may be applied during the decomposition step.

In this work, the influence of various chemical modifiers on the arsenic absorbance was investigated. The values of absorbance obtained in determination of standards without a modifier (in 0.75 mol L⁻¹ HCl) and with modifier such as Pd, Ni, the mixtures of Fe + triton X-100 and Ni + triton X-100 at the concentrations described above were compared. So, the calibration graphs of arsenic were obtained in these matrices.

The observed calibration curves for As solutions prepared in these matrix modifier solutions were given in Figs. 2–4. It was seen that the addition of nickel alone gave a positive effect in comparison with 0.75 mol L⁻¹ HCl matrix, but the addition of triton X-100 together with Ni gave a negative effect in comparison with alone nickel modifier (Fig. 2). The addition of Fe(NO₃)₃ together with triton X-100 gave a positive effect as high as the addition of nickel (Fig. 3). In addition, the calibration graph of As with nickel modifier does not pass the origin. The effect of molybdenum was similar to Fe(NO₃)₃ together with triton X-100 and the calibration graph passes at the perfect origin (Fig. 4). Finally, the addition of palladium

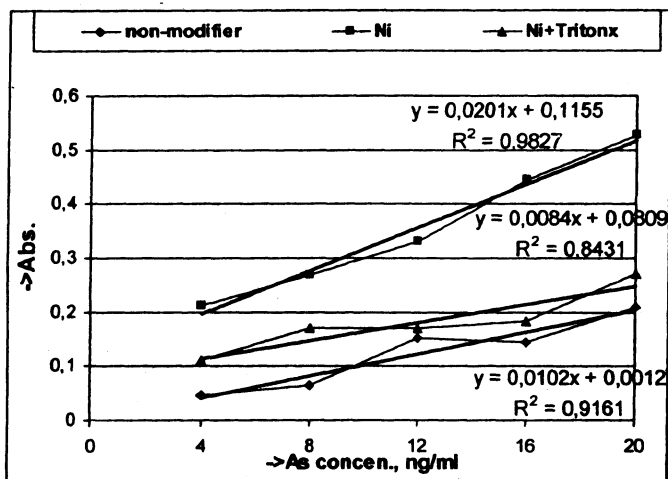


Fig. 2. A comparison of the effects of different modifiers in determination of As in 0.75 M HCl. ■ : in 50 mg/L of Ni(NO₃)₂, ▲ : in 50 mg/L of Ni(NO₃)₂ + 0.5% triton X-100 as modifier and ◆ : without modifier

modifier was superior (Fig. 4). Thus, $\text{Pd}(\text{NO}_3)_2$ was chosen for the determination of arsenic in the solid samples because of the higher sensitivity than the other modifiers and the calibration graph obtained in its matrix passes perfect origin.

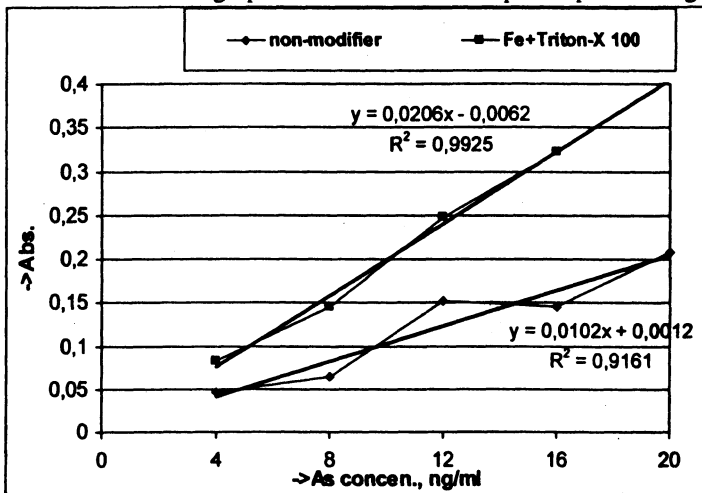


Fig. 3. A comparison of the effects of different modifiers in determination of As in 0.75 M HCl. ■ : in 50 mg/L of $\text{Fe}(\text{NO}_3)_2$ + 0.5% triton X-100 as modifier and ♦ : without modifier

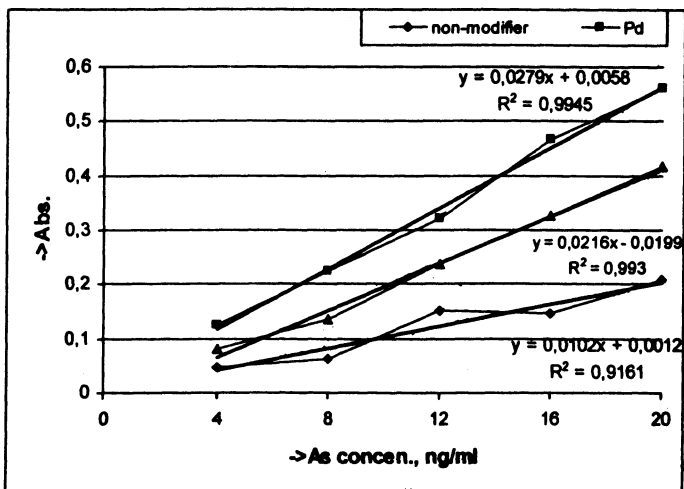


Fig. 4. A comparison of the effects of different modifiers in determination of As in 0.75 M HCl. ■ : in 10 mg/L of $\text{Pd}(\text{NO}_3)_2$ as modifier, ▲ in 50 mg/L of Mo and ♦ : without modifier

It was described that almost all of As or 60% at least in coal is volatile with fly ash¹⁷. In addition, it is reported that the exposure to high environmental arsenic levels as consequence of a coal burning power plant causes non-melanoma skin carcinoma¹⁸. The optimized method was applied to the determination of arsenic in solid samples such as copper mining slag, copper raw material, soil, fly ashing, coal, coal bottom ashing and the cement raw materials such as gypsum and tras.

The results obtained were given in Table-2. It is seen that arsenic concentration of the copper mining slag was higher than 10000 mg As kg^{-1} . In the literature,

similar results¹⁹ as high as 7000 mg kg⁻¹ were found in the mining slag and average concentration of 2500 (539–9380) mg As kg⁻¹ in the mine dump soil in the vicinity of Cu-W mine in Korea was reported²⁰. Bech *et al.*²¹ reported the arsenic concentrations up to 7670 mg kg⁻¹ in the soil around the copper mine. In addition, the arsenic concentration of 150 mg kg⁻¹ was found for the raw copper ore, in the current work. So, it can be said that arsenic in the raw copper ore was enriched in slag in the steps of the copper mining. As concentrations in the soil samples were found lower than the average toxicity threshold of 40 mg kg⁻¹ established for crop plants²². It is observed that there is no important hazardous arsenic concentration around the ferrochromium factory.

TABLE-2
ARSENIC CONCENTRATIONS IN THE STUDIED SAMPLES (DRIED BASIS)

Sample	As concn. in this work (mg/kg)	As concn. in literature (Ref.)
Dust around cement factory	53 ± 5	
Cement	43 ± 5	
Cement clay	44 ± 5	
Cement calcareous sample	44 ± 4	
Cement tras	42 ± 4	
Cement gypsum	36 ± 4	
Coal	46 ± 5	4.6-18.5 mg/kg ¹⁷
Coal bottom ash of power plant	52 ± 5	
Raw copper ore	150 ± 13	
Copper slag	10500 ± 850	539-9380 mg/kg for mine dump soil ²⁰ up to 7670 mg/kg for soil around Cu mine ²¹
Chromite ore	37 ± 4	
Ferrochromium factory slag	39 ± 4	
Soil around ferrochromium factory	35 ± 3	
Ferrochromium tras	40 ± 4	
Agricultural soil near the power plant	32 ± 3	Threshold value: 40 mg/kg for crop plants ²²
Raw soil around Hazar lake	26 ± 3	0.2–40 mg/kg for uncontaminated soil ³
Soil taken from Sivrice town Elazig	36 ± 4	

In conclusion, we have found that palladium was the best chemical modifier among the studied reagents. In addition, copper mining slag was extremely polluted with arsenic whereas such a pollution was not observed around cement and ferrochromium plants.

REFERENCES

1. IARC, Monographs on the Evaluation of the Carcinogenic Risk of Chemicals humans, WHO, Lyon, France, Vol. 1-2, Suppl. 7, pp. 100-106 (1984).
2. Health Assessment Document for Inorganic Arsenic, Research Triangle Park, NC, US-EPA, p. 351 (1984) (Final Report, No. EPA-600/7-83-021F).
3. Arsenic, WHO Regional Office for Europe, Copenhagen, Denmark (2000).
4. W. Mertz, Trace Elements in Human and Animal Nutrition, 5th Edn., Academic Press San Diego, California, Vol. 1-2 (1987).
5. E. Furimsky, *Fuel Proc. Technol.*, **63**, 29 (2000).
6. R.P. Turco, Earth under Siege from Air Pollution to Global Change, Oxford University Press (1997).
7. Environmental Protection Agency, Federal Register, Vol. 66 (14) (2001), Rules and Regulations <http://www.epa.gov/safewater/arsenic.html>.
8. K. Christen, *Environ. Sci. Technol.*, **34**, 291A (2000).
9. Li Li Yang and D.Q. Zhang, *Anal. Chim. Acta*, **491**, 91 (2003).
10. H.Th. Uggerud and W. Lund, *Spectrochim. Acta*, **54B**, 1625 (1999).
11. E. Vassileva, H. Baeten and M. Hoenig, *Fresenius J. Anal. Chem.*, **369**, 159 (2001).
12. H.M. Ortner, E. Bulska, U. Rohr, G. Schlemmer, S. Weinbruch and B. Welz, *Spectrochim. Acta*, **B57**, 1835 (2002).
13. G. Schlammer and B. Welz, *Spectrochim. Acta*, **41B**, 1157 (1986).
14. R.D. Ediger, *At. Absorpt. Newslett.*, **14**, 127 (1975).
15. A.B. Volynsky, S. Akman, C. Dogan and U. Koklu, *Spectrochim. Acta*, **56B**, 2361 (2001).
16. A.B. Volynsky, *Spectrochim. Acta*, **53B**, 139 (1998).
17. L. Ebdon and J.R. Wilkinson, *Anal. Chim. Acta.*, **194**, 177 (1987).
18. B. Pesch, U. Ranft, P. Jakubis, M.J. Nieuwenhuijsen, A. Hergomoller, K. Unfried, M. Jakubis, P. Miskovic, T. Keegan and the EXPASCAN study group, *Am. J. Epidemiol.*, **155**, 798 (2002).
19. C. Roussel, H. Bril and A. Fernandez, *J. Environ. Qua.*, **29**, 182 (2000).
20. M.C. Jung, I. Thorton and H.T. Chon, *Sci. Total Environ.*, **295**, 81 (2002).
21. J. Bech, C. Poschenrieder, M. Llugany, J. Barcelo, P. Tume, F.J. Tobias, J.L. Barranzuela and E.R. Vasquez, *Sci. Total Environ.*, **203**, 83 (1997).
22. S.C. Sheppard, *Water Air Soil Pollu.*, **64**, 539 (1992).

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