

E. STEFANOV¹, S. GEORGIEVA^{1*}

SPECIATION ANALYSIS OF ARSENIC IN SOIL SAMPLES BY LIQUID-LIQUID EXTRACTION AND ELECTROCHEMICAL DETECTION WITH GOLD MICRO-WIRE ELECTRODE

Soil collected from random areas of non-ferrous mines and smelters was studied in order to develop a low-cost but effective method for quantifying arsenic (III), arsenic (V), and total arsenic in contaminated soil. Hydrochloric acid microwave extractions have been used as a method to digest arsenic from soil in a form of solution suitable for speciation. Arsenic (III) is selectively extracted into benzene as arsenic trichloride from a highly concentrated hydrochloric acid solution. This was followed by the arsenic being extracted back into water. The total inorganic content of arsenic (V) can be directly determined by anodic oxidation of a gold screen-printed electrode using electrochemical detection. The amount of available Arsenic (III) in the sample is determined by pre-oxidation with KMnO_4 directly added to the electrochemical cell or by directly increasing the pH of the medium. ICP-MS was used to confirm all analyses for the various arsenic species as well as the discovery of total arsenic in the soil. It was discovered that the electrochemical method used allows for the cheap, quick, and selective determination of micro amounts of arsenic forms in contaminated soils.

Keyword: Arsenic species; soil; voltammetry; scTrace electrode; liquid extraction

1. Introduction

Arsenic is an essential, immunotoxic element. Arsenic has been shown to interact with thiol groups in proteins, cysteine, glutathione, and lipoic acid. It influences oxidative activities in the mitochondria and is engaged in various other critical metabolic processes. The hazardous dose for humans is 5-50 mg, while the fatal dose is 50-340 mg [1]. Arsenic is known as a “thiol poison” and its toxicity is caused by a disruption in the metabolism of sulfur, selenium, and phosphorus. Poisoning with this element can develop as a result of consuming contaminated food and drink, inhaling arsenic compounds like dust in the workplace, or using certain drugs. Arsenic poisoning harms the bone marrow, gastrointestinal tract, skin, lungs, and kidneys. There is ample evidence that inorganic arsenic compounds are carcinogenic. To date, more than 300 arsenates and As-containing minerals have been discovered [2]. Some arsenic is included in industrial cycles and then enters the soil and soil water due to mineral disintegration. After Pb, arsenic is the second most commonly reported inorganic contaminant in soil [2]. The primary source of technical arsenic is As-containing ore. As a result, the examination of arsenic forms in waste rock and mining waste, which are

the most harmful technogeochemical anomalies in the soil cover, receives a lot of attention. Severe environmental pollution with natural arsenic is also found at times Arsenic-contaminated soil and water have been reported to be catastrophic in a number of Asian countries in recent years [3,4]. There are various possible explanations for the high concentration of dissolved As. Among them is the participation of competing anions in the release of sorbed arsenate, As-oxidation pyrite with high redox potential, reduction of freely adsorbed arsenate to arsenite, and reductive dissolution of iron hydroxides containing arsenic at low redox potential [5-10].

Some mining wastes are the most enriched in As. The shape of the dominant As is mainly determined by the medium's pH. Arsenate is primarily found as H_3AsO_4 in an aqueous environment with a neutral pH; in a reducing atmosphere, arsenite H_3AsO_3 is generated [11] Arsenite in its reduced form is more poisonous than arsenite in its oxidized form. Both types of As have a great affinity for iron oxides, although they react in opposing ways to pH variations. The amount of arsenate adsorbed on iron oxides decreases with increasing pH in the pH range of 3-10. However, arsenite adsorption increased with pH, peaking at pH 9 [12].

¹ UNIVERSITY OF CHEMICAL TECHNOLOGY AND METALLURGY, DEPARTMENT OF ANALYTIC CHEMISTRY, 8, ST. KLIMENT OHRIDSKI BLVD, 1756, SOFIA, BULGARIA

* Corresponding author: st.georgieva@uctm.edu



The importance of investigating arsenic soil pollution is significant due to its impact on the food chain. Arsenic enters plants through the soil, as highlighted in a study [13]. The mechanism of how arsenic is transported from soils to plants was explored, revealing that the form of arsenic matters. For instance, As(V) uses phosphate transporters to enter root cells, while As(III) enters via aquaporins. It's noted that As(III) is more harmful than As(V) because of its higher water solubility. Inorganic forms of arsenic are more toxic than organic forms because they readily react with proteins, hindering cellular processes [14]. These findings underline the necessity for further investigation and the development of new methods to determine inorganic arsenic species in soils.

The following are the primary methods used in practice for determining arsenic in samples with varying matrix compositions [15-17]: 1) Titrimetric analysis is used to determine high and medium concentrations. This method has several advantages: it requires only a small amount of arsenic for examination, it is expressive, and it is simple to perform. Disadvantages of the approach include limited selectivity, which necessitates the isolation of arsenic prior to titrimetric measurement. The analytical results have a relative root mean square error of 0.1-0.5%; 2) Photometric methods of analysis are utilized to determine low concentrations. The photometric approach of this assay has the benefit of covering a very wide range of detectable concentrations. The method's high sensitivity allows it to detect arsenic in materials containing up to 1×10^{-5} - 1×10^{-7} % arsenic; 3) The polarographic method is used to detect arsenic in numerous industrial, natural, and food goods. The advantage of this method is its great selectivity, although its application to arsenic determination is limited. Regardless of the materials being studied, most procedures use three steps of analysis: – oxidative dissolution of an assessed material sample to obtain an aqueous solution of arsenic (V), – reduction of arsenic (V) to arsenic (III) or release of volatile arsenic compounds and absorption by the polarographic background; 4) X-ray fluorescence analysis methods have been widely used in recent years. The approach has several advantages, including great speed and precision of results. The disadvantages of the procedure are that it is less sensitive than emission spectral analysis and atomic absorption spectroscopy in terms of sensitivity; thus, in order to assess the content of arsenic in small quantities, it is pre-concentrated. The margin of error is 5 to 10%; 5) Emission spectrum analysis (AES) approaches are now frequently used. The ability to simultaneously determine a large number of elements is a significant benefit of the technology, and depending on the aim of the study, arsenic can be measured in concentrations ranging from 1×10^{-2} to 1×10^{-4} % with a relative standard error of determination of 20-30%; 6) Atomic Absorption Spectrometry (AAS) is based on the rapid measurement of the absorption of resonant radiation by free atoms in the gas phase. The method's advantages are its excellent selectivity, sensitivity, and speed [18-20].

Examining both forms of arsenic is becoming increasingly important, particularly in its speciation at low concentrations in soil samples, to analyze, anticipate, and avoid the buildup

of the poisonous form in such quantity as to be detrimental to biological life forms. Considering the shortcomings of the above-mentioned methods for the analysis of arsenic forms, the primary purpose of this manuscript is to present a low-cost, yet practical approach for assessing arsenic (III), arsenic (V), and total arsenic in contaminated soils.

2. Experimental

2.1. Materials

All reagents and solvents were analytical grade. Double distilled water was used for the preparation of the solutions. Hydrochloric acid, 37% ($=1.19 \text{ g mL}^{-1}$) p.a., benzene, 99.7% ($=0.879 \text{ g mL}^{-1}$) p.a., and hydrogen peroxide, 30% p.a. were utilized for liquid-liquid extraction of arsenic forms. CRM As 100.090.95 mg L^{-1} (CPAchem) and CRM Rh 99.980.39 mg L^{-1} (CPAchem) were used as reference analyte solutions. NIST 2710a and 2711a CRMs of polluted soils were employed as standard reference materials.

2.2. Apparatus

A 797 VA computrace, Metrohm voltammeter with a three-electrode electrochemical cell was utilized for the electrochemical detection: a screen-printed gold electrode (gold wire microelectrode, scTrace gold electrode, Metrohm) as the working electrode and a platinum auxiliary electrode. A calomel electrode ($\text{Hg/Hg}_2\text{Cl}_2$, KCl) with a potassium chloride concentration of 1.00 mol L^{-1} was used as a reference electrode. The ICP-MS method was employed as a comparison method, with spectra acquired using a Thermo Scientific iCAP RQ Quadrupole instrument. The following parameters were used: nebulizer K-type, auxiliary gas $1.5 \text{ L} \cdot \text{min}^{-1}$, nebulizer gas $0.7 \text{ L} \cdot \text{min}^{-1}$, RF power 1.2 kW , pump rate 50 rpm , sample uptake time 30 sec , integration time 30 sec radial view. SIAD BG supplied high-quality Ar 99.999% for plasma maintenance and as a carrier gas. The analytical signal was measured using two-point background adjustment and three replicas.

2.2.1. Electrochemical detection

Electrochemical detection was carried out in accordance with the methodology described in [21]. A solution of sulfuric acid (0.5 mol L^{-1}) and potassium chloride (0.05 mol L^{-1}) was produced to activate the microelectrode. As an electrolyte, a solution of sulfamic acid (1.00 mol L^{-1}), citric acid (0.5 mol L^{-1}), and potassium chloride (0.45 mol L^{-1}) was utilized.

Procedure: aliquots of the previously prepared soil sample extracts were sequentially added to 6.0 mL of electrolyte solution, previously purged with pure nitrogen to remove oxygen from the working solution. The signals were recorded in square

wave (SW) mode using the following parameters: Pretreatment mode: cleaning potential: -1.00 V, cleaning time: 60 s, deposition potential: -0.300 V, and deposition time: 10 s; potential step: 0.01 V s^{-1} , frequency: 100 Hz, and pulse amplitude: 0.02. The electrode was cleaned after each signal recording using a cleaning solution containing 0.5 mol L^{-1} sulfuric acid and 0.05 mol L^{-1} potassium chloride.

2.2.2. ICP-MS measurement

The arsenic signal in the sample was detected using the ICP-MS technique with the operating parameters specified in TABLE 1.

TABLE 1

ICP-MS method: chosen working characteristics for As determination in soil samples

Interface cones	Ni sampler and skimmer (with High Matrix insert 3.5 mm)
Nebulizer and spray chamber	Micromist and Quartz cyclonic spray chamber
Spray chamber temperature	$2.7^{\circ}C$
Cool gas	14.0 L min^{-1}
Auxilliary gas	0.8 L min^{-1}
Plasma power	1550 W
Nebulizer flow rate	1.015 L min^{-1}
Reaction cell gas	He
Reaction cell gas flow rate	4.034 mL min^{-1}
Measurement mode	Kinetic energy discrimination (KED)
Pump rate	40 rpm
Interna standard	Rh ¹⁰³

The calibration of the apparatus was carried out with calibration standard solutions (Fig. 1): all calibration solutions were prepared in 5% v/v hydrochloric acid from stock solution CRM As 100.09 ± 0.95 mg L^{-1} CPAchem. The used points for calibration: 0, 10, 25, 50, 75, 100 $\mu g L^{-1}$. Internal standard approach of calibration was used. For this purpose, Rh solution with concentration of 20 $\mu g L^{-1}$ was prepared.

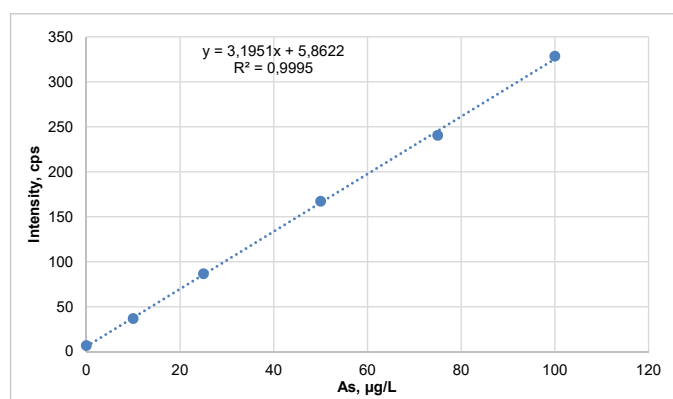


Fig. 1. Calibration curve of ICP-MS for As concentration measurement

2.3. Procedure for sample analysis

2.3.1. Sampling and sample locations

Soil samples were collected near a copper smelter and an old arsenic waste depot near Pirdop, Bulgaria (GPS coordinate $42^{\circ}42'52.5''N$ $24^{\circ}09'06.4''E$). Soil samples were taken from the soil surface (where possible, from the first 10-20 cm). All samples for analysis were stored in closed polyethylene containers at $4^{\circ}C$. Before analysis, the samples were dried at $105^{\circ}C$ for 4 h, was milled and was sieved through a 150 μm sieve.

2.3.2. Procedure for sample preparation

Analytical portion of 2 g soil sample was weighed on analytical balance. The portion was transferred into PTFE vessel of 50 ml for microwave digestion. For the digestion nonoxidizing hydrochloric acid was used in order to preserve the species of arsenic in their original oxidation state. To the sample portion 15 mL concentrated hydrochloric acid were added. Digestion in closed vessel was conducted – thus the volatile $AsCl_3$ could not be lost. The microwave digestion system (Multiwave 5000 by Anton Paar) was set on 500 W, $175^{\circ}C$ for 30 min. On Fig. 2 are present the power and temperature monitoring during digestion of samples. After digestion the solution was transferred into volumetric flask of 50.00 mL, the flask was filled up to the mark with concentrated hydrochloric acid.

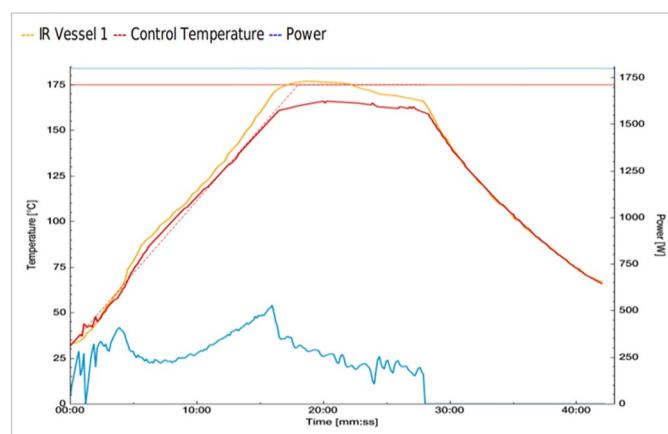


Fig. 2. Power and temperature monitoring during digestion

2.3.3. Procedure for liquid-liquid extraction

An aliquot of 5,00-25.00 mL fresh sample was added to 20 mL of concentrated hydrochloric acid HCl (37%, Merk). Extraction of arsenic was carried out with 15.0 mL benzene at room temperature and vigorous stirring for 5 min. After that the solution was placed to a separating funnel where the two phases were separated. The aqueous phase (raffinate) was stripped and subjected to a further extraction twice with 15.0 mL of benzene at the same conditions. After that the raffinate (containing As(V))

was transferred to the 100.0 mL volumetric flask and diluted to the mark with distilled water. The organic phase was re-extracted twice with 45.0 mL distilled water at room temperature and vigorous stirred for 3 minutes. After separating of two phases, the aqueous phase (extract) was collected again. To ensure complete extraction of As(III), this procedure was repeated two more time by adding benzene to the aqueous phase. The extract (containing As(III)) was transferred to 200.0 mL volumetric flask and diluted to the mark with distilled water. The extract and the raffinate were analyzed after appropriate dilution by voltamperometry and ICP-MS method as comparative one. On Fig. 3 are presented the stages of total sample analysis.

2.3.4. Determination of soil characteristics

For the purpose of this work two certificate reference soil materials (CRMs) were used – Montana soil 2710a and 2711a by NIST [22]. The first used CRM NIST 2710a has been collected from USA, Montana state, Silver Bow Creek where soils are highly contaminated with heavy metals such As, Pb, Zn, Cu etc. [23]. The material of second used CRM NIST 2711a has been collected from field located near a site formerly used

by a smelting plant, in east Helena, Montana, USA. The used CRMs contents are presented in TABLE 2.

2.4. Statistical analysis

The analytical aspects of the implemented method were statistically evaluated using the mathematical software Origin-Pro8.0 (ANOVA).

2.4.1. Results and discussions

2.4.1.1. Development of liquid-liquid extraction method for As determination with microwave decomposition of the soil sample and voltammetric detection.

2.4.1.1.1. Analytical performance

The sample was collected for analysis nearby a copper smelter and an old arsenic waste dump near Pirdop, and it contained the principal chemical components. Fig. 4 compares the chemical content of the samples taken to that of the used certi-

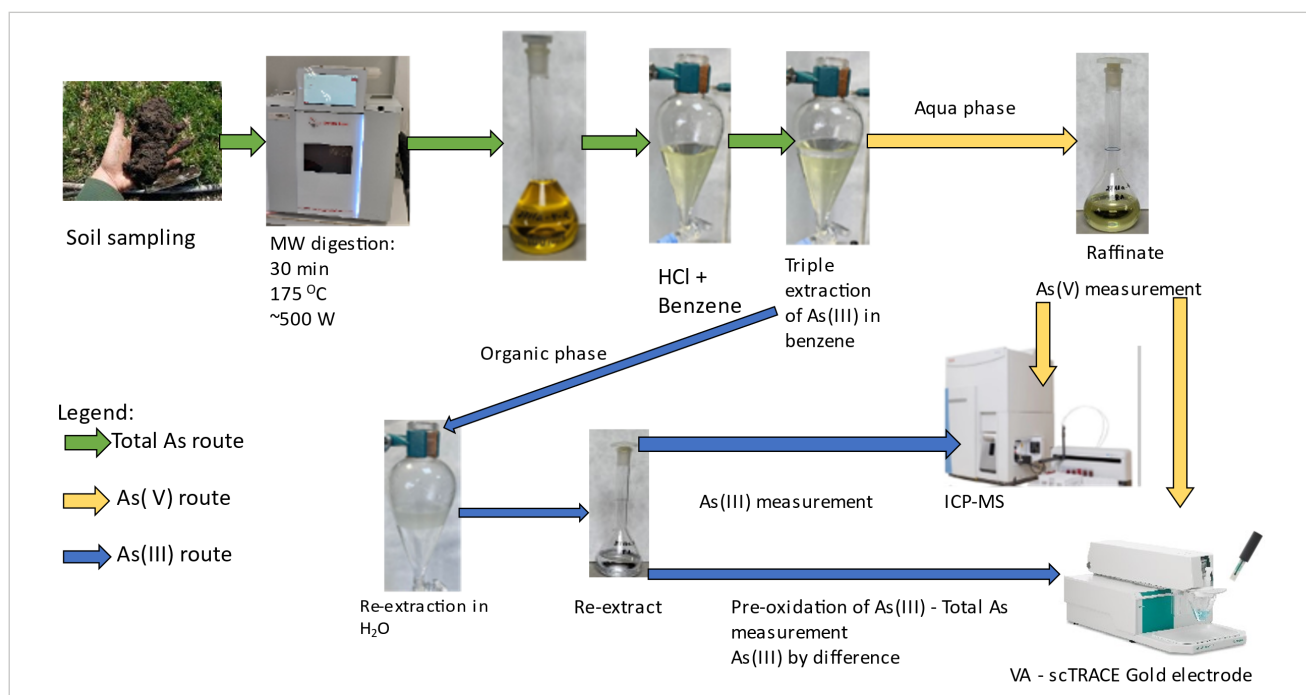


Fig. 3. Stages of analytical procedure for speciation analysis of arsenic in soil samples

TABLE 2

The main component content in used CRM soil samples NIST 2710a and NIST 2711a

Element	Al, %	As, %	Ca, %	Cu, %	Fe, %	Pb, %	Mg, %	Mn, %
NIST 2710a	5,95	0,154	0,964	0,342	4,32	0,552	0,734	0,214
NIST 2711a	6,72	0,0107	2,42	0,014	2,82	0,14	1,07	0,0675
Element	P, %	K, %	Si, %	Na, %	Ti, %	Zn, %	Others, %	—
NIST 2710a	0,105	2,17	31,1	0,894	0,311	0,418	51,8	—
NIST 2711a	0,0842	2,53	31,4	1,2	0,317	0,0414	51,2	—

fied reference soil materials. As seen in the samples, numerous other metal components are present in addition to the analyte, which would have an effect on the registration of the analytical signal of arsenic when using methods for its identification. For example, it has been found that the presence of Fe in the system affects arsenic determination in soils, and the effectiveness of its extraction is dependent on the soil-to-acid ratio and acid concentration. This necessitates the use of selective and sensitive technologies for determining both the total concentration of arsenic and its various forms.

In previous investigations, we demonstrated that preliminary sample preparation, consisting of liquid-liquid extraction using a non-polar organic solvent, entirely extracts the two forms of arsenic found in copper electrolytic bath samples. A sample preparation approach and ICP-OES method operating parameters for detecting arsenic signals in extract and raffinate were established [24]. J. Chappell et al. offer a method for analyzing arsenic forms in soil samples that involves extracting the analyte

with hydrochloric acid to remove arsenic from the soil in a form appropriate for speciation [25]. Arsenic (III) is selectively extracted into chloroform from a highly concentrated hydrochloric acid solution as arsenic trichloride, and total inorganic arsenic is determined after reducing arsenic (V) to the trivalent state with potassium iodide. As (V) is calculated as the difference between As(III) and total inorganic arsenic. The signals of various types of arsenic are detected using the atomic-absorption spectroscopy-hydride technique and X-ray fluorescence spectrometry [25]. Soil samples were prepared for examination in the present manuscript using microwave digestion in the presence of hydrochloric acid using the operating settings listed in Section 3.2. Digesting the sample in a closed vessel prevents volatility of the resulting AsCl_3 and, as a result, losses of As(III) – volatile AsCl_3 cannot be lost. Voltammetric detection of arsenic analytical signals was accomplished using a microelectrode composed of gold nanoparticles. According to the literature, As(V) produces a well-shaped anodic peak at roughly -0.1V in an acidic electrolyte environ-

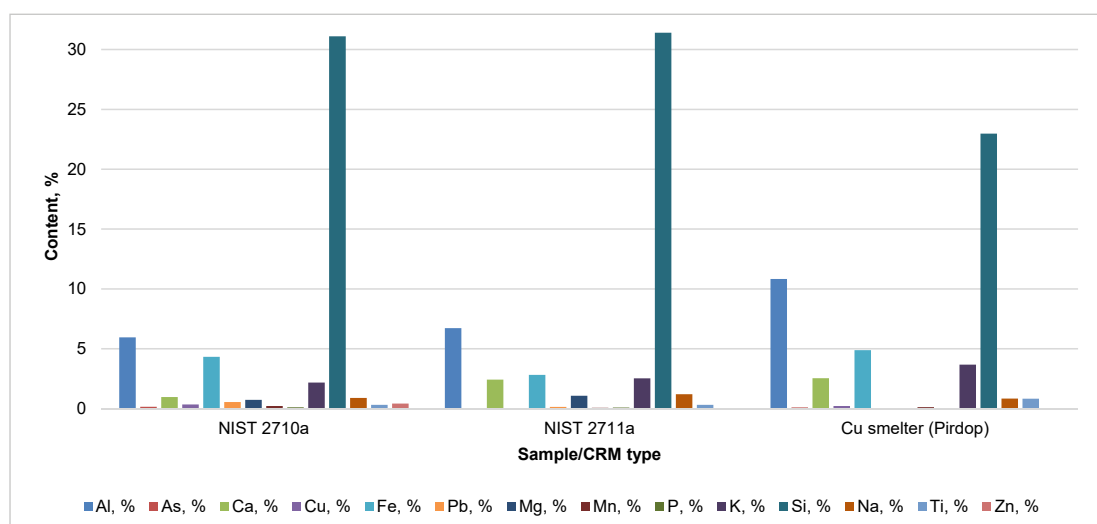


Fig. 4. Chemical content of the analyzed sample and of used certified reference soil materials

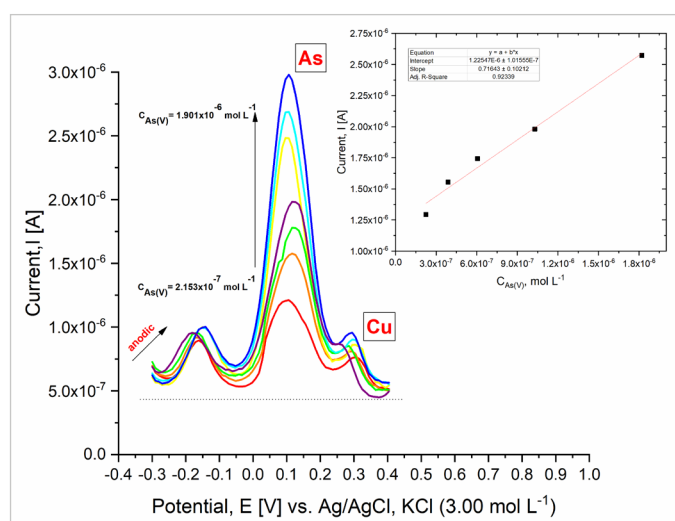


Fig. 5. SW voltamperograms of As(V) at different analyte concentration and a plot of current intensity vs. arsenic concentration (mol L^{-1}) (inserted graphic)

ment. Fig. 5 depicts the signals of standard As(V) solutions with increasing concentration. As can be observed, the intensity of the present peak grows proportionally to the concentration of the analyte. The calibration graph in the concentration range 2×10^{-7} – $2 \times 10^{-6} \text{ mol L}^{-1}$ is also shown in Fig. 5 (inset graph), and the analytical function coefficient was found to be 0.716 ± 0.102 . The analysis of As(III) in soil samples (As(III) as an extract) was done in the same electrolyte medium by pre-oxidizing As(III) to As(V) with potassium permanganate and detecting the signal of the greater degree of arsenic as previously reported.

2.4.1.1.2. Analytical characteristics of the method

TABLE 3 shows the data for the quantitative determination of As (III), As (V), and total arsenic (As(III)+As(V)) in one sample using microwave digestion of the sample for efficient storage of arsenic, subsequent extraction, and direct voltam-

metric method for arsenic determination. The sensitivity, accuracy, and repeatability of the novel approach were assessed in order to evaluate its analytical features for arsenic species in soil samples. By testing three samples from the same soil samples on different days, the efficacy of the used arsenic species extraction method was confirmed. The mean values from three parallel determinations of As(III), As(V), and total arsenic are as follows: $(3.19 \pm 0.06) \text{ g L}^{-1}$ for As(III); $(4.83 \pm 0.05) \text{ g L}^{-1}$ for As(V) and $(8.02 \pm 0.08) \text{ g L}^{-1}$ for total arsenic, respectively. The obtained relative standard deviation was $s_r = 0.57\%$. The total arsenic levels determined by the extraction voltammetric method were compared to those determined by the extraction ICP-MS analysis of the same sample (TABLE 3). One can conclude that the results obtained by both methods are identical within the limit of random errors (TABLE 3). Eq. (1) was used to calculate the percentage ($R\%$) of arsenic from six repeats of each analysis, and the results are also shown in TABLE 3:

$$R = \frac{C_{\text{As(III)}} + C_{\text{As(V)}}}{C_{\text{Total}}} \times 100, \% \quad (1)$$

2.4.1.1.3. Evaluation of the selectivity of the method

Fig. 4 illustrates the percentage contents of accessible metal ions in all soil samples investigated. As can be seen, all samples include large concentrations of potassium, phosphorus, aluminum, and iron, as well as a lesser amount of copper ions, which is why the method's selectivity was tested. Only copper ions produce a signal similar to arsenic in the examined potential window. In the Fig. 6 it can be seen that there is a shoulder on the main peak at about 0.2 V, which is caused by the presence of copper ions. When detecting arsenic on a gold electrode in the presence of copper ions in concentrations greater than 10 times the concentration of the analyte, an interfering impact on the arsenic signal is found, according to data in the literature. As a result, we suggest a signal differentiation (Fig. 7), in which it is noticed that the interfering copper ion concentrations indicated in the literature no longer affect the recording of the As(V) signal.

TABLE 3

Results for difference forms of As and total arsenic in analysis soil sample and referent materials by determine by different analytical methods

Sample	Method	Analyte			As(V), mg kg ⁻¹	n	S	Sum As(III)+As(V), mg kg ⁻¹	CRM (Total As), mg kg ⁻¹	Recovery, %
		As(III), mg kg ⁻¹	n	S						
CRM 2710a	L-L extraction and ICP-MS	1573	5	22	45	5	16	1618	1540	105
	L-L extraction and Voltammetry	1557	3	1.53	29	3	2.52	1586	1540	103
CRM 2711a	L-L extraction and ICP-MS	105	5	8	6,5	5	0,5	112	107	105
	L-L extraction and Voltammetry	102	3	0.98	5.5	3	0.21	108	107	101
Pirdop smelter soil	L-L extraction and ICP-MS	113	5	7	7	5	0,4	120	125	96
	L-L extraction and Voltammetry	120	4	1.20	6.7	3	0.17	127	125	102

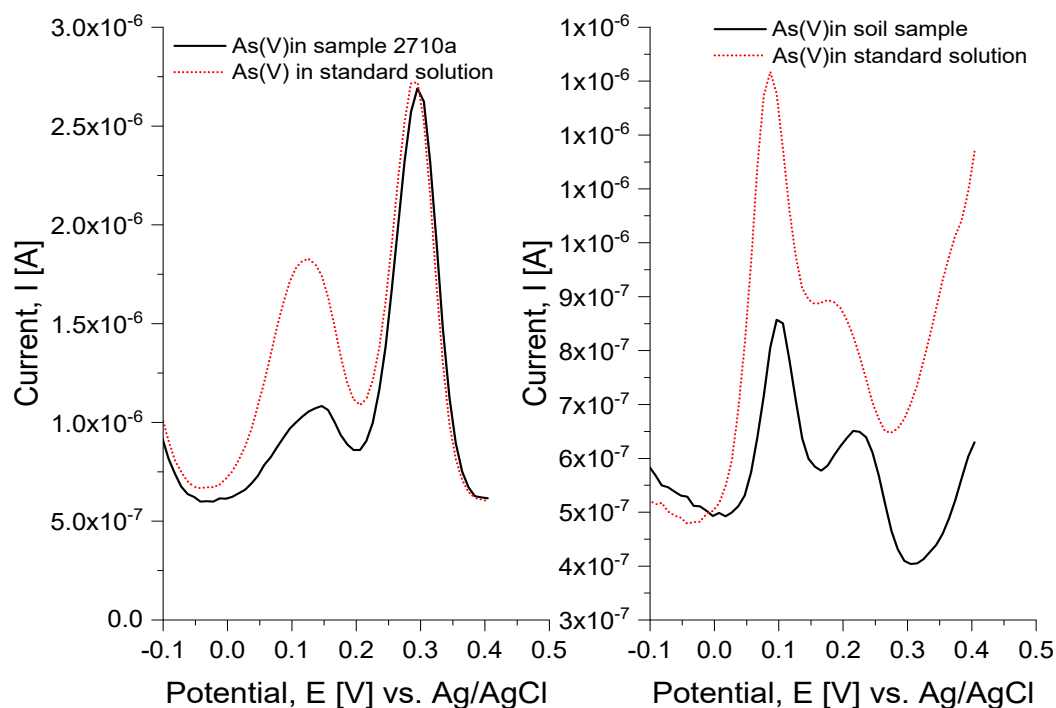


Fig. 6. Voltammetric determination (SW) of As(V) in soil sample and reference soil material 2710a by method of standard addition

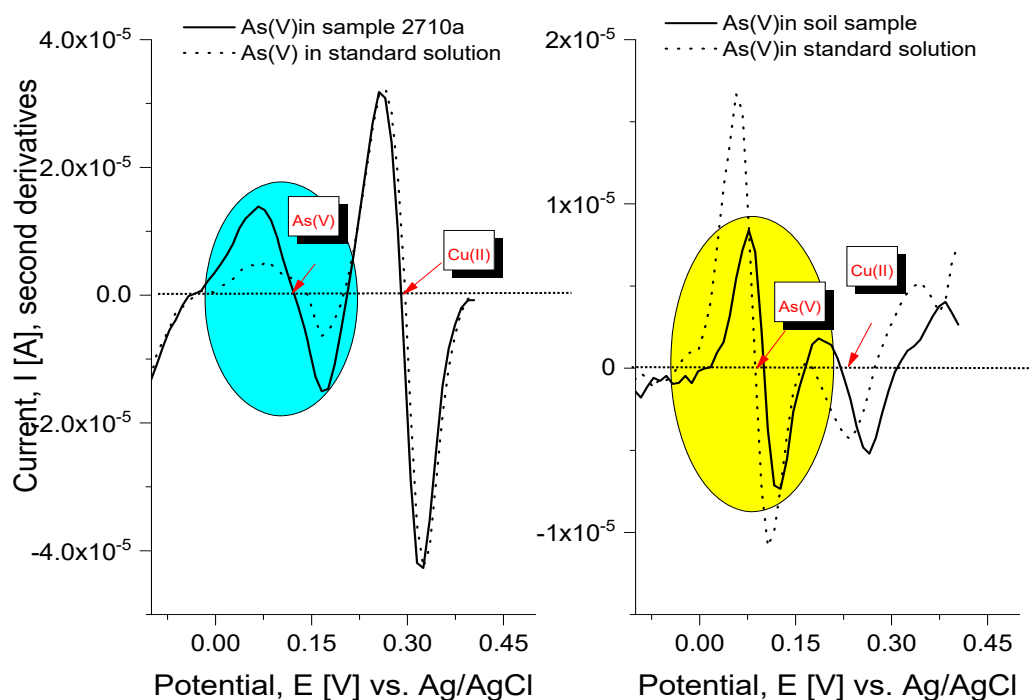


Fig. 7. Plot of first derivative of current [A] of voltammetric signals vs. potential, E [V]

For demonstration of selectivity of extraction procedure, to the aliquots of 5 mL, H_2O_2 30% were added. Then the samples with addition H_2O_2 was heated in order to destroy excess of peroxide. After that the aliquots were passed through whole procedure. The results are summarized in TABLE 4.

To further assess the method's selectivity and to demonstrate the complete extraction of As(III), a standard addition of As(III) was added to the extracted soil materials, and the total mass of arsenic in the sample was determined voltammetrically. It should be noted that the additional arsenic is likewise subjected to the extraction reagent exposure protocols mentioned. The influence of matrix components was assessed by measuring sample recovery after spiking. Eq. (2) was used to calculate the recovery, and the results of the analysis are shown in TABLE 5.

$$R = (m_{a+spike} - m_a) / m_{spike} \quad (2)$$

where $m_{a+spike}$ is the mass of As(V) after spiking, m_a – the mass of As(V) and m_{spike} – mass of analyte in spike. The recovery results are also presented in TABLE 5.

2.4.1.2. Checking the method's accuracy

The ICP-MS method confirmed the results of the used voltammetric method for detecting arsenic forms. Extracts and raffinates from certified reference materials, as well as investigated soil samples of various weights, were tested spectrometrically for this purpose, and the results obtained from many parallel determinations at various studied values are provided in TABLE 6. The obtained results were statistically analyzed, and the relative error values were determined and compared with the analytical properties of the voltammetric method (Figs. 8 and 9).

TABLE 4
Results for arsenic determination in reference soil materials and investigated soil sample after adding H_2O_2 30%

Sample	As(III), g/t	As(V), g/t	As (As(III)+As(V), g/t	As certified value, mg/kg	Recovery, %	As(V) distribution, %
2710a	<1	1580	1580	1540	103	100
2711a	<1	108	108	107	100	100
Cu smelter soil	<1	110	110	99	111	100

TABLE 5
Percentage recovery of As(V) in spiked sample, using spiking levels of 0.0001423, 0.003296 and 0.008994 g obtained by direct voltammetric detection

Solution	mass of As(V) total (Real sample + spike), g	mass obtained, g	mass recovered, g	Recovery, %	Relative error, %
1	0.0004856	0.0004861	0.0001428	100.3	0.3
2	0.003378	0.003392	0.003263	100.2	0.2
3	0.01001	0.009987	0.008998	99.7	-0.3

Figs. 8 and 9 show the percentage distribution of arsenic in the samples as well. There is a recognized actual value (μ) in the results for total arsenic, which is acquired by direct examination

of the sample by ICP-MS method (TABLE 7). The difference is calculated as the absolute error ($|\Delta C| = |C - \mu|$), and the relative percentage error ($\% \delta = |\Delta C| \times 100 / \mu$) is 0.28% (TABLE 7). The

TABLE 6

Results for parallel determinations of different soil materials obtained by comparative ICP-MS method

Sample	mass, mg	V, ml	Aliquote, ml	Vextr., ml	Vraf., ml	As(III), $\mu\text{g/L}$	DF	As(V), $\mu\text{g/L}$	DF	As(III), g/t	As(V), g/t	As (As3+As5), g/t	As (III), %	As (V), %	CRM, mg/kg	Recovery
2711a	1999.5	50.00	25.00	200	100	46.02	10	33.412	2	92.06302	6.684071	98.7	93.2%	6.8%	107	92%
2711a	1998.6	50.00	25.00	200	100	47.774	10	31.024	2	95.61493	6.209146	101.8	93.9%	6.1%	107	95%
2711a	2000.7	50.00	25.00	200	100	47.587	10	29.491	2	95.1407	5.896136	101.0	94.2%	5.8%	107	94%
2711a	1999	50.00	25.00	200	100	45.594	10	30.62	2	91.23362	6.127064	97.4	93.7%	6.3%	107	91%
2711a	1998.2	50.00	25.00	200	100	46.805	10	27.525	2	93.69432	5.509959	99.2	94.4%	5.6%	107	93%

Sample	mass, mg	V, ml	Aliquote, ml	Vextr., ml	Vraf., ml	As(III), $\mu\text{g/l}$	DF	As(V), $\mu\text{g/l}$	DF	As(III), g/t	As(V), g/t	As (As3+As5), g/t	As (III), %	As (V), %	CRM, mg/kg	Recovery
2710a	2000.8	50	5	200	100	68.333	20	30.699	2	1366.114	30.68673	1396.8	97.8%	2.2%	1540	91%
2710a	2001	50	5	200	100	68.65	20	33.491	2	1372.314	33.47426	1405.8	97.6%	2.4%	1540	91%
2710a	2001	50	5	200	100	70.857	20	32.783	2	1416.432	32.76662	1449.2	97.7%	2.3%	1540	94%
2710a	1999.2	50	5	200	100	70.975	20	32.543	2	1420.068	32.55602	1452.6	97.8%	2.2%	1540	94%
2710a	2001.4	50	5	200	100	69.874	20	32.576	2	1396.502	32.55321	1429.1	97.7%	2.3%	1540	93%

Sample	mass, mg	V, ml	Aliquote, ml	Vextr., ml	Vraf., ml	As(III), $\mu\text{g/L}$	DF	As(V), $\mu\text{g/L}$	DF	As(III), g/t	As(V), g/t	As (As3+As5), g/t	As (III), %	As (V), %	CRM, mg/kg	Recovery
Cu smelter soil	2000.7	50	25	200	100	47.595	10	32.612	2	95.1567	6.520118	101.7	93.6%	6.4%	99	103%
Cu smelter soil	1999.2	50	25	200	100	49.307	10	36.538	2	98.65346	7.310524	106.0	93.1%	6.9%	99	107%
Cu smelter soil	1999.7	50	25	200	100	45.79	10	33.099	2	91.59374	6.620793	98.2	93.3%	6.7%	99	99%
Cu smelter soil	2000.2	50	25	200	100	50.488	10	27.897	2	100.9659	5.578842	106.5	94.8%	5.2%	99	108%
Cu smelter soil	2001	50	25	200	100	48.384	10	30.252	2	96.71964	6.047376	102.8	94.1%	5.9%	99	104%

Montana soil 2711a			
N	As(III), mg/kg	As(V), mg/kg	Total As, mg/kg
1	92	7	99
2	96	6	102
3	95	6	101
4	91	6	97
5	94	6	99
Average, mg/kg	94	6	100
S, mg/kg	2	0	2
RSD, %	2	7	2
Confidential interval, mg/kg	2	1	2
Recovery, %	NA	NA	93

Montana soil 2710a			
N	As(III), mg/kg	As(V), mg/kg	Total As, mg/kg
1	1366	31	1397
2	1372	33	1406
3	1416	33	1449
4	1420	33	1453
5	1397	33	1429
Average, mg/kg	1394	32	1427
S, mg/kg	25	1	25
RSD, %	2	3	2
Confidential interval, mg/kg	31	1	31
Recovery, %	NA	NA	93

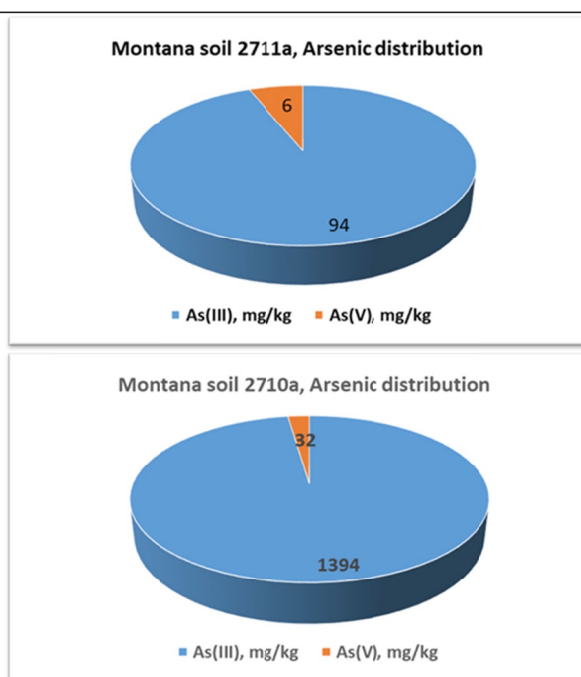


Fig. 8. Statistically evaluation of the results of referent samples 2711a and 2710a and pie diagrams of the relative error percentage distribution of arsenic in the samples

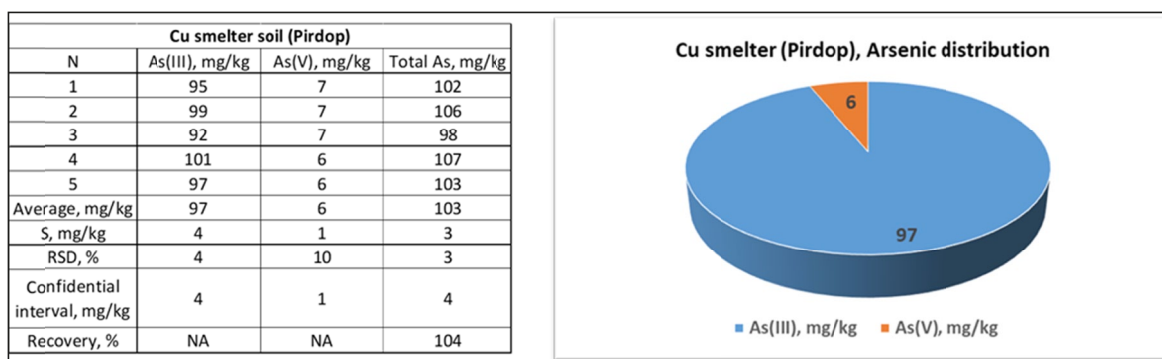


Fig. 9. Statistically evaluation of the results of analyzed soil sample and pie diagram of the relative error percentage distribution of arsenic in the sample

TABLE 7

Statistical characteristics for evaluation of accuracy of the voltammetric method applied at analysis of soil sample

Statistical characteristics	Concentration of As(III) $\times 10^{-5}$, g L ⁻¹	Concentration of As(V) $\times 10^{-5}$, g L ⁻¹	Concentration of total As $\times 10^{-5}$, g L ⁻¹
\bar{X} (at $n = 3$)	3.19	4.83	8.02
S	0.0326	0.0285	0.0461
S_r , %	1.02	0.59	0.57
t_{table} ($P = 95\%$)	3.18	2.57	2.57
confidence interval (at $P = 95\%$)	± 0.06	± 0.05	± 0.08
true content, μ	N/A	N/A	8.04
$ \Delta C = C - \mu $	N/A	N/A	0.02
$\% \delta = \Delta C \times 100 / \mu$	N/A	N/A	0.24

Student's test was used to statistically evaluate the accuracy of the results obtained by developed method. The empirical value of Student's test (t_{table}) does not exceed the tabular value for the specified number of parallel analyses, indicating that there are no system errors. The confidence interval for As (III) and As(V) was determined for the other two studies (results for content of As (III) and As (V)). The computed mean values for As(III), As(V) and total arsenic were obtained within the limits of the voltammetric method's confidence interval, confirming the accuracy of the used detection method.

3. Conclusions

This paper describes a method for determining As(III) and As(V) in industrially polluted soils. The sample preparation method utilizes novel non-oxidizing microwave digestion. The extraction method relies on liquid-liquid extraction and voltammetric detection. Because basic chemicals and common techniques are used, the proposed method is simple, economical, and accessible. Soil materials from contaminated soils in the Pirdop region of Bulgaria were evaluated in the development of the procedure, and the forms of arsenic were determined by direct voltammetric detection of As(V) in the raffinate and derived by pre-oxidation of arsenic 3 in the extract. The As(III) and As(V) forms were determined using square wave voltammetry (gold screen-printed electrode; 50 Hz, amplitude

–50 mV) in an electrolyte with pH 2.34. The amount of accessible Arsenic (III) in the sample is determined by pre-oxidation with KMnO_4 immediately added to the electrochemical cell or by changing the pH of the medium. The results obtained for As(III) and As(V) forms by the present electrochemical method were within the confidence interval given by ICP-MS method used as a comparative method. The results were satisfactory and demonstrated that nearly all of the arsenic contained was in the trivalent state (97%). The method has advantages over other methods such as: determination of arsenic species in soils samples in lower concentration ranges comparable with ICP-MS but the method is cheaper and easier for application. It has been demonstrated that the suggested voltammetric method produces accurate and precise and that the method may be successfully employed in the measurement of arsenic forms in contaminated soil materials in the presence of metals such as Cu, Fe, Al, Mg, Ca and Mn.

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