the crystalline phase to the amorphous one that speeds up the transport of allyl centres during their decay. This DSC evidence supports conclusions following from both interpretations of Arrhenius parameters. From a microscopic point of view it means that at temperatures 313 K and 323 K the phase transformation, *i.e.* the decay of crystallites increases the molecular mobility in the matrix. Consequently, the rate of migration of allyl macroradicals is in their decay reaction enhanced.

On the basis of the present results from the study of the decay of allyls in chemically cross-linked PE, we can state that this reaction proceeds dominantly in amorphous regions and is affected by crosslinking and by the course of phase transition.

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Determination of Arsenic in Soils by Cathodic Stripping Voltammetry

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An analytical procedure has been developed for determination of low contents of As in soils by the cathodic stripping voltammetry method using HMDE. Arsenic was determined after $AsBr_3$ extraction from the medium of 11.5 M-H_2SO_4, 0.05 M-NaBr, and 0.002 M-$NH_2NH_2 \cdot H_2SO_4$ into toluene and back-extraction into the solution of 1.5 M-HCl and 0.03 M-$NH_2NH_2 \cdot H_2SO_4$. Optimum procedure for decomposition of the soil sample and for separation of As from the interfering components as well as optimum conditions for electrochemical determination itself were investigated. Deposition of As on HMDE was achieved in the presence of Cu(II) by electroreduction in the form of intermetallic compounds from the medium of 1 M-HCl, 0.02 M-NH_2NH_2 H_2SO_4, and 0.0002 M-$CuCl_2$. Concentration of As was evaluated by the method of standard additions on the basis of the signal arising on reduction of As to AsH_3. The developed procedure is simple as to the number of operations preceding the determination itself and reliable, as evidenced by low values of relative standard deviations (1.1 to 3.2 %) and by the results of analyses of standard materials.

For determination of trace amounts of inorganic components in real samples of various origin, beside atomic spectrometry also differential pulse polarography and stripping voltammetry are used, the latter enabling *in situ* preconcentration of the component to be determined. In polarographic and voltammetric determinations in common base electrolytes only As(III) provides a signal. Therefore, when determining total amount of As in samples, it is necessary to reduce the inactive As(V) to electroactive As(III). This may be achieved by using various reductants (NaHSO$_3$, Na$_2$SO$_3$, NH$_2$NH$_2 \cdot$ H$_2$SO$_4$, Cu(I) in concentrated HCl, *etc.*)

and procedures. The reductant should be chosen so that its excess or the by-products of the reduction reaction might not interfere with the determination of As.

In voltammetric determinations As(III) is deposited by electroreduction mostly on solid electrodes, *e.g.* Au [1], Au film [2—4], graphite [5—7], and Pt [1, 8, 9], and the anodic polarization curves are evaluated. Insolubility of As in Hg means a limited use of the hanging mercury drop electrode (HMDE). The presence of Cu(II) [10—12] or Se(IV) [13] in the base electrolyte brings about a noticeable increase of the preconcentrating factor as a

consequence of formation of intermetallic compounds and, thus, enables to use also this electrode in trace analysis of As [11—13] . When using HMDE, evaluated is the signal arising on cathodic stripping of the deposited As on the basis of the $As^0 \rightarrow As^{3-}$ reduction.

Voltammetric determination of As requires separation of As from the matrix in most real samples. This is achieved by distillation in the form of $AsCl_3$ [2] or $AsBr_3$ [14], coprecipitation with hydroxides and hydrated oxides [4], and extraction of arsenic halides into nonpolar solvents [3, 12, 15, 16]. Arsenic separated by extraction is determined either directly in nonaqueous medium [16] or, more often, after back-extraction into the aqueous phase [3, 12, 15]. The advantage of extractive separation lies in that it is not time-consuming and that reduction of the inactive As(V) to active As(III) takes place simultaneously with separation.

EXPERIMENTAL

Analyzed were soil samples from different horizons (1st horizon = 10—20 cm, 2nd horizon = 30—40 cm, 3rd horizon = 50—60 cm) and the standard materials ECH No. 12-1-03 and EOP No. 12-1-02 (Institute of Radioecology and Utilization of Nuclear Technique, Košice). The soil samples were dried, homogenized, and sieved (0.2 mm mesh).

HCl and HNO_3 were of height purity, H_2SO_4 of reagent grade, and the other chemicals used were of anal. grade. The standard As(III) solution ($c = 5 \times 10^{-3}$ mol dm^{-3}) was prepared by dissolving As_2O_3 (0.2473 g) in 2 M-NaOH (10 cm^3). After dilution with deionized water to 100 cm^3 and acidifying with 3 M-H_2SO_4 (5 cm^3) the solution was made up to 250 cm^3 The standard solutions of lower concentrations (2.5×10^{-5}, 5×10^{-5}, 10^{-4} mol dm^{-3}) were freshly prepared before analysis by diluting the stock solution. In order to prevent oxidation of As(III) to inactive As(V), the standard solutions were stabilized by addition of $NH_2NH_2 \cdot H_2SO_4$.

Voltammetric measurements were performed on a PA 4 polarographic analyzer (Laboratorní přístroje, Prague) with three-electrode system consisting of static mercury drop electrode, saturated silver chloride electrode, and Pt supporting electrode, connected to an XY 4105 recorder. The conditions of measurements were the following: deposition potential $E_e = -0.475$ V, drop size (160 ms; 2.3 mg), deposition time $t_e = 40$ s, pulse amplitude – 50 mV, voltage scan rate 20 mV s^{-1}, current sensitivity 1—2 nA mm^{-1}, time constant of memory 100 ms. The method used was the fast scan differential pulse cathodic stripping vol-

tammetry. The solutions were deareated by bubbling through with prepurified nitrogen.

Extractions were performed in 25 cm^3 volumetric flasks and back-extractions in 10 cm^3 volumetric flasks fitted with polyethylene stopper. Additions of small quantities of solutions were made with UNI micropipettes (Plastomed, Poland).

Complete Decomposition of Samples

To the soil sample (0.3—0.4 g) or to the standard material (0.1 g) and contaminated soil in teflon crucible concentrated H_2SO_4 (2 cm^3) was added, followed by gradual addition of concentrated HF (2 cm^3) in small portions. After decomposition of silicates, the sample was heated on a sand bath under addition of concentrated HNO_3 (1.5—2.0 cm^3) until total decomposition. Traces of HNO_3 were removed by heating with concentrated HCOOH (1 cm^3).

Extraction and Voltammetric Determination of As

The sample after complete decomposition was quantitatively transferred into a 25 cm^3 volumetric flask and concentrated H_2SO_4 (14 cm^3) was added so that the final concentration of H_2SO_4 in the solution was 11.5 mol dm^{-3}. After cooling to room temperature 0.7 % $NH_2NH_2 \cdot H_2SO_4$ (1 cm^3) in 1.25 M-NaBr and toluene (1.5 cm^3) were added. The reaction mixture was then diluted to 25 cm^3 with deionized water and shaken vigorously for 5 min. After separation of phases, the organic phase (1 cm^3) was transferred with a dry pipette into a volumetric flask containing 10 cm^3 of solution of 1.5 M-HCl and 0.03 M-$NH_2NH_2 \cdot H_2SO_4$. Back-extraction of As(III) into aqueous phase lasted 2 min. For one determination 1—3 cm^3 of aqueous phase was pipetted and made up to 10 cm^3 so that the resulting concentration of HCl in the analyzed solution was 1 mol dm^{-3} After deaeration of the sample 0.04 M-$CuCl_2$ (50 mm^3) was added. The As(III) peak was recorded at the conditions mentioned above in the potential range of – 0.475 to – 0.875 V by cathodic stripping voltammetry with fast scan differential pulse record of the stripping step. For determination of As the method of standard additions was used. It was realized by five additions (20 mm^3) of 2.5×10^{-5} to 10^{-4} M-As(III). The As content was found out by treatment of concentration dependence by linear regression as intercept on the concentration axis. Analyzed were at least three different amounts of each sample.

RESULTS AND DISCUSSION

Very low contents of As may be determined by the method of stripping voltammetry using HMDE only in the presence of compounds which make easier the deposition of As in the form of inter-metallic compounds soluble in Hg. As follows from papers [10—12], Cu(II) has such an ability. In this work its favourable effect on the As(III) signal was utilized for voltammetric determination of As in soils.

Two-step electroreduction of As(III) ($As^{3+} \rightarrow As^0$, $As^0 \rightarrow As^{3-}$) makes possible to determine As(III) after deposition on HMDE by both anodic and cathodic stripping of the electrolysis product. However, Cu(II) present in the base electrolyte interferes with determination of As by anodic stripping voltammetry. On the contrary, in cathodic stripping voltammetry (CSV), due to further reduction of As^0 to As^{3-}, selective stripping of As from the deposited product takes place, which is indicated by a signal arising at the potential of -0.67 to -0.74 V in dependence on the Cu(II) concentration. In order to find out optimum con-
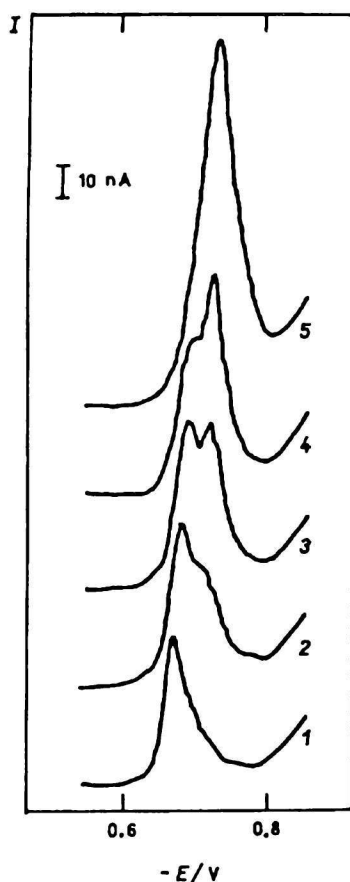

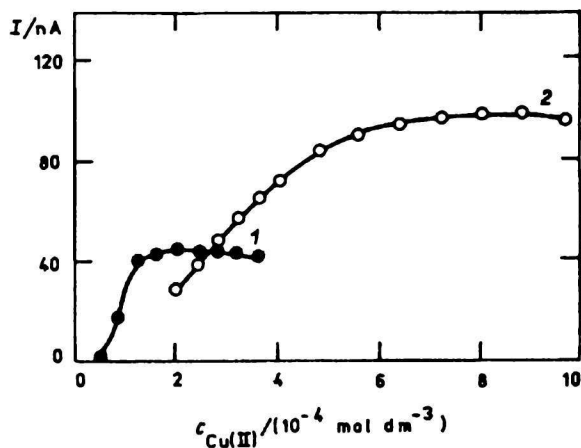**Fig. 2.** Dependence of the height of the As(III) peaks on concentration of Cu(II). $c_{HCl} = 1$ mol dm^{-3}, $c_{As} = 4 \times 10^{-7}$ mol dm^{-3}. *1.* Values for the As(III) peak at -0.68 V; *2.* values for the As(III) peak at -0.74 V.

ditions for determination of As by the CSV method on HMDE, the influence of concentrations of HCl and Cu(II) and of the deposition potential on the As(III) signal was investigated.

The concentration of Cu(II) in the base electrolyte is a decisive factor for sensitivity of determination of As(III) by the CSV method. Change in the Cu(II) concentration brings about a change of the height, shape, and position of the peak (Fig. 1). Because the data on optimum concentration of Cu(II) in papers [10—12] were controversial, in the present communication the effect of $c_{Cu(II)}$ on the As(III) signal was investigated and the optimum concentration was suggested. The As(III) peak appears at $c_{Cu(II)} \geq 8 \times 10^{-5}$ mol dm^{-3} and heightens with the increasing concentration of Cu(II) up to 10^{-3} mol dm^{-3}, except the narrow interval at $c = 2 \times 10^{-4}$ mol dm^{-3} (Fig. 2). With the change of $c_{Cu(II)}$ also the shape and potential of the peaks are changing, as indicated by the polarization curves in Fig. 1. At a certain $c_{Cu(II)}$ a second peak arises at more negative potential, which increases and shifts to more negative potentials with the increasing concentration of Cu(II), while the first peak disappears. Therefore, it is possible to assume the formation of two inter-metallic compounds with different ratios of Cu and As. The authors in [7] on the basis of X-ray structural analysis confirmed the formation of an intermetallic compound of Cu_3As composition on graphite electrode. In evaluation of As(III) by the method of calibration curve, it is advantageous to work at conditions when the As(III) signal does not change with the changing concentration of Cu(II). It follows from experimental measurements that the optimum concentration of Cu(II) for As(III) determination by the CSV method changes with
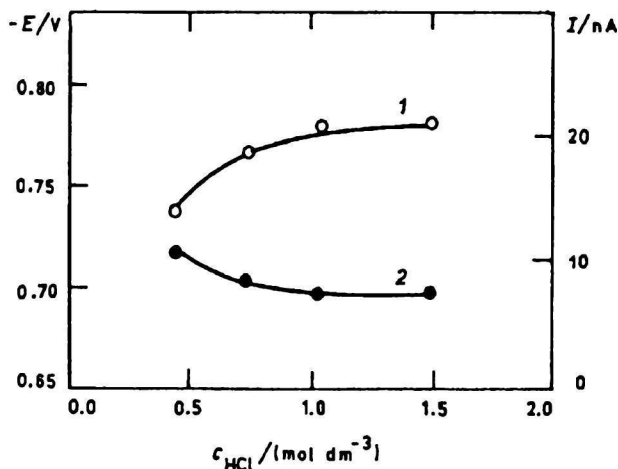

Fig. 1. Effect of concentration of Cu(II) on the nature of the As(III) signal. $c_{HCl} = 1$ mol dm^{-3}, $c_{As} = 4 \times 10^{-7}$ mol dm^{-3}, $c_{Cu}/(10^{-4}$ mol dm$^{-3})$: *1.* 1.2; *2.* 2.0; *3.* 2.8; *4.* 3.6; *5.* 5.6.

Fig. 3. Effect of concentration of HCl on the height I (1) and potential E (2) of the As(III) peaks. $c_{As} = 2 \times 10^{-7}$ mol dm^{-3}, $c_{Cu} = 2 \times 10^{-4}$ mol dm^{-3}.

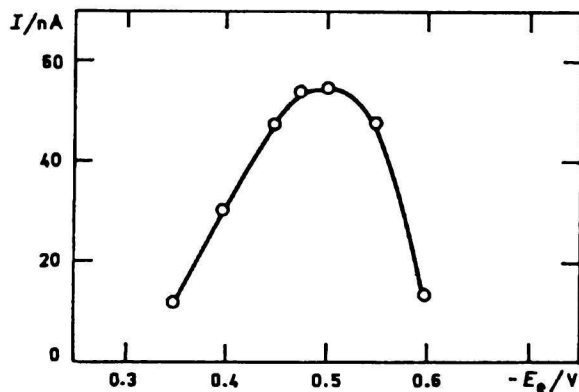**Fig. 4.** Dependence of the As(III) signal on deposition potential. $c_{HCl} = 1$ mol dm^{-3}, $c_{As} = 5 \times 10^{-7}$ mol dm^{-3}, $c_{Cu} = 2 \times 10^{-4}$ mol dm^{-3}.

the size of Hg drop and deposition time. For 160 ms Hg drop and deposition time $t_e = 40$ s, the advised concentration of CuCl$_2$ is 1.8×10^{-4} to 2×10^{-4} mol dm^{-3}. At higher concentrations of Cu(II) the sensitivity of determination is higher but the determination is less precise because the As(III) peak is located on the increasing part of the peak belonging to base electrolyte. As Cu(II) catalyzes the oxidation of As(III) to inactive As(V), the solution of the Cu(II) salt is added only after thorough deaeration of the sample.

It follows from the literature [10—12] as well as from our own experience with determination of As(III) by SW-polarography [17] that HCl is a suitable base electrolyte for determination of As(III). As the height of the As(III) peak depends on concentration of HCl, obviously as a consequence of changes of the ratio of chloro and hydroxo complexes of As(III), the optimum base electrolyte (1—1.5 M-HCl) was chosen on the basis of study of the influence of the HCl concen-

tration on the As(III) signal. The effect of concentration of HCl on the height and potential of the As(III) peaks is illustrated in Fig. 3.

The suitable working conditions for electrolytical deposition of As on HMDE have been chosen on the basis of the DPP curves in 1 M-HCl and of the dependence of the height of the As(III) peak on the deposition potential in CSV. The potential of the first peak on the DPP record, corresponding to As$^{3+} \rightarrow$ As^0 reduction, was -0.385 V. As follows from Fig. 4, the maximum signal in CSV was achieved in the narrow range of potentials (-0.475 to -0.5 V). Due to possible reduction of As to AsH$_3$, at more negative potentials the As(III) signal decreases.

The results of study of the effect of Cu(II) and HCl concentrations on the As(III) signal showed that the solution of 1 M-HCl and 0.0002 M-CuCl$_2$ was a suitable base electrolyte for determination of As(III) by the CSV method. In this medium the dependence of the peak height on concentration of As(III) was linear in the interval of $c = 10^{-7}$— 10^{-6} mol dm^{-3}.

Table 1. Results of Determination of As in Soils

	Sample	Horizon	$L_{1,2}$/ppm	$s_{\bar{x}}$ /%	e /%
Standard	ECH No. 12-1-03		58.6 ± 1.5	1.1	3.0
material	EOP No. 12-1-02		82.7 ± 3.4	1.7	4.6
Soil	N-1-TT	1	9.2 ± 0.5	2.5	
		2	10.1 ± 0.3	1.4	
		3	5.4 ± 0.3	3.2	
	N-2-LM	1	5.2 ± 0.2	2.3	
		3	5.0 ± 0.3	2.6	
	N-5-ZV	1	9.0 ± 0.5	2.7	
		2	8.8 ± 0.6	3.2	
		3	9.6 ± 0.4	2.1	
	N-3-PD	1	78.6 ± 2.8	1.6	

$L_{1,2}$ - confidence limit calculated for $\alpha = 0.05$, $s_{\bar{x}}$ - relative standard deviation of arithmetic mean, e - relative error.

In complex samples, such as soils, direct voltammetric determination of As after total decomposition of the sample is not possible. The determination itself has to be preceded by separation of As from the complex soil matrix and reduction of the inactive As(V) to As(III). Of several possible procedures, extraction of $AsBr_3$ from H_2SO_4 into toluene was chosen [15]. The extraction is not only rapid, selective, and highly effective (99—100 %), but As(V) is simultaneously reduced to As(III) with HBr, arising from NaBr in the presence of H_2SO_4. For quantitative separation one extraction is sufficient. At the given experimental conditions Sb and Sn are coextracted with As [15,18]. The efficiency of extraction depends on concentrations of H_2SO_4 and NaBr. The effect of concentration of H_2SO_4 on efficiency of extraction at three concentrations of NaBr (0.5, 0.1, and 0.05 mol dm^{-3}) was investigated with standard As samples. While at the As concentration $\rho = 1$—6 μg cm^{-3} for quantitative extraction $c(H_2SO_4) = 10$ mol dm^{-3} was sufficient [17], at $\rho = 30$—130 ng cm^{-3} 100 % extraction was achieved only at $c(H_2SO_4) >$ 11 mol dm^{-3}. On the basis of our experimental results for the given concentration level of As in soils the medium of 11.5 M-H_2SO_4 and 0.05 M-NaBr is suggested. On reduction of As(V) and other components present in the sample with HBr, a certain amount of Br_2 is always formed and coextracted. To prevent possible oxidation of As(III), prior to extraction NH_2NH_2 H_2SO_4 was added into aqueous solutions as well as into the base electrolyte. Arsenic was determined voltammetrically after back-extraction from toluene into the solution of 1.5 M-HCl and 0.03 M-$NH_2NH_2 \cdot H_2SO_4$.

Though Sb itself does not provide any signal in CSV, it affects the signal of As(III), mainly at concentrations higher than that of As(III). Therefore, only the method of standard additions was used for evaluation of the As concentration.

The developed procedure was tested by analysis of two standard materials EOP No. 12-1-02 and ECH No. 12-1-03 (light ash from thermal power stations) with the As content of (79.1 ± 6.6) ppm and (56.9 ± 4.3) ppm, respectively. The results obtained are in good agreement with the values declared (Table 1).

The results of determination of As in the analyzed soil samples after total decomposition at the described experimental conditions are summarized in Table 1. From the presented data it follows that the precision of determination is very good, the relative standard deviations vary from 1.1 to 3.2 %.

The analytical procedure developed for determination of low contents of As in complex soil matrices by the CSV method is reliable, the number of operations preceding the electrochemical determination itself is low, and the instrumentation simple.

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