DETERMINATION OF TRACE AMOUNTS OF HEAVY METALS IN FOODSTUFFS BY ANODIC STRIPPING VOLTAMMETRY. OPTIMIZATION OF APPARATUS PARAMETERS

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The use of differential pulse anodic stripping voltammetry in the determination of heavy metals (Cd, Pb, Cu, As) in foodstuffs was studied. Preconcentrating from solutions and dissolution took place on a thin film mercury electrode. A factorial experiment served to determine the effects of variable parameters of the apparatus, a polarographic analyzer: pulse amplitude, pulse period, and potential scan of the working electrode during dissolution. The first two parameters are significant but the scan rate is not. The apparatus parameters were optimized further by the method of response surface fitting near optimum.

For the determination of trace quantities of heavy metals in water, soil, and foodstuffs, an analytical method with a high enriching factor, accuracy, sensitivity, and relative simplicity must be used. Anodic stripping voltammetry (ASV) satisfies these conditions and it has been more extensively applied during last years thanks to the possibility of a simultaneous determination of several elements in concentrations lower than 1 ppb[1].

With respect to the interfering influence of the capacity current in the ASV method using a linear increase of the polarization voltage, different methods with a modulated polarization voltage were proposed, such as alternating current (AC), second harmonic alternating current (AC_2), normal pulse (NP), differential pulse (DP), square wave (SW), stepped voltage, and intermodulation methods[2-8]. Of these, the differential pulse anodic stripping voltammetry (DPASV) is most sensitive to both reversible and irreversible systems. With the use of a thin film mercury electrode[5,9], this method is very sensitive in the determination of heavy metals in water[10], biological materials[11], and foodstuffs[12].

EXPERIMENTAL

For the purification of volatile acids and bases, a method was elaborated based on transferring the vapour from a distillation bottle at a low temperature by means of stream of pure air to the surface of distilled water[13-16]. The same method was used in preparing very pure water from an alkaline solution containing potassium permanganate[16].

Standard solutions of Cd, Pb, and Cu (concentration 0·01 mol/l) were prepared by dissolving pure metals (99·999%, Research Institute of Metals, Panenské Břežany) in purified nitric acid. Lower concentrations were obtained by diluting with pure water.

The solutions were analysed in a glass vessel (Simax, Kavalier) whose lower was half conically constricted. Oxygen was removed by bubbling with pure nitrogen, which passed through an acidified solution of vanadyl sulphate containing a zinc amalgam[17].

Measurements were done on a polarographic analyzer of the type PA-2 with an EZ-7 recorder (Laboratory Work, Prague). The chart speed was always 2 cm/min. Further conditions are indicated below.

Glassy carbon (Carbon Loraine, France) in the form of a rod of 0·3 cm diameter was fastened in a Teflon holder (1 cm outer diameter and 6·7 cm length) and used as a rotating disc electrode. Prior to every measurement, the electrode was ground with a metallographic emery paper, polished with $CaCO_3$, rinsed with diluted HCl (1 : 1) and finally with distilled water[16]. A saturated calomel electrode joined with the measured solution by a salt bridge served as reference. The auxiliary electrode was of platinum.

RESULTS AND DISCUSSION

The height of the anodic dissolution current or the sensitivity of the measurement depends on many factors. Several of these, selected according to the literature data, were examined, for example the scan rate, the rotation speed of the electrode, and the pulse amplitude (for DPASV). With respect to the large number of influencing factors, it is difficult to select the experimental conditions so that only changes of a single factor could be studied. This is the reason for the diverging experimental data in the literature. To follow the influence of all the selected factors, a factorial experiment was used[18–20].

The reason for the use of the factorial experiment in the present work is that there is no mathematical relation according to which the influence of individual factors (both instrumental and chemical) on the sensitivity of the DPSAV method could be calculated. The known relations described only the influence of individual factors, for example the equation $I_p = 0{\cdot}138 Q_m/\tau_p$, where τ_p denotes the pulse duration[21], or $I_p = f(\Delta E)$, where ΔE denotes the pulse amplitude[22]. Since these equations do not involve the mutual effect of the factors, they cannot lead to optimization of the experiments with respect to the highest sensitivity. It was found, *e.g.*, that the influence of the scan rate on the sensitivity of the measurement is different at different pulse amplitudes[16].

The factors influencing the sensitivity of the DPASV method were divided into two groups: instrumental and chemical. Some of the instrumental factors, *e.g.* the pulse duration, are constants of the apparatus used. Variable factors are the pulse amplitude, the pulse period, and the scan rate. The second group involves the pH of the solution, the time of electrolysis, the concentration of Hg(II) ions, *etc.* For each group of factors, a special factorial experiment of the type 2^k was carried out. We assumed that no interactions exist between the chemical and the instrumental factors.

The chemical factors were kept constant in all experiments: concentration of Hg(II) ions $c_{Hg^{2+}} = 1 \cdot 10^{-4}$ mol/l, time of electrolysis (enrichment) $t_{el} = 80$ s, pH of the supporting electrolyte 4·6. Since the PA 2 apparatus enabled us to change the three parameters mentioned above, a factorial experiment of the type 2^3 was done.

The upper (+) and lower (−) limits of the instrumental factors were chosen according to Table I. The metal to be determined was Pb and each experiment was repeated twice a day. The results are given in Table II. The experiments were evaluated according to the sign scheme, where the individual results are replaced by the sums of the results of two measurements (Table III).

The calculated values of F according to ref.[19] in comparison with the tabulated critical value of $F_{\alpha=0.05}(1 \cdot 8) = 5 \cdot 3$ show that the amplitude (A) and pulse period (B) are significant for the sensitivity of the measurement. On the other hand, the scan rate

TABLE I

Upper and lower limits of apparatus parameters

	upper l.	lower l.
$E \equiv$ A pulse ampl.	100 mV	12·5 mV
$\tau \equiv$ B pulse period	4 s	1 s
$\beta \equiv$ C scan rate	5 mV/s	1 mV/s

TABLE II

Sign scheme for the factorial experiment

Exp. No	A	B	C	I_p (Pb),	μA
1	−	−	−	6·5	8·0
2	−	−	+	5·5	7·0
3	−	+	−	4·5	5·0
4	−	+	+	2·0	2·0
5	+	−	−	17·0	21·0
6	+	−	+	21·0	24·0
7	+	+	−	11·5	13·0
8	+	+	+	8·5	10·0

$c^{2+}_{Pb} = 1 \cdot 10^{-6}$ mol/l, $t_{el} = 80$ s, $E_{el} = -1 \cdot 0$ V, $c^{2+}_{Hg} = 1 \cdot 10^{-4}$ mol/l, pH of analysed solution 4·6.

of the PA 2 apparatus is not significant and does not influence the sensitivity of the measurement. It is also seen that a mutual interaction exists between the couples $\Delta E - \tau(AB)$ and $\tau - \beta(BC)$ (significant factors are denoted by an asterisk).

As a further step, it was necessary to find the optimum values of the instrumental parameters. Since the response of the apparatus is best under the conditions of the experiment 6 (Table I), we used the method of response surface fitting near optimum to determine the optimum region at the same scan rate[19]. The most preferable arrangement of experiments is a factorial experiment of the type 3^k (k denotes the num-

TABLE III

Analysis of the dispersion variance of the factorial experiment for the apparatus parameters

Source of variance	Sum of squares	Degree of freedom	Mean square	F
A	446·3	1	446·3	193·9*
B	172·3	1	172·3	66·3*
C	3·5	1	3·5	1·4
AB	40·6	1	40·6	15·6*
AC	3·5	1	3·5	1·4
BC	15·0	1	15·0	5·7*
ABC	4·5	1	4·5	1·7
residual	20·6	8	2·6	—

* Significant factor.

TABLE IV

Factorial experiment 3^2 for optimization of apparatus parameters

Exp. No	Factor		$I_p/\mu A$	Exp. No	Factor		$I_p/\mu A$
	ΔE/mV	τ/s			ΔE/mV	τ/s	
1	12·5	1	5·5	6	50	4	10·0
2	12·5	2	4·5	7	100	1	24·0
3	12·5	4	2·0	8	100	2	20·0
4	50	1	22·0	9	100	4	10·0
5	50	2	14·5				

$c_{Pb}^{2+} = 1 \cdot 10^{-6}$ mol l^{-1}, $c_{Hg}^{2+} = 1 \cdot 10^{-4}$ mol l^{-1}, $t_{el} = 80$ s, $\beta = 5$ mV/s, pH = 4·6.

ber of significant factors), where three levels correspond to each factor. The number of experiments carried out was equal to 3^2, the levels of the factors were 12·5, 50, and 100 mV for the amplitude and 1, 2, and 4 for the pulse period. Their combinations and the results of the measurements are given in Table IV.

Apparently, experiment 7 gave the best result, which corresponds to experiment 6 in Table II. The sensitivity increases with increasing amplitude (experiments 1, 4, 7, and 2, 5, 8), however the increase is less marked when the amplitude is higher than 50 mV, which is in accordance with theory[22]. The sensitivity increases also with decreasing pulse period, which is in accordance with ref.[15] but at variance with ref.[11]. Thus, the optimum parameters of the apparatus are $\Delta E = 100$ mV, $\tau = 1$ s, and $\beta = 5$ mV/s.

LIST OF SYMBOLS

A electrode surface
c concentration of the substance to be determined
E_{el} imposed electrolysis voltage
ΔE pulse amplitude
F distribution function
I_p peak dissolution current
Q_m charge consumed during electrolysis
τ pulse period
t_{el} time of electrolysis (enrichment)
β scan rate

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