THE DETERMINATION OF TRACE AMOUNTS OF HEAVY METALS IN FOODSTUFFS BY ANODIC STRIPPING VOLTAMMETRY: OPTIMIZATION OF CHEMICAL FACTORS

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A study was made of the use of differential pulse anodic stripping voltammetry (DPASV) for the determination of heavy metals (Cd, Pb, Cu) in foodstuffs. A thin-film mercury electrode was used for preconcentration from solution and dissolution. After prior optimization of the instrumental parameters, the effect of the following chemical factors was studied: concentration of mercury(II) ions, electrolysis (enrichment) time and the pH of the background electrolyte. It was found that all three factors affect the sensitivity of the determination of Cd and Pb, while only the electrolysis time and electrolyte pH are important for Cu. All three factors were optimized by the simplex method. The dependence between the concentration and the peak dissolution current was measured for all three metals and the detection and determination limits were found.

Chemical factors such as the composition of the base electrolyte, the pH of the analyzed solution, the thickness of the mercury film, the electrolysis (enrichment) time, stirring rate (mass transport to the electrode), indicator electrode potential during electrolysis, *etc.*, can affect measurements using the differential pulse anodic stripping voltammetric method (DPASV) using a thin-film mercury electrode (TMFE). In optimization of these factors, it is first necessary to determine whether they are important and whether their values affect the measuring sensitivity. For this purpose, similarly as in optimization of instrumental parameters, a series of measurements was carried out (factor experiment). Acetate buffer[1] was used as base electrolyte and its pH was considered as the first factor affecting the measuring sensitivity. The mercury film is deposited on the glassy carbon electrode either before the determination or during the determination simultaneously with the studied ionic metals. Comparison of these two methods has indicated that deposition of the mercury film prior to the determination is unsuitable[2]. In our procedure, mercury was deposited on the electrode simultaneously with the determined metals and the concentration of mercury(II) ions in solution (affecting the thickness of the mercury film) was the second factor studied. The potential of the indicator electrode during the electrolysis is a further important factor. In the determination of Cd, Pb and Cu, this value was maintained constant at $-1{\cdot}0$ V as the drops of deposited mercury are roughly of identical size and are evently distributed at this potential. The effect of stirring the solution during the electrolysis was studied separately and the solution was stirred at the same electrode rotation rate (155 rpm) during all the experiments. It was assumed that there is no interaction between the rate of electrode rotation and the other factors. The final parameter studied was the electrolysis time t_{el}.

The effects of these factors on the determination of individual metals (Cd, Pb and Cu) may differ and thus factor experiments were carried out simultaneously for all three metals. It was assumed that there is no interaction between the metals at a concentration of $1 \,.\, 10^{-7}$ mol l^{-1} and that no intermetallic compounds are formed.

RESULTS AND DISCUSSION

The following upper and lower limits of the tested factors, *i.e.* concentration of Hg^{2+} ions (A), electrolysis time (B) and pH of the base electrolyte (C) were selected:

$c_{Hg^{2+}}$ (A) $4 \,.\, 10^{-5}$ mol l^{-1} and $4 \,.\, 10^{-6}$ mol l^{-1};
t_{el} (B) 360 s and 80 s;
pH (C) 5·8 and 3·6.

Experiments were carried out according to a sign scheme for Cd, Pb and Cu. All the measurements were repeated twice over one week The results are given in Table I. Table II gives evaluation of the experiments for these metals.

TABLE I

Sign scheme for the factor experiment on the chemical parameters (2^3)

Exp. No	A	B	C	I_p(Cd), μA		I_p(Pb), μA		I_p(Cu), μA	
				I	II	I	II	I	II
1	−	−	−	0·0	0·1	0·0	0·2	0·2	0·2
2	+	−	−	0·1	0·2	0·1	0·2	0·2	0·3
3	−	+	−	0·3	0·4	2·3	2·0	2·5	1·8
4	+	+	−	1·3	1·5	4·1	3·9	2·5	2·3
5	−	−	+	0·7	1·0	2·2	1·8	1·5	1·6
6	+	−	+	1·3	1·4	3·0	2·7	1·7	1·6
7	−	+	+	4·5	6·0	8·5	8·0	7·6	7·0
8	+	+	+	7·8	7·0	9·0	10·8	8·0	8·0

$c_{Cd^{2+}} = c_{Pb^{2+}} = c_{Cu^{2+}} = 1 \,.\, 10^{-7}$ mol/l; $E_{el} = -1·0$ V; $V = 25$ ml.

Instead of carrying out the calculation for the individual data, calculations were based on the sum of two identical measurements, where a total number of measurements of $2 \times 2^3 = 16$ was considered for statistical evaluations.

Comparison of calculated values of the Fisher distribution F from ref.[4] with the tabulated critical value $F_{\alpha=0\cdot05}(1\cdot8) = 5\cdot3$ indicates that the concentration of mercury(II) ions (*A*), electrolysis time (*B*) and pH value (*C*) affect the sensitivity of the determination of cadmium and lead, while only factors *B* and *C* are important for copper. In the range tested, the concentration of mercury(II) ions does not affect the sensitivity of the determination of copper, possibly because of the low solubility of copper in mercury. This observation is in agreement with the results in Fig. 1,

TABLE II

Analysis of the scatter in the factor experiment on the chemical parameters

Source of change	F Cd	 Pb	 Cu
A	18·9*	20·2*	5·2
B	188·5*	384·0*	1 131·2*
AB	8·8*	7·0*	2·4
C	217·8*	287·0*	786·6*
AC	2·9	—	1·0
BC	103·6*	57·0*	275·8*
ABC	0·6	1·0	0·6
Residual	—	—	—

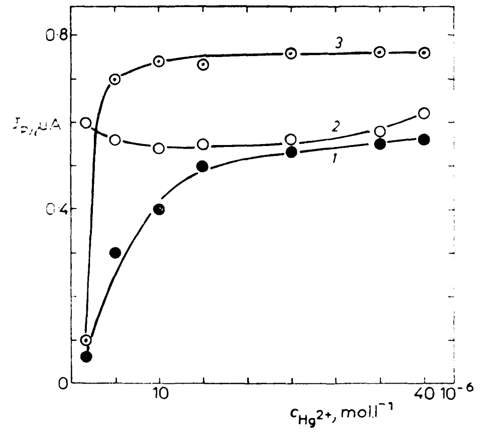

FIG. 1

Dependence of the sensitivity of the determination of *1* Cd, *2* Cu and *3* Pb on the concentration of mercury(II) ions; $c_{Cd^{2+}} = c_{Pb^{2+}} = c_{Cu^{2+}} = 1 \,.\, 10^{-7}$ mol l^{-1}, $t_{el} = 6$ min., pH 4·6 depicting the dependence of the peak dissolution current I_p (peak height) on the concentration of mercury ions at constant values of the other chemical factors.

No theory has been developed for the effect of the pH of the base electrolyte on the sensitivity of determinations using the DPASV method. It has been suggested that the optimal pH value in an acetate medium lies between 5 and 5·8 (ref.[5,6]), but adequate reasons have not been given. The pH value can affect the pre-electrolysis, anodic dissolution, or both of these steps. Thus two more experiments were carried out, with constant pre-electrolysis potential and different pH values during the anodic dissolution.

The results in Table III indicate that the sensitivity of the determination is sensitive to the pH during the anodic dissolution rather than during the pre-electrolysis. This observation can be explained on the basis of knowledge of the equilibrium compositions of complexes of acetate at pH 3·6 and 5·8 with these metals.

The stability constants for the complexes of Cd, Pb and Cu with acetate ions were obtained from the literature[7] and the compositions of the complexes with acetate ions were calculated according to ref.[8]. The results obtained are listed in Table IV.

Reactions occurring at the boundary between the electrode and the solution during anodic dissolution can be expressed as:

1. Anodic oxidation $M = M^{n+} + ne$
2. Complex formation $M^{n+} + mAc^- = M(Ac)_n^{n-m}$ $(m = 1, 2, \ldots, 4)$.

It is necessary that the rate of the second reaction be much greater than that of the first reaction[9], and thus the equilibrium conditions for the composition of the complexes with acetate ions were calculated. The calculated data indicate that, at pH 5·8 the great majority of the oxidized metal formed during anodic dissolution forms a complex with acetate ions, increasing the rate of anodic dissolution and improving the sensitivity of the determination; at pH 3·6, the opposite effect is operative.

After determination of the important factors affecting the sensitivity of the measurement, it was necessary to find the optimal values. For this purpose, the simplex method[10-12] was used and lower and upper limits were found for each factor. The factors were normalized[12] (to ensure same weight for each factor during optimization) using the relationship

$$F_M = m - m_D/m_H - m_D \,,$$

where m is the actual value, m_H and m_D are the upper and lower limit of the factor. For K factors, K + 1 points were employed with various levels of these factors. After measuring the anodic dissolution current for the individual points, the point with the smallest response was eliminated and a new point was found using relationship[11]: $R = P + \gamma(P - W)$, where R is the level of the factor for the new point and P is the average of the values (levels) of the factors (except for the excluded point) and W is that of the excluded point. A value of 1 was selected for coefficient γ.

The initial point in the first simplex was selected as point 8 in the factor experiment (Table I), corresponding to the largest anodic dissolution current. Further simplexes were measured until the anodic dissolution current increased no longer.

The step chosen for $c(\mathrm{Hg})^{2+}$ (factor A) was 0·1 mg Hg^{2+} in a volume of 25 ml, for factor t_{el} (B), 80 s and for the pH (factor C), 1 degree.

Factors A, B and C were normalized in the following manner:

TABLE III

Analysis of the effect of the pH value on the sensitivity of the determination of Cd, Pb and Cu

pH During electrolysis	3·6			3·6		
pH During anodic dissolution	3·6			5·8		
I_p, μA	Cd	Pb	Cu	Cd	Pb	Cu
	1·2	2·4	2·2	7·5	9·0	8·1

TABLE IV

Compositions of the Cd, Pb and Cu complexes with acetate ions at pH 3·6 and pH 5·8

Cadmium	Cd^{2+}, %	CdAc^{+}, %	$\mathrm{Cd(Ac)}_2$, %	$\mathrm{Cd(Ac)}_3^-$, %	$\mathrm{Cd(Ac)}_4^{2-}$, %
pH 3·6	83·67	14·30	2·00	0·03	—
pH 5·8	16·24	30·80	45·76	6·80	0·50
Lead	Pb^{2+}, %	PbAc^{+}, %	$\mathrm{Pb(Ac)}_2$, %	$\mathrm{Pb(Ac)}_3^-$, %	$\mathrm{Pb(Ac)}_4^{2-}$, %
pH 3·6	32·86	47·05	20·09	—	—
pH 5·8	0·85	17·40	81·75	—	—
Copper	Cu^{2+}, %	CuAc^{+}, %	$\mathrm{Cu(Ac)}_2$, %	$\mathrm{Cu(Ac)}_3^-$, %	$\mathrm{Cu(Ac)}_4^{2-}$, %
pH 3·6	49·30	43·03	7·32	0·31	—
pH 5·8	2·33	25·35	47·72	22·27	2·63

TABLE V

Simplex method for optimization of the chemical factors in the determination of Cd, Pb and Cu by the the DPASV method on a mercury film electrode

Simplex No 1	Peak No	μA			Factors		
		Cd	Cu	Pb	A	B	C
	1	7·8	8·0	10·0	1·000	1·000	1·000
	2	7·2	8·0	9·0	0·444	1·000	1·000
	3	6·1	6·4	8·0	0·722	0·753	1·000
	4	7·0	7·4	8·5	0·722	0·917	0·629
Sum of retained coordinates = S					2·166	2·917	2·629
$p = S/K$					0·722	0·972	0·876
Excluded apex	3				0·722	0·753	1·000
New apex	5				0·722	1·191	0·752
Simplex No 2	1	7·8	8·0	10·0	1·000	1·000	1·000
	2	7·2	8·0	9·0	0·444	1·000	1·000
	4	7·0	7·4	8·5	9·722	0·917	0·629
	5				0·722	1·191	0·752
	5′	7·4	7·8	9·5	0·722	1·000	0·752
Sum of retained coordinates = S					2·166	3·000	2·752
$P = S/K$					0·722	1·000	0·917
Excluded apex	4				0·722	0·917	0·629
New apex	6				0·722	1·274	1·205
Simplex No 3	1	7·8	8·0	10·0	1·000	1·000	1·000
	2	7·2	8·0	9·0	0·444	1·000	1·000
	5′	7·4	7·8	9·5	0·722	1·000	0·752
	6				0·722	1·274	1·205
	6′	7·6	8·0	9·5	0·722	1·000	1·000
Sum of retained coordinates = S					2·444	3·000	2·752
$P = S/K$					0·815	1·000	0·917
Excluded apex	2				0·444	1·000	1·000
New apex	7				1·186	1·000	0·834
Simplex No 4	1	7·8	8·0	10·0	1·000	1·000	1·000
	5′	7·4	7·8	9·5	0·722	1·000	0·752
	6′	7·6	8·0	9·5	0·722	1·000	1·000
	7				1·186	1·000	0·834
	7′	7·6	8·2	9·5	1·000	1·000	0·834
Sum of retained coordinates = S					2·722	3·000	2·834
$p = S/K$					0·907	1·000	0·945
Excluded apex	5′				0·722	1·000	0·752
New apex	8				1·092	1·000	1·148
					1·000	1·000	1·000

$$F_A = (M-4\,.\,10^{-6})/(4\,.\,10^{-5}-4\,.\,10^{-6}) = (M(mg)-0{\cdot}02\ mg/25\ ml)/(0{\cdot}2-0{\cdot}02) = (M-0{\cdot}02)/0{\cdot}18$$

$$F_B = (t_{el}-80)/(360-80) = (t_{el}-80)/280$$

$$F_C = (pH\text{-}3{\cdot}6)/(5{\cdot}8-3{\cdot}6) = (pH\text{-}3{\cdot}6)/2{\cdot}2$$

The actual value of each factor was calculated according to the relationship, $m = m_H - f\,.\,q$, where f is found according to ref.[12] and q is the selected step. The results of the simplex method are given in Table V.

It can be seen that new apex 8 is roughly identical with apex No 1. This point was considered to be the maximum in the simplex method. The following optimal conditions for the chemical factors in the determination of Cd, Pb and Cu were

TABLE VI

Concentration range for value *a* and *b*

Element	$c\,.\,10^{-9}$, mol l^{-1}	*a*, μA	*b*, μA mol l^{-1}
Cd	1– 10	−0·122	$0{\cdot}83\,.\,10^8$
	10– 100	−0·16	$0{\cdot}86\,.\,10^8$
	100–1 000	−1·62	$0{\cdot}994\,.\,10^8$
Pb	1– 10	−0·119	$1{\cdot}41\,.\,10^8$
	10– 100	0·34	$1{\cdot}16\,.\,10^8$
	100–1 000	−0·49	$1{\cdot}247\,.\,10^8$
Cu	10– 100	3·87	$0{\cdot}64\,.\,10^8$
	100–1 000	−7·44	$1{\cdot}869\,.\,10^8$

TABLE VII

Limits of detection and determination for Cd, Pb and Cu

Ion	Average I_b μA	S_b	Detection limit mol l^{-1}	Determination limit mol l^{-1}
Cd	—	—	$1{\cdot}4\,.\,10^{-9}$	$4{\cdot}2\,.\,10^{-9}$
Pb	0·4	0·05	$0{\cdot}3\,.\,10^{-9}$	$0{\cdot}9\,.\,10^{-9}$
Cu	1·8	0·70	$0{\cdot}4\,.\,10^{-9}$	$1{\cdot}2\,.\,10^{-9}$

found by the simplex method:

$$A = c_{Hg^{2+}} = 0{\cdot}2\ \mathrm{mg/25\ ml} = 4 \,.\, 10^{-5}\ \mathrm{mol\ l^{-1}}\,, \quad F_A = 1$$

$$B = \text{electrolysis time} = t_{el} = 360\ \mathrm{s}\,, \quad F_B = 1$$

$$C = \text{solution pH during anodic dissolution} = 5{\cdot}8, \quad F_C = 1\,.$$

All subsequent measurements for cadmium, lead and copper were carried out under these conditions.

Calibration Curve for the Determination of Cd, Pb *and* Cu

The dependence between concentration c and the peak dissolution current I_p for the determination of Cd, Pb and Cu was found using the optimal instrumental parameters and optimal values of the chemical factors. The calibration curves obtained for Cd and Pb have 3 linear regions with various slope values. The calibration curve of copper has two linear regions. These linear regions can be described by the simple relationship

$$I_p = a + bc\,,$$

where I_p is in μA and c in mol l^{-1}, so that the values for a and b for the individual metals and concentration ranges are given in Table VI.

Detection Limits and Determination Limits for Cd, Pb *and* Cu

For most instrumental methods, the detection limit is depedent on the blank values for the analyzed ion and its deviation[13]. The anodic dissolution current obtained for Cd, Pb and Cu in the base electrolyte (blank) was measured under optimal instrumental and chemical factor conditions. The measurement was repeated 5 × and the standard deviation was calculated. The current corresponding to the detection limit I_d was calculated using the relationship[14]:

$$I_d - I_b = 2\sqrt{(2)}\, S_b\,,$$

where S_b is the standard deviation of the blank and I_b is the average anodic dissolution current for the blank for the given metal. The current corresponding to the determination limit I_s was calculated using the relationship[13]:

$$I_s - I_b = KS_b\,, \quad \text{where} \quad K = 10\,.$$

Results for the detection limit and determination limit for Cd, Pb and Cu are listed in Table VII. The detection and determination limits for Cd were found using the calibration curve.

REFERENCES

1. Aliakbar A.: *Thesis*. Prague Institute of Chemical Technology, Prague 1981.
2. Batley G. E., Florence T. M.: J. Electroanal. Chem. Interfacial Electrochem. *55*, 23 (1974).
3. Štulíková M.: J. Electroanal. Chem. Interfacial Electrochem. *48*, 33 (1973).
4. Felix M., Bláha K.: *Matematicko-statistické metody v chemickém průmyslu*, p. 205. Published by SNTL, Prague 1962.
5. Copeland T. R., Christie J. H., Osteryoung R. A., Skogerboe R. K.: Anal. Chem. *45*, 2171 (1973).
6. Pinchin M. J., Newham J.: Anal. Chem. Acta 90, 91 (1977).
7. Budevsky O.: *Foundations of Chemical Analysis*, p. 348. Wiley, New York, 1979.
8. Šůcha L., Kotrlý S.: *Teoretické základy analytické chemie*, p. 60. Published by SNTL, Prague 1971.
9. Brainina Kh. Z.: Talanta *18*, 513 (1971).
10. Deming S. N., Morgen S. L.: Anal. Chem. *45*, 278A (1973).
11. Long E.: Anal. Chim. Acta *46*, 193 (1969).
12. Morgen S. L., Deming S. N.: Anal. Chem. *46*, 1170 (1974).
13. *Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry*: Anal. Chem. *52*, 2242 (1980).
14. Florence T. M.: J. Electroanal. Chem. Interfacial Electrochem. *27*, 273 (1970).

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