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**SOME NEW METHODS  
OF INDIRECT DETERMINATION OF METALS  
BASED ON ADSORPTION AND COMPLEXATION  
PROPERTIES OF ARSENAZO III AZO DYE**

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*Voltammetric properties of Arsenazo III were studied in view of its exploitation for trace analysis of metal ions using adsorptive stripping voltammetry. Conditions for determinations of uranium and aluminium were optimized and the corresponding procedures suggested.*

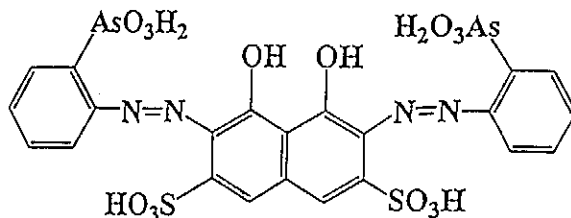
### **Introduction**

Arsenazo III (chemically 1,8-dihydroxy-2,7-bis-(2-arsonophenylazo)-naphthalene-3,6-disulfonic acid or its disodium salt, see formula) was synthesized at the end of fifties during a search for new metalochromic indicators and organic

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reagents as a compound derived from chromotropic acid [1,2]. In the solid state, it has a form of dark red crystalline powder soluble in water, its neutral solutions are stable. The solutions are coloured from pink to dark red at pH < 4 and from violet to blue at pH > 5. Analytical significance of this azo dye follows from its ability to form complexes with numerous cations which can be used for the tests and photometric determinations of uranium, titanium, zirconium, hafnium and thorium, lanthanoids, and others [3-34].



Arsenazo III

Chemical equilibria of Arsenazo III (AZIII) are rather complicated and, although investigated in detail, many significantly different data, especially for its acid-base reactions, are given in literature [6,10,27,35]. These contradictions are usually explained by an inadequate purity of the reagent samples used [35]. Depending on pH, AZIII is able to form nine species from  $H_9L^+$  to  $L^{8-}$  liable to eight protonation and/or dissociation equilibria. The corresponding dissociation constants were calculated on the basis of spectrophotometric measurements; it follows that the dissociation of  $-SO_3H$  groups can be expected in strongly acidic media, hydrogen atoms of  $-AsO(OH)_2$  groups dissociate in the pH range of 2–8, and hydroxyl groups bound to the naphthalene ring can release protons in alkaline media at pH > 8. The absorption maximum of the free dye is shifted to ca. 540 nm in acidic media (with molar absorption coefficient of ca. 30 000  $l\ mol^{-1}\ cm^{-1}$ ), or to 700 nm in extremely acidic solutions [35].

Similarly, complexation equilibria of AZIII are also quite complex as the dye can offer rich possibilities for the rise of several chelate rings due to the presence of numerous donor atoms. As described in literature [3,4,10,16] the reaction between the reagent and metal ions leads usually to the complexes with 2 : 1, 1 : 1 (or 2 : 2), and 1 : 2 ligand-to-metal ratios, the 3 : 1 ratio being less frequent. Absorption maxima of the complexes were found at wavelengths of ca. 650 nm with molar absorption coefficients of about 130 000  $l\ mol^{-1}\ cm^{-1}$  for Th(IV) and U(IV), 50 000  $l\ mol^{-1}\ cm^{-1}$  for  $UO_2^{2+}$  and cations of rare earths, and 1000–10 000  $l\ mol^{-1}\ cm^{-1}$  for bivalent and trivalent cations [10,26]. An optimum pH value for the complex formation generally decreases with increasing valency

of the corresponding cation. Thus, the optimum pH range is 4–5 for bivalent, 1–4 for trivalent (including ions of lanthanoids and also  $\text{UO}_2^{2+}$ ), and  $< 1$  for tetravalent cations [10].

As it follows from the previous text, both acid-base and complexing properties of this azo dye were investigated several times from the spectrophotometric point of view but no attention was paid to its electrochemical behaviour. The only mention we found was that dealing with utilization of AZIII in the determination of uranium in river water by capillary electrophoresis [36]. In that paper, it was also shown that while the  $\text{AZIII-UO}_2^{2+}$  complex is charged negatively (and its mobility is only slightly lower than that of the free dye), the complexes of AZIII with other cations are mostly neutral or positively charged. Basic electrochemical properties of AZIII in view of its exploitation for the determinations of metal ions by adsorptive stripping voltammetry are described in this paper.

## Experimental

### *Reagents*

Arsenazo III was of analytical-reagent grade (Fluka). All other chemicals were of analytical reagent grade (Lachema Brno) and were used without further purification. Stock 0.001 M AZIII solution was prepared by dissolving the weighed amount of its disodium salt in redistilled water. Redistilled deionised water was used throughout.

The supporting electrolyte was a 0.1 M KCl solution which was prepared by dissolving KCl in redistilled water, pH being adjusted with 0.1 M HCl. The solution was deaerated with argon (Synthesia Pardubice).

### *Apparatus*

For all voltammetric measurements, a PC-controlled polarograph (model Eco-Tribo, Polaro Sensors, Prague) was used. The cell consisted of a conical glass vessel (50 ml). All measurements were carried out in three-electrode configuration using a platinum plate and a saturated calomel electrode (SCE) as auxiliary and reference electrodes, resp. A pen-type renewed hanging mercury drop electrode (UM $\mu$ E, Polaro Sensors) in SMDE (stationary mercury drop electrode) mode was used as working electrode.

All laboratory glass was treated with diluted  $\text{HNO}_3$  and rinsed with redistilled water. Dosing of small volumes was performed by micropipettes.

## Procedures

A supporting electrolyte (20 ml) was placed into the electrolytical cell, AZIII solution was added and the mixture was deaerated with argon for 15 min. Hydrodynamic convection during preconcentration step was effected by bubbling argon through the solution. All measurements were performed using FSDPV (fast scan differential pulse voltammetry) mode. The peak heights were evaluated automatically by fitting a tangent to the peak base.

## Results and Discussion

### *Electrochemical Behaviour of Arsenazo III*

Electrochemical behaviour of AZIII in a solution could be expected to be extremely complicated with regard to the structure of AZIII molecule including a number of possible electroactive centers, the abundance of several dissociation degrees in the solution, the presence of several tautomeric forms, the adsorption abilities of this azo dye at the electrode surface, and the incidental formation of the complexes with electrode material. The cyclic voltammogram of the AZIII solution (Fig. 1) illustrates the complicated electrochemical behaviour mentioned above. Many peaks recorded in the poten-

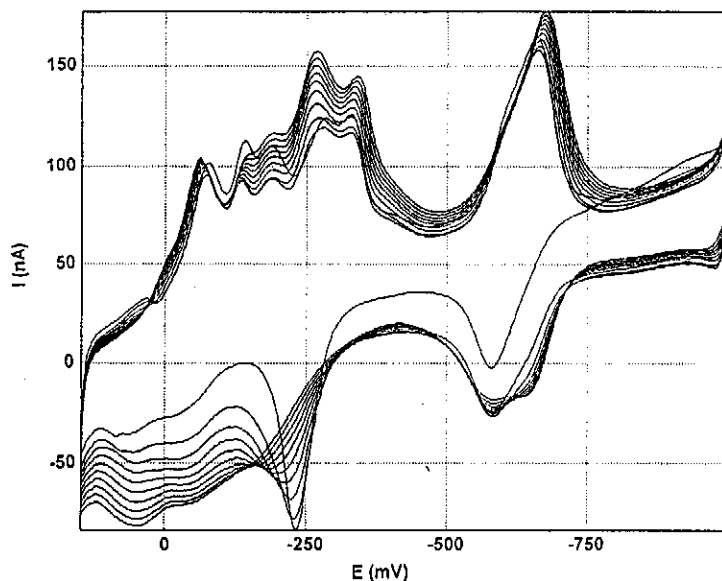


Fig. 1 Cyclic voltammogram of AZ III ( $2.5 \times 10^{-6} \text{ mol l}^{-1}$ ). Supporting electrolyte 0.1 M KCl + 0.1 M HCl (pH 1.85), scan rate  $50 \text{ mV s}^{-1}$ , initial potential  $-1000 \text{ mV}$ , final potential  $+150 \text{ mV}$ , 10 cycles

tial range from -1000 mV to +150 mV and their gradual change indicate quite a lot of electrochemical processes and their affecting by adsorption. A shape of cyclic voltammetric curves is affected by a number of other experimental parameters such as pH, the AZIII concentration, the delay between individual cycles, the scan rate and the presence of other cations in the supporting electrolyte. Cations forming complexes with AZIII strongly affect the peak occurring at -270 mV. This peak is well reproducible and its height decreases with increasing concentration of the cations present in the supporting electrolyte. It was just this peak that was chosen for the determination of several metal ions.

The dependence of the peak height on the accumulation potential (using  $t_{acc} = 120$  s and scan from -400 mV to 0 mV) has a somewhat unexpected shape (Fig. 2), showing two maxima (peaks with half-width of ca. 200 mV) at approx. -400 and 0 mV. The maximum at 0 mV is significantly higher. Almost zero current can be expected at  $E_{acc} < -600$  mV and  $E_{acc} \approx -200$  mV. The next minimum is at +150 mV. Both maxima achieve the highest value at  $E_{in} \approx -400$  mV. The shape of this dependence is unique but no explanation was found for that. Using accumulation under open circuit, the peak height is

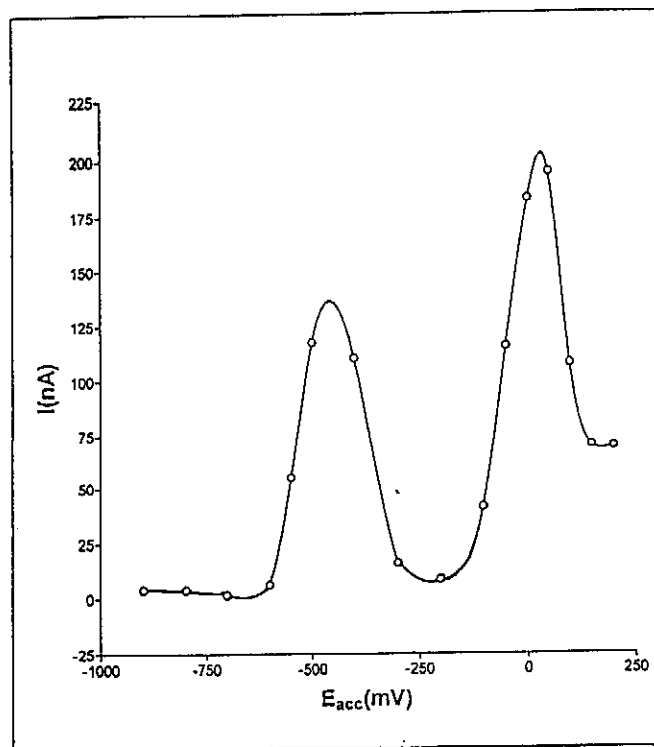


Fig. 2 The dependence of the current response of AZ III on the accumulation potential. Supporting electrolyte 0.1 M KCl + 0.1 M HCl (pH 1.85),  $c_{AZIII} = 5.7 \times 10^{-7}$  mol l<sup>-1</sup>, accumulation time 120 s, scan rate 20 mV s<sup>-1</sup>, pulse 50 mV, initial potential -400 mV, final potential 0 mV

lower (approx. 70% of the value obtained at the accumulation potential of 0 mV).

The pH dependence of the peak height or peak potential, respectively, is also interesting (Fig. 3). Peak of AZIII can only be observed in pH range 0.5–4, the maximum current response can be achieved at pH 1.8–2.2. The dependence  $E_p$  vs. pH probably shows several breaks. The most significant break occurs at pH  $\approx$  1.2. The approximately parabolic course of peak current ( $I_p$ ) vs. pH reminds the dependence of adsorption of the complexes on pH and could indicate that groups (bonds) responsible for electrochemical behaviour of investigated AZIII peak also participate on the complex formation.

At lower pH values, the initial segment of the dependence  $I_p$  vs.  $t_{acc}$  (Fig. 4) is linear, then the peak increase retards until the maximum current value is achieved and the current response slowly decreases almost to zero current at extremely long  $t_{acc}$ . At higher pH values, the initial segment has a sigmoidal course. These types of the dependences are usual in adsorptive voltammetry. The dependence  $I_p$  vs. concentration of Arsenazo III ( $c_{AZIII}$ ) in the supporting electrolyte has a similar course (Fig. 5). The initial segment is linear at lower pH values and sigmoidal at higher pH values. In a narrow range of the

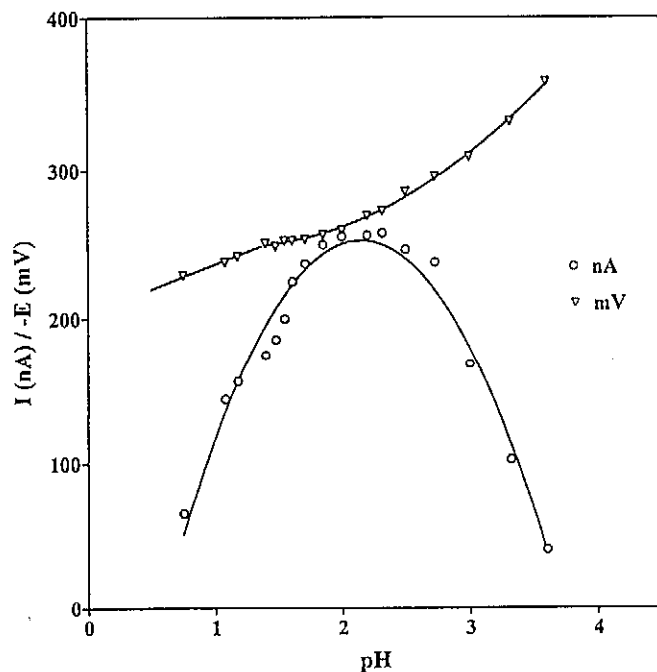


Fig. 3 Influence of pH on the current response of AZIII a peak potential. Supporting electrolyte 0.1 M KCl, pH 1.85 adjusted by HCl addition,  $c_{AZIII} = 5.7 \times 10^{-7} \text{ mol l}^{-1}$ , accumulation time 120 s, accumulation potential 0 mV, scan rate  $20 \text{ mV s}^{-1}$ , pulse 50 mV, initial potential  $-400 \text{ mV}$ , final potential 0 mV

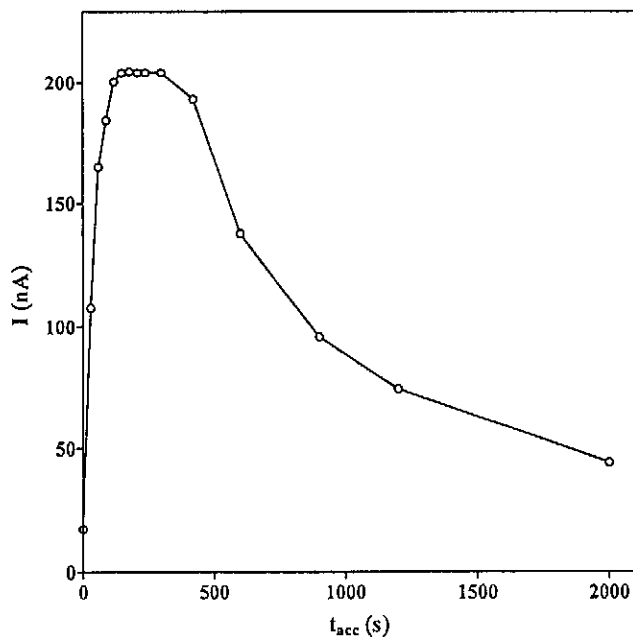


Fig. 4 The dependence of the current response of AZIII on the accumulation time. Supporting electrolyte 0.1 M KCl, pH 1.85 adjusted by HCl addition,  $c_{AZIII} = 5.7 \times 10^{-7} \text{ mol l}^{-1}$ , accumulation potential 0 mV, pulse 50 mV, scan rate  $20 \text{ mV s}^{-1}$ , initial potential -400 mV, final potential 0 mV

maximum, the current response is almost independent on AZIII concentration. Further increase of the AZIII concentration causes a "break down" of adsorption isotherm, i.e. gradual decrease in the peak height. Both phenomena, the decrease of the peak height at higher values of  $t_{acc}$  or  $c_{AZIII}$ , could be explained by multilayer adsorption. An exact explanation of the cyclic voltammogram of AZIII cannot be presented here as the electrochemical behaviour of the dye is really not simple. It will surely be a subject of next investigations using some electrochemical as well as spectral methods together with mathematical simulations.

#### *Determination of Metals*

The AZIII peak occurring at approx. -270 mV decreases significantly after additions of the cations forming complexes with the dye. This effect could probably be explained by the formation of complexes which have similar adsorptive properties as the free azo dye but significantly different electrochemical behaviour. Thus, the competitive adsorption equilibria at the electrode

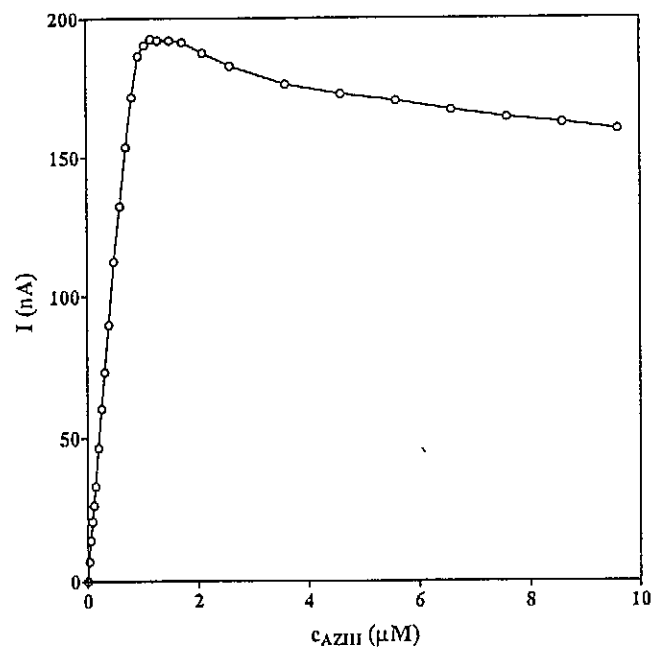


Fig. 5 The dependence of the current response on the concentration of AZIII in the supporting electrolyte. Supporting electrolyte 0.1 M KCl + 0.1 M HCl (pH 1.85), accumulation time 120 s, accumulation potential 0 mV, scan rate 20 mV s<sup>-1</sup>, pulse 50 mV, initial potential -400 mV, final potential 0 mV

Table I Influence of some bivalent and trivalent cations to the Arsenazo III current response (peak height of the free AZIII = 1.00)

	0.1 mM	1 mM	10 mM
Ca(II)	0.95	0.83	0.61
MN(II)	0.98	0.84	0.65
Zn(II)	0.94	0.78	0.54
Ba(II)	0.92	0.79	0.56
Ni(II)	0.92	0.78	0.33
Fe(II)	0.91	0.76	0.30
Fe(III)	0.50	0.10	0.05
Al(III)	0.36	0.05	-



surface could be responsible for the decrease of the peak height. The shape of dependence of the peak current vs. cation concentration is significantly affected by accumulation time, pH of a supporting electrolyte and concentration of Arsenazo III. At higher values of these three parameters, the dependence is sigmoidal. At the optimum conditions, the initial segment is linear and can be exploited for the determination of cations in solution.

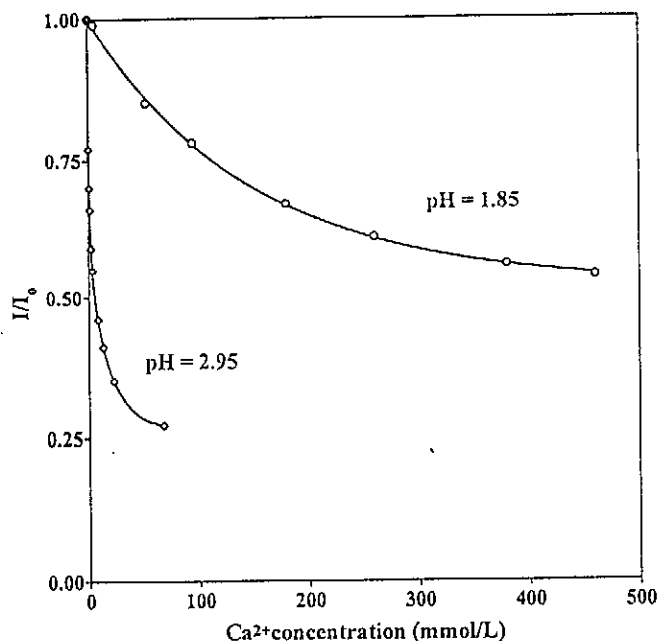


Fig. 6 Influence of pH on the interferences of bivalent cations. Supporting electrolyte 0.1 M KCl adjusted by 0.1 M HCl,  $c_{AZIII} = 5.7 \times 10^{-7} \text{ mol l}^{-1}$ , accumulation time 120 s, accumulation potential 0 mV, scan rate  $20 \text{ mV s}^{-1}$ , pulse 50 mV, initial potential  $-400 \text{ mV}$ , final potential 0 mV. Current response with interfering ions (I) was recalculated to the current response of Arsenazo III ( $I_0$ ).  $Ca^{2+}$  ion was chosen as a model bivalent cation

The decrease in the peak current generally depends on a cation valency (Table I) and the pH value. The effect of bivalent cations is insignificant and can strongly be suppressed by lowering the pH value of the supporting electrolyte (Fig. 6). The influence of trivalent cations is much stronger. Both  $UO_2^{2+}$  and U(IV) have the most significant effect, which probably corresponds with stability of their complexes. As it can be seen from Figs 7 and 8, the peak current decreases linearly with both  $UO_2^{2+}$  and  $Al^{3+}$  additions approx. to one quarter of the original signal.

Table II Influence of some anions to the arsenazo III current response (peak height of the free AZIII = 1.00)

	0.1 mM	1 mM	10 mM
Fluoride	0.99	0.96	0.21
Oxalate	1.00	1.01	0.77
Sulfate	1.01	1.03	0.85
Thiocyanate	1.01	1.09	1.31
Acetate	0.98	1.00	0.98
EDTA	0.98	0.92	0.82
Phosphate	1.03	1.00	0.79
Ascorbate	1.01	1.03	1.01

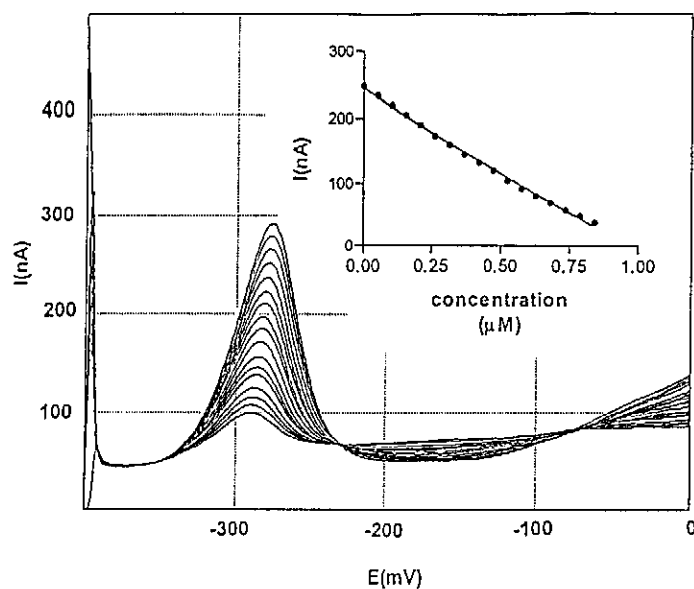


Fig. 7 Differential pulse voltammograms in the presence of uranium, and calibration curve for uranium. Supporting electrolyte 0.1 M KCl + 0.1 M HCl (pH 1.75),  $c_{AZIII} = 5.7 \times 10^{-7} \text{ mol l}^{-1}$ , standard solution of  $\text{UO}_2^{2+}$  added by steps (each 0.25 ppb), accumulation time 120 s, accumulation potential 0 mV, scan rate  $20 \text{ mV s}^{-1}$ , pulse 50 mV, initial potential -400 mV, final potential 0 mV

The influence of anions on the peak height is insignificant (Table II). In most cases, the anions slightly decrease the current response, only the presence of  $\text{SCN}^-$  ions having an opposite effect. Fluorides present in concentrations

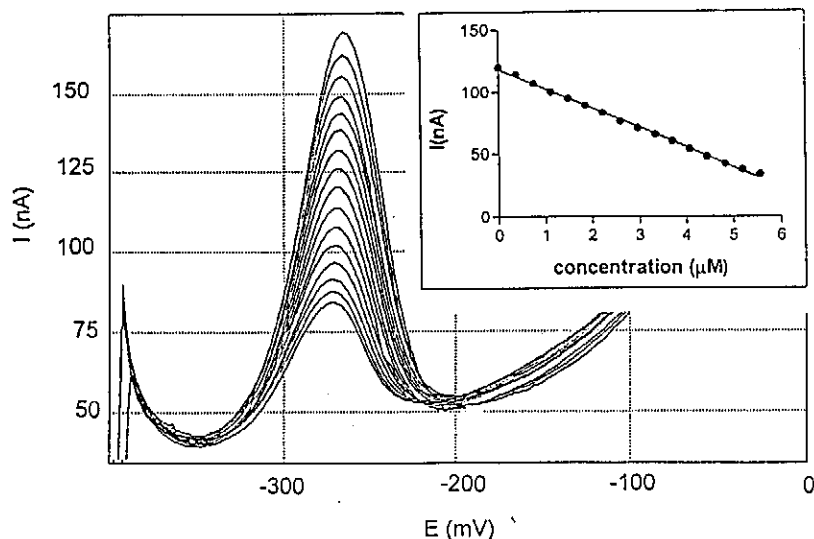


Fig. 8 Differential pulse voltammograms in the presence of aluminium, and calibration curve for aluminium. Supporting electrolyte 0.15 M acetate buffer (pH 3),  $c_{\text{AZIII}} = 1.7 \times 10^{-7} \text{ mol l}^{-1}$ , standard solution of  $\text{Al}^{3+}$  added by steps (each 10 ppb), accumulation time 120 s, accumulation potential 0 mV, scan rate  $20 \text{ mV s}^{-1}$ , pulse 50 mV, initial potential -400 mV, final potential 0 mV

higher than  $10^{-3} \text{ mol l}^{-1}$  decrease the peak height significantly.

Based on the facts described above, the procedures for determinations of uranium [37] and aluminium [38] were suggested. The optimized conditions of these determinations are shown in Table III; linear calibration curves were obtained with the use of these parameters. The peak height of AZIII alone is well reproducible (RSD = 0.6%) but for evaluation of concentrations, a modified standard addition method had to be used. The sample and standard solution must alternately be added to the supporting electrolyte and the decrease of the peak height must be evaluated. Of course, interferences of numerous cations are quite important and must be eliminated [37,38].

Finally, with regard to the interfering effects mentioned, the procedures allowing determinations of some other metal ions based on both adsorption and complexation properties of Arsenazo III could be elaborated.

Table III Optimized experimental conditions for the determination of uranium and aluminium

	Uranium	Aluminium
Supporting electrolyte	0.1 M KCl + HCl	0.15 M acetate buffer
pH	1.85	3
Accumulation potential $A_{acc}$	0 mV	0 mV
Initial potential $E_{in}$	-400 mV	-400 mV
Final potential $E_{fin}$	0 mV	0 mV
Accumulation time $t_{acc}$	120 s	120 s
Scan rate	20 mV s <sup>-1</sup>	20 mV s <sup>-1</sup>
Pulse amplitude	50 mV	50 mV
Pulse duration	100 ms	100 ms
Pulse interval	100 ms	100 ms

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### References

1. Savvin S.B.: Dokl. Nauk SSSR **127**, 1231 (1959).
2. Savvin S.B.: Talanta **8**, 684 (1961).
3. Savvin S.B.: Zavod. Lab. **29**, 131 (1963).
4. Nemodruk A.A., Palei P.N.: Zh. Anal. Khim. **18**, 480 (1963).
5. Savvin S.B.: Talanta **11**, 7 (1964).
6. Palei P.N., Udalcova N.I., Nemodruk A.A.: Zh. Anal. Khim. **22**, 1797 (1967).
7. Chudnov E.G., Yakovlev G.I.: Radiokhimiya **4**, 505 (1962).
8. Nemodruk A. A., Kochetkova N. E.: Zh. Anal. Khim. **18**, 333 (1963).
9. Nemodruk A.A., Palei P.N., Kochetkova N.E.: Radiokhimiya **5**, 335 (1963).
10. Buděšinský B.: Collect. Czech. Chem. Commun. **28**, 2902 (1963).
11. Savvin S.B., Bagreev V.V.: Zavod. Lab. **26**, 412 (1960).
12. Volyneec M.P.: Zavod. Lab. **26**, 1109 (1960).
13. Polyakov A.I., Volyneec M.P.: Geokhimiya (1961) 426.

14. Dukyanov V.F., Savvin S.B., Nikolskaya I.V.: *Zavod. Lab.* **25**, 1155 (1959).
15. Vladimirova V.M., Davidovich N.K.: *Zavod. Lab.* **26**, 1210 (1960).
16. Duklanov V.F., Nikolskaya I.V., Kozlova E.S.: *Radiokhimiya* **3**, 239 (1961).
17. Kuznetsov V.I., Akimova T.G., Eliseeva O.P.: *Radiokhimiya* **4**, 188 (1962).
18. Lukyanov V.F., Savvin S.B., Nikolskaya I.V.: *Zh. Anal. Khim.* **15**, 311 (1960).
19. Palei P. N., Nemodruk A. A., Davidov A.V.: *Radiokhimiya* **3**, 181 (1961).
20. Goryushina V.G., Romanova E.V.: *Zavod. Lab.* **26**, 415 (1960).
21. Goryushina V.G., Romanova E.V., Archakova T.A.: *Zavod. Lab.* **27**, 794 (1961).
22. Elinson S.V., Mirsoyan N.A.: *Zavod. Lab.* **27**, 798 (1961).
23. Palshin E.S., Myasoyedov B.F., Palei P.N.: *Zh. Anal. Khim.* **17**, 471 (1962).
24. Goryushina V.G., Savvin S.B., Romanova E.V.: *Zh. Anal. Khim.* **18**, 1340 (1963).
25. Singer E., Mareček J.: *Fresenius Z. Anal. Chem.* **196**, 321 (1963).
26. Nn: Arsenazo III, Spolana, Neratovice 1968.
27. Spitsyn P.K., Svarev V.S.: *Zh. Anal. Khim.* **22**, 1797 (1967).
28. Poluektov N.S., Kirilov A.I., Makarenko O.P., Vlasov N.A.: *Zavod. Lab.* **37**, 536 (1971).
29. Kuzin E.L., Lichonina E.A., Savvin S.B.: *Zh. Anal. Khim.* **27**, 350 (1972).
30. Surin I.G., Spitsyn P.K., Barkovskij V.F.: *Zh. Anal. Khim.* **34**, 1103 (1979).
31. Savvin S.B., Petrova T.V., Dzerajan T.G.: *Zh. Anal. Khim.* **35**, 1485 (1980).
32. Spitsyn P.K.: *Zavod. Lab.* **45**, 689 (1979).
33. Spitsyn P.K.: *Zh. Anal. Khim.* **36**, 1330 (1981).
34. Lopez-de-Alba P. L., Lopez-Martinez L., Wrobel K., Wrobel K., Amador-Hernandez J.: *J. Radioanal. Nucl. Chem.* **220**, 167 (1997).
35. Jančář L., Černocká H., Šulová R., Jančářová I., Kubáň V.: *Scripta Fac. Sci. Nat. Univ. Masaryk. Brun.* **26** (Chem.), 43 (1996).
36. Colburn B.A., Sepaniak M.J., Hinton E.R.: *J. Liq. Chromatogr.* **18**, 3699 (1995).
37. Komersová A., Bartoš M., Kalcher K., Vytřas K.: *Electroanalysis*, accepted for publication.
38. Komersová A., Bartoš M., Kalcher K., Vytřas K.: prepared for publication.