

## VA-METRIC DETERMINATION OF BENZ(a)PYRENE IN RICE, GRAIN, AND PROCESSED PRODUCTS

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Polycyclic aromatic hydrocarbons (PAH), in particular, benz(a)pyrene (BZP), are commonly accepted indicators of environmental contamination, including that of food products. Therefore, determining the BZP concentration is sufficient to judge the level of contamination by cancer-causing PAH in general [1, 2].

Knowledge of the quantitative PAH content in biological items, especially agricultural, enables the nature of the diseases caused by them to be predicted and diagnosed. In addition, the source terms and the uptake pathways of toxic and cancer-causing substances into the organism and the dynamics of their accumulation can be followed.

Therefore, we studied the electro-oxidation of BZP in various aprotic media at a solid carbon-paste electrode. The cation-radical forms through one-electron transfer. The electrochemical process of BZP in general is irreversible. It was also found that the oxidation potential of BZP is determined by its structure and depends linearly on its ionization potential and energy of the highest molecular orbitals.

VA-grams of BZP were recorded by a PU-1 polarograph with a PDP-4 potentiometer using a solid carbon-paste electrode in a three-electrode system. The reference electrode was an AgCl electrode; the auxiliary electrode, Pt. The microelectrode was dipped in a mixture of hot concentrated HNO<sub>3</sub> and HCl (1:1) for 3-5 min and then thoroughly rinsed with doubly distilled water before measurements. The supporting electrolytes were alkali-metal and ammonium acetates, chlorides, nitrates, and perchlorates.

The limiting anodic current is proportional to the BZP concentration in the studied supporting electrolytes not only at the limiting current but also at any optimal potential of the carbon-paste electrode in the range 0.55-1.65 V.

A standard BZP solution was made up using reagent from Fluka Buchs (Switzerland). The working surface of the electrode was cleaned before each measurement with filter paper moistened with a saturated solution of the appropriate supporting electrolyte.

Preliminary experiments showed that substances that are oxidized at the modified carbon-paste electrode can interfere with the BZP determination. However, only molecules with phenyl rings can be oxidized because metal ions in the studied items are in their highest oxidation state and organic compounds are in principle structurally similar to the electrode. Thus, phenols, aromatic amines, and their analogs can interfere. The analyzed samples were treated with acid and base before the VA-grams were recorded in order to convert phenols and amines to water-soluble compounds and remove them from the non-aqueous solution to be analyzed.

The analytes were rice, grain, and processed products. These were ground to a homogeneous mass with particle sizes of several microns. The next operation was carried out according to the literature method [3]. The literature method was used to extract and concentrate BZP [4].

The extraction of the substance to be determined from the sample to be analyzed is very important. The uncertainty in performing this procedure can significantly affect the accuracy of the method. The BZP concentration coefficient reaches  $5 \cdot 10^3$  if 500 ml of sample to be analyzed is treated with a hexane solution (5-10 ml, 25%) or its mixture with *n*-propanol (1:1) and another solvent in acetone. This causes practically complete transfer of BZP into the extract. The hexane solution or hexane:*n*-propanol (1:1) mixture of the extract is evaporated at low temperature to 30 ml. Supporting electrolyte (5 ml) is added. The solution is transferred into the electrolyzer. The VA-grams are recorded four times.

TABLE 1. Determination of Benz(a)pyrene by VA-metry and the Shpol'skii Method in Rice, Grain, and Processed Products

Analyte	Found benz(a)pyrene, $n \cdot 10^{-9}$		$n$	$S$	$S_r$
	Shpol'skii method	voltammetry			
Viet Nam rice	1.3	2.9±0.60	3	0.24	0.083
Rye	2.8	3.5±0.78	4	0.49	0.140
Wheat	1.0	1.6±0.13	5	0.12	0.080
Oats	3.9	4.7±0.68	4	0.43	0.091
Barley	1.8	2.8±0.23	5	0.21	0.075
Rye bread	3.6	4.3±1.61	3	0.65	0.151
Fine rye bread	3.2	3.4±0.51	4	0.32	0.094
Wheat bread	1.5	1.9±0.17	5	0.16	0.085

Note:  $n$  is the number of parallel determinations;  $S$  is the standard deviation, dispersion, scatter;  $S_r$  is the relative standard deviation.

Some of the experimental data from the analysis of rice, grain, and processed products are listed in Table 1. It can be seen that the results are reliable and reproducible with a relative standard uncertainty <0.33.

Thus, the developed VA-metric methods for determining toxic BZP in agricultural products can be used to estimate the degree of ecological danger of the Central Asiatic region [5].

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