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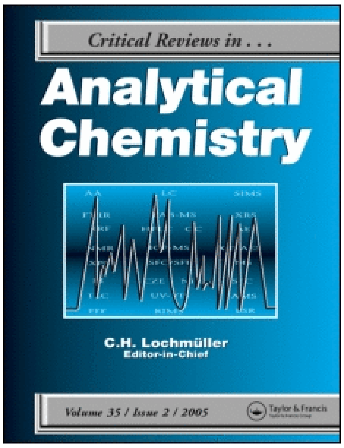

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DETERMINATION OF NITRATED POLYCYCLIC AROMATIC HYDROCARBONS AS A NEW CLASS OF ENVIRONMENTAL CARCINOGENS

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Nitrated polycyclic aromatic hydrocarbons (NPAHs) are relatively new class of environmental carcinogens [1,2] and there is an ever increasing demand for the determination of their trace concentrations. So far mostly chromatographic methods, such as GC-MS or HPLC with fluorimetric detection are used for these purposes [3], while differential pulse voltammetry (DPV) and adsorptive stripping voltammetry (AdSV) methods for the determination of these substances were developed only recently [4]. As can be seen from Table I, the sensitivity of DPV or AdSV is sufficient. However, inherent low selectivity of these methods has lead us to investigate their combination with liquid extraction or solid phase extraction. This combination enabled us to determine as low as 1.10^{-10} mol.l^{-1} 9-nitroanthracene in highly polluted Vltava river [5] in Prague. The sensitivity of HPLC with UV detection of NPAHs is too low for environmental applications. However, HPLC with electrochemical detection after preliminary reduction of NPAHs to the corresponding aminoderivatives (APAHs) is more sensitive and fluorescence or chemiluminescence detection is even more sensitive as demonstrated in Table I. A new type of platinum tubular voltammetric detector [6] and procedures for precolumn reduction and chemical derivatization [7] were developed in our laboratory for these purposes and tested on nitronaphtalenes and nitrobiphenyls as model substances.

Beside the extreme sensitivity required for the determination of environmental carcinogens, there is another rather special problem. Any contact with a chemical carcinogen presents certain risk to an analyst. This risk can be minimised by a careful observing of appropriate safety regulations and by development and proper use of methods for laboratory decontamination and destruction of carcinogens in laboratory wastes. These methods are developed in the framework of a programme co-ordinated by International Agency for Research on Cancer (IARC) in Lyon.

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Table I. Selected examples of NPAH and APAH determination

Analyte	Method	Conditions	LOD (M)	Ref
1-nitropyrene	DPV	BR buffer - MeOH (1:1), pH 2.7	7.10^{-8}	9
	AdSV	BR buffer - MeOH (99:1), pH 2.2	1.10^{-9}	9
	HPLC	UV detection at 240 nm	1.10^{-7}	9
9-nitroanthracene	DPV	BR buffer - MeOH (1:1), pH 9.2	2.10^{-7}	5
	AdSV	BR buffer - MeOH (9:1), pH 7.1	2.10^{-9}	5
	HPLC	UV detection at 252 nm	$4{,}10^{-6}$	5
1-aminopyrene	HPLC	UV detection at 240 nm	1.10^{-7}	9
	HPLC	fluoresc. det. exc. 345 nm; em. 415 nm	1.10^{-9}	9
	HPLC	thin layer elchem. det. at + 0.8 V	4.10^{-8}	9
4-nitrobiphenyl	HPLC	UV detection	$\sim 10^{-6}$	7
	HPLC	reductive amperometry	$\sim 10^{-6}$	7
	HPLC	precolumn reduction to amines followed by		7
		oxidative amperometry	$\sim 10^{-7}$	7
		fluorometry	$\sim 10^{-9}$	7
		derivatization and chemiluminescence	$\sim 10^{-10}$	7

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We have investigated the following methods of destruction of model NPAH´s [8,9] :

1. Chemical reduction by zinc powder followed by chemical oxidation by permanganate
2. Chemical reduction by zinc powder followed by enzymatic oxidation by hydrogen peroxide
3. Chemical oxidation by Fenton reagent
4. Electrochemical reduction followed by chemical oxidation by permanganate
5. Photochemical destruction using UV irradiation

According to our experience, the first three methods are suitable for practical applications, the degree of destruction being higher than 99%.

We have developed several methods to monitor the efficiency of the destruction based on UV spectrophotometry, differential pulse polarography at dropping mercury electrode, differential pulse voltammetry at hanging mercury electrode or carbon paste electrode and HPLC with spectrophotometric, fluorimetric or electrochemical detection.

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