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# Extraction of the insecticide dieldrin from water and biological samples by metal affinity chromatography

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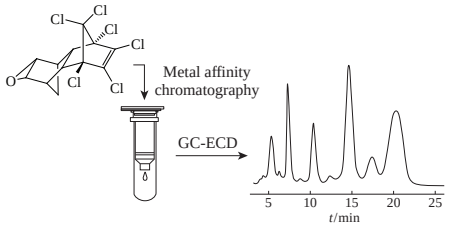
**A new simple and efficient procedure for the determination of dieldrin in water, milk and blood plasma using metal affinity sorbent based on monolayers of nickel stearate has been proposed.**




Dieldrin† is a resistant toxic chlorinated insecticide that acts on the nervous system and internal organs. Despite the forbiddance of using dieldrin in many countries, it still can be found in soil, open water and, as a consequence, in living organisms. Dieldrin has a capacity for bioaccumulation, and it can migrate over long distances due to climatic and ecological processes.[1]

The permissible insecticide aldrin serves as a constant source of dieldrin because it can be oxidized under acidic conditions to form the latter. The methods used to extract dieldrin from water and milk (the main source of dieldrin contamination) are characterized by complexity and low specificity owing to the presence of a significant amount of impurities that often interfere with analysis.[2] Moreover, the degree of extraction from water and milk does not exceed 80%.[3]

We propose a new approach to the extraction of dieldrin from water, milk and blood plasma using a metal-affinity sorbent based on collapsing monolayers of nickel stearate (Langmuir–Blodgett films, LBF $Ni^{II}$). Based on the various affinities of organic compound heteroatoms to metal ions,[4] metal affinity chromatography is a more specific and selective extraction method than conventional liquid-liquid and solid-phase extraction (C-18). The sorbent has the following properties: the surface preferably consists of metal atoms;[5] the mass of 1 $dm^2$ is 0.022±0.003 mg; the isoelectric point is reached at pH 3.5; the sorption capacity for hemoglobin is 1.38 mmol $g^{-1}$; and the degree of extraction of aminomethylphosphonic acid from water is 86±4%.[6,7]

We additionally studied the surface morphology of the sorbent. The monolayers of nickel(II) stearate were produced using the Langmuir–Blodgett method.[8] After collapsing, these structures were examined by scanning electron microscopy (Inspect S, FEI). Figure 1 shows that the collapsing monolayers of nickel(II) stearate have folding nature; sections with a smooth surface are also distinguishable. Thus, the surface of collapsing LBF is accessible to analyte molecules.

To study the extraction of dieldrin from aqueous solutions, we performed a model experiment under conditions specific for classical metal affinity chromatography: incubation with sorbent (sorption) in the presence of trifluoroacetic acid (TFA) at pH 2.5 and desorption with 0.4 M aqueous ammonia (pH 9).[9] The dieldrin concentration in solutions varied from 0.01 to 1 ng $ml^{-1}$. Note that the minimum concentration of dieldrin (0.01 ng $ml^{-1}$) corresponded to the maximum permissible concentration of dieldrin in natural samples based on the data of the World Health Organization.[10]

As a method of quantitative analysis, gas chromatography with an electron capture detector was used (Shimadzu, GC-2010). The standard solutions of dieldrin (0.1, 0.25, 0.5, 0.75, and 1 ng $ml^{-1}$; the injected volume was 1 μl) were analyzed, and a standard curve was plotted. The calibration curve was linear ($R^2$ = 0.998) in a calibration range of 0.01–500 ng on column. The relative standard deviations (RSD) of the peak area of dieldrin demonstrated the good precision and repeatability of the method (< 10%). LOD was 0.01 ng $ml^{-1}$ on the column, LOQ was 0.1 ng $ml^{-1}$ on the column for standard solutions of dieldrin. The intra-day relative standard deviation was 8%; inter-day relative standard deviation was 5%. The number of measurements $N$ = 4.

A linear correlation between dieldrin concentrations in flow through fraction and dieldrin concentration in the initial solutions

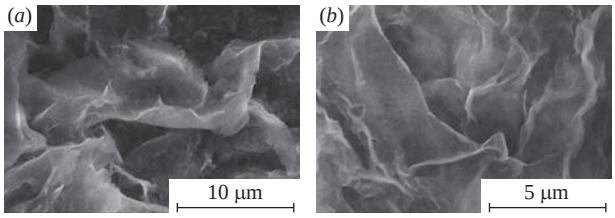



**Figure 1** Micrographs of collapsing LBF $Ni^{II}$.

† IUPAC name of dieldrin is (1a*R*,2*R*,2a*S*,3*S*,6*R*,6a*R*,7*S*,7a*S*)-3,4,5,6,9,9-hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-2,7:3,6-dimethanonaphtho-[2,3-*b*]oxirene.

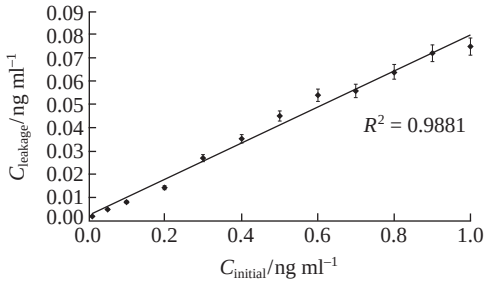



**Figure 2** Dieldrin concentration in flow through fraction depending on initial concentration.

on nickel sorbents (Figure 2) indicates that sorbent saturation was not achieved and a further increase of the initial concentration of the toxic substance was not possible due to reaching the solubility limit in water. Thus, after equilibration, the dieldrin content of solution did not exceed 10% of the initial concentration.

Note that we failed to successfully perform desorption under the conditions of classical metal affinity chromatography. In solutions obtained after sorbent treatment with 0.4 M aqueous ammonia, dieldrin was detected in trace amounts; therefore, the next step was to optimize the desorption of dieldrin with LBF Ni$^{II}$. Elution with metal affinity sorbents can be carried out in several ways: significantly change the pH compared to the conditions of sorption, modify donor force of eluents or use salt solution in high concentrations.[11] We have previously shown that a combination of different eluents leads to a more efficient elution of substance from the sorbent and, consequently, increases the degree of extraction.[12]

In this work, we used the following solutions sequentially: 0.4 M aqueous ammonia; a 0.015% solution of perfluorooctanesulfonic acid (PFOS) with a 0.5% aqueous solution of piperidine and 0.1% TFA in acetonitrile (Figure 3). The obtained fractions were analyzed by gas chromatography as described above.

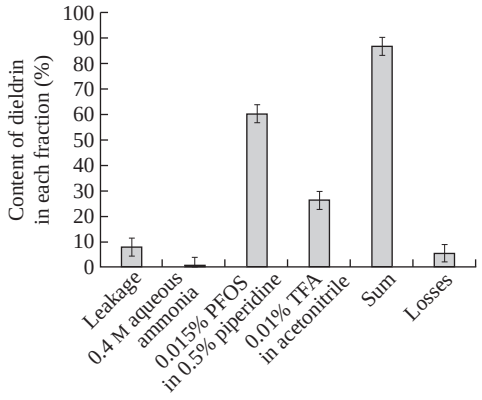



**Figure 3** Diagram of dieldrin extraction from water solution.

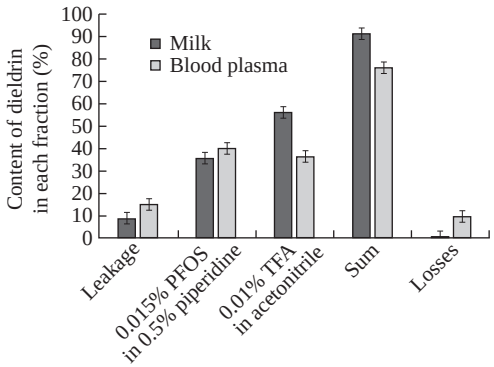



**Figure 4** Diagrams of dieldrin extraction from milk and rat blood plasma.

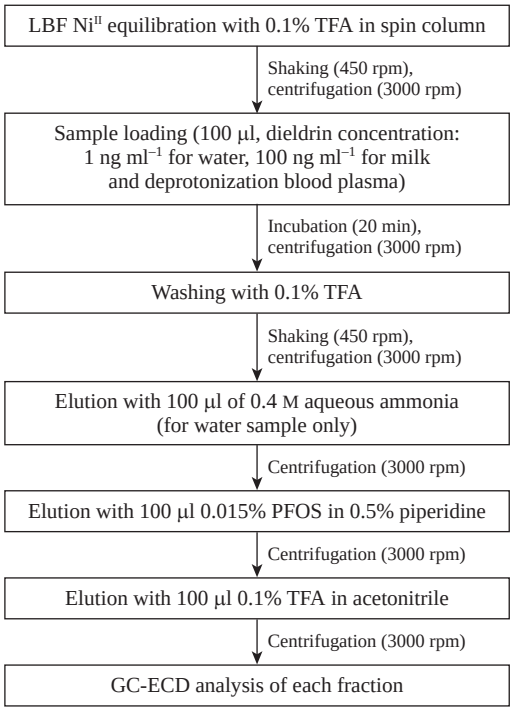



**Figure 5** Procedure of dieldrin separation from water, milk and blood plasma.

The results are consistent with the previous experimental data: the concentrations of dieldrin in a flow through fraction (leakage) and in the first fraction (0.4 M aqueous ammonia) were 7.8 and 0.2%, respectively. At the same time, the largest amount of dieldrin was determined in the piperidine–PFOS fraction. Sorbent treatment with a 0.1% solution of TFA in acetonitrile allowed us to additionally extract 26.3% dieldrin. Thus, the total recovery rate was 86.7% with minimal losses on the sorbent (5.5%). According to the results of the experiment, we decided to eliminate the step of elution with aqueous ammonia because of its inefficiency.

Along with water solutions, the main source of dieldrin contamination is milk, which is a complex matrix containing proteins, lipids, carbohydrates and mineral substances. In addition, it is interesting to explore the possibility of dieldrin extraction from more complex matrices such as blood plasma.

A concentration of 100 ng ml$^{-1}$ was chosen because the solubility of dieldrin in milk is much higher than in water; dieldrin in food in this concentration may cause intoxication and this amount of dieldrin can often be found in contaminated milk in Asia, Brazil, *etc*.[3] According to the above procedure, dieldrin was extracted from cow milk [GOST (State Standard) 31450-2013] and rat blood plasma followed by gas-chromatographic (GC) analysis with ECD (calibration functions for milk: $y = 745329x - 2\times10^{-10}$, $R^2 = 0.9974$; for blood plasma: $y = 692138x - 3\times10^{-10}$, $R^2 = 0.9812$) (Figure 4).

Thus, the application of metal affinity chromatography using LBF Ni$^{II}$ to extract dieldrin from milk allowed us to increase the degree of extraction to 91.4% with minimal losses on the sorbent (0.2%). In the case of blood plasma, the degrees of extraction were 76.1 and 9.2%, respectively. Hence, we proposed a new protocol for the extraction of dieldrin from water, milk and blood plasma (Figure 5).

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