THE CONCEPTION OF GAS-CHROMATOGRAPHIC AND CHROMATO-MASS-SPECTROMETRIC DETECTION OF POLYCHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS IN DRINKING WATER

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Despite certain progress made in this country in the organization of research on detecting trace quantities of dioxins, at least, three causes do not allow this analysis to be performed on a large scale and be feasible for laboratories working in the system of nature and health protection services: high cost of analysis; difficulties in preparation of samples; inavailability of imported chromato-mass-spectrometric equipment.

The territory of Russia and the former USSR remains a blank space which is potentially contaminated with an unknown quantity of dioxins and may be dangerous for its own population and for the populations of the neighbouring states. It is necessary to have a governmental programme aimed at equipping specialized laboratories and enabling them to perform mass analyses on these large areas. A multi-level conception is proposed:

1st level: Preliminary gas-chromatographic mass analyses on sites. Commercial production of gas devices (3700 and Kristall-2000) with an electron-capture detector and silica capillary columns (50-80 m long, inner diameter 0.20, 0.32 and 0.52 mm) the cost of which doesnot exceed 2000 $. In 1992, 100 such devices have been furnished. Unification of a procedure for preparation of drinking water samples. The work on the development of an enzyme immunoassay kit for group and individual express-detection of dioxins.

2nd level: A unified procedure of sample preparation. A low-resolution chromato-mass-spectrometer. About 10 equipped centres. The work on the development of a domestic device.

3rd level: High-resolution chromato-mass-spectrometry with a unified procedure of sample preparation and separation. 2-3 equipped centres. The work on the development of a domestic device.

Gas-chromatographic analysis. The critical ecological situation is intensified today by the aggravation of the political and aconomical life in the countries of the former USSR, by their common poor technical development and, in particular, by the lack in them (except for Russia) of commercial production of chromatographic and chromato-mass-spectrometric equipment. However paradoxical it is, but the main services engaged in nature protection, such as sanitary-epidemiological, ecological, agrochemical stations and laboratories, do not possess modern capillary gas-chromatographic equipment and have no experience in employing this method at all although it is absolutely necessary for separation of complex mixtures of polychlorinated aromatic hydrocarbons. Analyses of dioxins performed in the country in the recent time were carried out with the use of earlier purchased imported equipment and chromatographic materials which practically exhausted their resources.

All this makes the task of organization of services for control of dioxins and other superecotoxicants in the environment of such an enormous part of the territory of Europe and Asia under conditions of political, economical and technical instability in the country highly difficult.

To equip the most effective nature-controlling services, such as sanitary-epidemiological stations, we have chosen as a basic one the device (model 3700) commercially produced by the Moscow plant "Chromatograph" and developed on the basis of the specifications of the firm Varian, USA. But our domestic device is additionally supplied with a unit for sample injection into the capillary column and with a highly sensitive electron-capture detector (detection limit $2 \cdot 10^{-14}$ g/sec). The procedure of water sample preparation, separation and detection of the mixture ingradients permits us to determine 2,3,7,8-tetrachlordibenzo-p-dioxins on the level of 0.01 ng/l (1,2).

We used the known method of water extraction by hexane with subsequent evaporation and purification of the extract on a column with silica gel treated in succession with alkali and sulfuric acid (1). For separation of dioxin and dibenzofuran mixtures silica capillary columns produced by us (3) were used. They are up to 80 m long and are treated with polar and non-polar stationary phases and their mixtures. Their use has increased the reliability

of identification of some almost inseparable sample components (toxic components, in particular). The cost of gas-chromatographic determination in this case does not exceed 100-150 $, which has permitted the use of mass analysis of a large number of samples with required sensibility and a relatively high reliability. To reduce the cost of dioxin analysis, it is supposed to supply sanitary laboratories with enzyme immunoassay diagnostic kits for the most toxic isomers or a group of isomers.

For increasing the reliability of identification of dioxins or for confirming the data of gas-chromatographic analyses carried out on sites, an imported chromato-mass-spectrometric equipment was used available, as a rule, in large centres of the country (1)

Chromato-mass-spectrometric analysis. The following equipment was used for identification: 5988A (Hewlett-Packard), 11D-700, MAT-311A and the Varian 3400 system with a mass-spectrometer with double focusing (HS-Q-30) permitting a detection threshold of 1 pg Research and instrument-making organizations of the Ministry of Health and Academy of Sciences of Russia have designed a special apparatus for analysis of dioxins on the basis of the gas chromatograph Kristall-2000/3000 (4) and a compact mass-analyser with double focusing of an ionic bunch reaching a detection limit of $2 \cdot 10^{-10}$ g upon ionization by an electron stroke, a range of mass numbers 1-3000, a maximal resolution of 800 on the level of 10% of the peak height.

For identification and quantitative calculations we have organized the production of kits of mixtures of dioxins and dibenzofurans as well as individual compounds.

Results and conclusions. The developed analytical procedures and complex laboratories are mainly intended for controlling the quality of drinking water and water from the sources of urban water supply. The analyses of drinking river water from the main rivers of Russia, Ukraine, Siberia and Uzbekistan performed in 1990-1992 showed the presence of some polychlorinated dibenzo-p-dioxins and dibenzofurans practically in all tested samples often in concentrations exceeding the maximally permissible ones. Samples of tap drinking water in such large and important centres as Moscow, St.Petersburgh, Volgograd, Kiev, Ufa, Tashkent, Sevastopol made no exception. Even higher concentrations of dioxins were found by us in different soils and silts, especially in

regions of intensive agriculture and wastes discharges. Below, the data characterizing the qualitative and quantitative composition of some dioxins in water samples from a number of regions of Russia and Ukraine are presented (see Table).

Of particular concern is the state of the Ufa region where chemical substances containing high concentrations of dioxins have been produced for many years. The Moscow water supply also excites apprehension for, at least, in one of four reservoirs trace quantities of tetrachlordioxins are regularly recorded.

Thus, the data obtained prove convincingly the contamination with dioxins of the basic sources of water supply in the largest cities of the former USSR. At the same time, the knowledge of the true ecological state in the country and of its water sources cannot be obtained now because of the poor technical equipment of organizations engaged in nature protection and the general poor development of the country in the field of analytical instrument-making. Realization of the 1st level of analysis will make it possible to perform semi-quantitative studies in the nearest 1.5-2 years with the use of domestic gas-chromatographic devices. Chromato-mass-spectrometric investigations (2nd and 3rd levels) will require a cooperation with western firms.

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Table

DATA ILLUSTRATING THE PRESENCE OF DIOXINS IN DRINKING AND RIVER WATER, ng/l.
PERMISSIBLE LEVEL (USSR, 1991) FOR 2,3,7,8-TClDD - 0.020 ng/l

Poly-ClDD	Ufa river. South Reserv.		Moscow river, reservoir November-91	Moscow city, tap water, Novem.-91	Dnieper river, Cherkassy city, May-91	Volga river, Volgograd city, May-91	Neva river, St.Peters-burgh, June-91	Sevastopol city, tap water, June-91
	April-90	May-91						
tetra					0.650	0.740	0.430	0.510
1,3,6,8 -	-	-	0.080	-				
1,3,7,9 -	-	-	0.190	-				
1,3,6,8 -	-	-	-	0.080				
1,4,6,9 -	-	-	-	0.090				
1,2,3,4 -	-	-	0.620	-				
2,3,7,8 -	-	-	-	-	0.001	0.01	0.01	-
pentha	-	-	-	-	0.130	0.160	-	0.180
hexa	88.0	-	-	-	0.130	0.320	0.15	-
hepta	120	-	-	-	0.170	0.210	-	-
octa	760	-	-	-	-	-	-	-
equiv. contamination		0.007			0.015	0.014	0.021	0.008