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Problems of the development of ecological instrument making

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The attention devoted to the development of new analytical methods and instruments for ecology has been aroused by the appearance in the waste from economic activity of a large amount of highly toxic pollutants, which are dangerous to man and the environment even in very small amounts. The detection of these substances at the level of limiting permissible concentrations against the background of interfering substances is a very complex scientific and technical task. Bearing in mind that about 70 000 organic compounds are being used throughout the world and are therefore present in the environment and that their number increases by 1–2000 annually,[1] the necessity for newer modern approaches to ecological analyses becomes evident. For such studies, it is essential to have at one's disposal a set of fairly universal methods and instruments with a high sensitivity and selectivity. The results should be interpreted on a computer. Furthermore, it is essential to possess a data bank for the identification of substances.

The development of analytical methods in ecology has been stimulated by a series of accidents in chemical undertakings and by the results of their investigation. The results of a study of the accident in Seveso (Italy) in 1976,[2,3] where the latest advances in chromatography and mass spectrometry had to be used in order to detect traces of dioxins, which poison human beings and pollute the locality, have appeared in print to the greatest extent. The consequences of the agricultural pollution and of the use of chemicals (herbicides) during most recent wars have also served as stimuli.[4] All these major catastrophic pollutions have led to a sharp increase in the number of scientific publications on the development of analytical methods using the latest instruments: highly effective gas and liquid chromatograph and mass spectrometers, which are used in more than half the instances where analytical methods are needed.[5]

The increasing complexity of the ecological situation and frequent accidents in chemical undertakings have induced a rapid growth of the industrial manufacture of analytical apparatus in various countries. The quality of the apparatus has been increasing significantly as a result of a large number of service devices: devices for sampling and preparation of samples and a sophisticated system for the interpretation of data on computers with extensive program libraries, data bands, and systems for the identification of substances.

The achievements in instrument making and electronics enabled a number of firms to develop mobile laboratories equipped with chromatographs and mass spectrometers. The best known of these is the TAGA-3000 Laboratory (Canada). It uses as the detector a mass spectrometer with a device for the automatic injection of samples from the atmosphere, which ensures a high sensitivity (10^{-15} g cm^{-3}). The presence of a navigating device makes it possible to plot maps of contamination in the given locality. The MM-1 mobile laboratory of the Bruker Company (Federal Republic of Germany) has effective analytical characteristics. It uses as the detector a quadrupole mass spectrometer with sample injection through a capillary column and with heating at the sampling site. This laboratory is designed for the rapid identification and estimation of the amount of organic substances in water, air, and on the surface. It can be used to analyse the distribution of dioxins.[6]

The use of modern analytical methods and apparatus combined with well thought out organisational measures is undoubtedly the most promising trend in ecology, which has already frequently led to positive results, and not only in the case of industrial accidents already mentioned. The significant improvement of the ecological situation in the region of the Greak Lakes (USA) and the Mississippi River may serve as an example. The combination of modern physicochemical and biological analytical methods and international cooperation has made it possible to investigate fairly rapidly the causes of the death of seals in Lake Baikal.[7]

The use in ecology of the majority of analytical instruments is limited by their high cost, the need for special accommodation, and the unduly laboratory-oriented design of the instruments as well as the need for highly qualified specialists to carry out the analyses. For the mass application of analytical instruments in ecology, the designers must significantly reduce the cost of the apparatus without loss of their quality, reduce their weight and size, and expand their operating conditions.

The small batches of chromatographs and mass spectrometers produced by Soviet industry do not satisfy the requirements of ecologists either as regards their functional possibilities or their operating characteristics. Essential instruments such as chromatograph-linked mass spectrometers and quadrupole mass spectrometers are not produced at all. There is a particularly serious lack in the field of assembly and interpretation of data on the basis of modern advances in computer techniques. Devices for continuous monitoring based on laser techniques and small cheap and selective sensors of different types are completely lacking.

One of the main reasons why Soviet industry lags behind in ecological instrument making is the absence of a scientific-technical base and of permanent specific organisational stimuli, which, on the one hand, would stimulate the demand for ecological instruments because of the need to carry out measures to protect nature and, on the other hand, would stimulate the manufacture and improvement of their quality.

The Siberian Division of the USSR Academy of Sciences prepared the program "Development of Methods, Instruments, and Mobile Laboratories for the Analysis of the Pollution of the Environment", which can be regarded as the first stage of work designed to create a

base for ecological instrument making. The program included 34 research and experimental-design studies which are planned for 1989–1991. The program of the development of studies in the subsequent period will be prepared in 1990 using the experience gained.

The main executor of the program is the Limnological Institute of the Siberian Division of the USSR Academy of Sciences. The overall cost of the studies is 23 million roubles (7.7 million roubles annually). The main bulk of the studies are being performed by members of the Institute of the Siberian Division of the USSR Academy of Sciences, the Geophysical Instrument Making Division of the Tochnash Design Bureau at the Institute of Geology and Geophysics of the Siberian Division of the USSR Academy of Sciences, the EKOTEK Company, and the experimental factory of the Irkutsk Scientific Centre.

It is proposed initially to set up and standardise a limited list of toxicants, each of which will represent a specific group of ecological toxicants of prime importance, classified in relation to the analytical methods and instruments. Such a list is necessary for laboratory tests of instruments and should be reduced to a minimum in order to diminish the cost of the development of the metrological aspect of the work.

In addition, it is necessary to set up an information data bank for the study of the advances in the field of ecological instrument making and for the refinement of different aspects of the research. In the course of the studies, it is proposed to develop a packet of programs for personal computers, to carry out bibliographic and patent searches, and to introduce the information into the data base and analyse it.

The next group of studies is designed to create instruments for the analysis and monitoring of prime toxicants in the gas phase.

In order to construct the gas chromatographs, it is essential to employ the experience gained in the development of the "Ekho" gas analyser-identifier, whose design is so advanced that it can become the basis for a series of universal an specialised chromatographs which are not inferior to the best devices throughout the world. The design of the "Ekho" gas analyser is protected by a patent.[8] The instrument employs novel units: a device for sample injection from a concentrator, polycapillary columns, an improved electron capture microdetector, and a microprocessor device for controlling the apparatus and for interpretation of data, which are also protected by patents. Further improvements to the design of the apparatus will make it possible to extend the range of substances analysed and to improve the sensitivity of the determination of impurities in the atmosphere to 10^{-15} g cm^{-3} (combined with a resolving capacity ranging from thousands of plates in portable versions of the apparatus to tens of thousands of plates in stationary designs). The detector being developed on the basis of molecular condensation nuclei possesses unique sensitivity and is capable of detecting a wide range of substances. The set of existing technical solutions, the degree of elaboration of the components of the apparatus, and the design as a whole make it possible to create an instrument which will not be inferior to the best devices available throughout the world as regards its characteristics.

Rapid performance (a fraction of a second for the entire range of substances detected) and a high sensitivity (10^{-13} g cm^{-3}) are combined in the novel instrument called "drift spectrometer", where the substances are separated on the basis of the non-linear dependence of the mobilities of their ions in specially generated electric field pulses.[9,10] The instrument operates with air being continuously pumped through it and is designed to analyse the composition of the air on board moving carriers. The studies being performed should lead to the construction and tests of a prototype of the instrument. The instrument has no analogues abroad.

For remote-control analyses, it is proposed to construct a batch of atomic-absorption mercury Zeeman analysers in air which have proved very satisfactory in a whole series of tests on the detection of mercury vapour in the atmosphere performed on an aeroplane (developed by the Institute of the Optics of the Atmosphere, Siberian Division of the USSR Academy of Sciences, Tomsk).

Members of the Krasnoyarsk Scientific Centre of the Siberian Division of the USSR Academy of Sciences have been investigating new principles of the analysis of air and liquid media using the resonance effects in laser spectroscopy and microwave spectroscopy. It is proposed to construct analysers with a very simple design and easy to operate.

It is proposed to construct several prototypes of a lidar for remote-control measurements of the amounts of sulphur dioxide, nitrogen oxides, and aerosols in the atmosphere and to test them in Tomsk, Novosibirsk, and Irkutsk. The instrument has been developed by the Institute of the Optics of the Atmosphere of the Siberian Division of the USSR Academy of Sciences and is designed to monitor the state of the atmosphere in the vicinity of major industrial undertakings, heat and power generating plant and urban regions.

Yet another group of studies has been devoted to the development of means for the analysis of liquids. These studies should result in the modernisation of the electronic units of the "Milikhrom" liquid chromatograph, the development of which led to the award of the USSR State Prize. The novel units and blocks of the chromatograph, patented in major capitalist countries[12–18] and protected by USSR patents, ensure effective characteristics of the instrument: sensitivity down to 10^{-9} g with respect to nucleotides, duration of analysis from 2 to 20 min, and selectivity equivalent to 4000 plates.[11] After modernisation, the instrument should be produced commercially.

It is also proposed to use the best advances in the development of the units of the "Milikhrom" chromatograph to improve the efficiency of the ionic chromatograph in a flow-injection analyser. By virtue of the employment of the principle of microcolumn chromtography, a tenfold saving has been achieved in the reagents and sorbents in the ionic chromatograph compared with the best foreign analogues. The flow-injection analyser is based on the detector of the "Milikhrom" chromatograph incorporating a 2:μl cell and a small-size system for the supply of the solution of the solvent and for injection.

An attempt has been made to devise an apparatus for the neutron-activation analysis of admixtures of chemical elements in water under field operating conditions. For this purpose, one uses small neutron generators with a flux $>10^8$ neutron s^{-1}. Similar generators are used for the neutron bore hole logging. In the above study a novel design of a generator with a gas-filled tube was employed. The study led to the creation of a mock-up of the apparatus.

The most complex problems have to be solved in the studies designed to devise different types of mass spectrometers. The principal difficulties arise in the creation of transportable versions of the apparatus for mobile ecological laboratories and in the development of devices for the introduction of samples. It is proposed that both direct sample injection from the atmosphere and sample injection via chromatographic columns be employed, as well

as a novel hydrodynamic procedure for the introduction of liquid samples into the mass spectrometer.

The possibility of devising a Soviet-produced transportable quadrupole mass spectrometer has been investigated. The MM-1 mass spectrometer, developed by the Bruker Company (Federal Republic of Germany), may serve as a model.

It is proposed to develop an analytical system based on a static mass spectrometer with a samarium magnet, which is equipped with a device for the introduction of samples from the atmosphere, a line of receivers for the simultaneous recording of the mass spectra, a device for coupling to a personal computer in order to interpret the information and identify the substances, and a vacuum system capable of working as a part of the equipment of a mobile ecological laboratory. The study should be completed by the construction and test of the system as part of an ecological laboratory. The system is designed for the analysis of toxicants of prime importance in the gas and liquid phases.

The problems concerning the testing and calibration of instruments for the analysis of traces of substances in the gas phase are being solved. Generators of standard concentrations of prime toxicants, based on the constancy of the concentration of the vapour of a solution at a given temperature, are being developed for the purpose of the tests. The solution is deposited on a large surface,[19] in the given instance on the channels of a polycapillary plate. The generators are first calibrated against a radioactive label. A calibration table, indicating the concentration of the toxicant vapour at a specified temperature to within $\pm 10\%$, is assigned to each generator. It is possible to construct in this way generators for the determination of the concentrations of substances down to 10^{-14} g cm^{-3} in air. Sets of such generators, designed for different concentrations, make it possible to test the linearity and sensitivity of instruments over a wide dynamic range.

Fluorine-graphite matrices, maintaining a constant flux of an evaporating substance for up to 6 months, are prepared by a special technology and are used for the sorption of volatile substances. The advantages of the sorption generators of standard concentrations are their small size and ease of operation, which makes it possible to incorporate them directly into the automatic calibration apparatus.

In the course of these studies, measures will be taken to ensure the metrological certification of the generators and sets of generators in the required numbers will be constructed.

A large series of studies is being performed on the creation of chromatographic phases and different types of capillary and polycapillary columns for gas chromatography. The results obtained at the Institute of Organic Chemistry of the Siberian Division of the USSR Academy of Sciences in the synthesis of polysiloxane liquid phases, reagents in the deactivation of the surfaces of glass and quartz using a specially developed technology for the deposition and stabilisation of phases, made it possible to set up the manufacture of columns which are not inferior to the best foreign examples either as regards selectivity or as regards the range of working temperatures (from -60 to 320 °C). The principal task at the present stage is to ensure the provision of highly effective chromatographic columns in all the developments involved in the given programme.

In order to improve the characteristics of a traditional analytical instrument — the emission spectrometer — a study has been undertaken to construct a mock-up of such a spectrometer in which all the latest advances in this field are employed: holographic grids, a recorder with a line of photodiodes for the simultaneous recording of the MASI spectra, and the assembly and interpretation of information with the aid of microprocessor computers. The size of the apparatus is significantly reduced and the requirements as regards vibration stability are less stringent, which makes it possible to employ the device in mobile laboratories.

A large series of studies has to be carried out on the development of methods for the analysis of toxicants of prime importance (it is proposed to involve in this investigation a large team of members of the Institutes of the Novosibirsk, Krasnoyarsk, and Tomsk Scientific Centres). The analytical methods should be based on the devices developed in accordance with the given programme and should employ the latest advances in the computer interpretation of information. A data bank should be set up for use in personal computers in order to identify the substances analysed. In the first stage of the investigation, it is proposed to create data banks and systems for the identification of substances against the background of impurities.

Two studies are designed to develop hydroacoustic devices for hydrobiological studies and for the estimation of the stock of fish and the state of water-containing areas.

The development of a mobile ecological laboratory is the most complex component among those planned in the programme "development of methods, instruments, and mobile laboratories for the analysis and monitoring of pollutants in the environment". The laboratory should be placed in a specially equipped automobile (bus). In the first stage of the development, it is proposed that the laboratory should incorporate (after structural modification) the following instruments: a modernised Ekho-M gas chromatograph, a modernised Millikhrom liquid chromatograph, a drift spectrometer, a mass spectrometer with sample injection from the atmosphere, a bioluminometer, an aerosol counter, devices for the selection and preparation of samples, and a set of personal computers within the automobile. The laboratory is designed for the operational analysis of the state of the environment. In the first stage of these studies, it is also necessary to revise the necessary set of apparatus, to specify the unsolved problems, and to formulate the task for the next stage.

The programme is completed by a series of studies designed to prepare for the construction of a scientific-industrial base for ecological instrument making at the Irkutsk Scientific Centre. In accordance with the resolutions of the Praesidium of the Siberian Division of the USSR Academy of Sciences, it is proposed to create the Irkutsk Engineering-Ecological Centre, in which the total number of engineers and other workers employed will be up to 1000. The tasks in the Centre are the development of modern methods for the analysis and monitoring of the state of the environment, the coordination of the work of the organisations participating in the execution of the programmes, the construction and testing of prototypes of the apparatus, the incorporation in commercial production of the developments achieved at the Centre, and cooperation in the practical employment of such developments by the monitoring organisations.

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Brief communications

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Chromatography in ecology

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The solution of the problem of ecology in all countries, namely the creation of waste-free technologies the utilisation of the materials obtained, the study of their metabolism under operating conditions, their regeneration, and their disposal, is impossible without chemical analysis of complex organic mixtures, which permits not only the determination of the overall content of the organic substance but also the establishment of the presence and the determination of the concentrations of specific mixture components. Chromatography combined with mass spectrometry, IR Fourier spectroscopy, UV spectroscopy, etc. has become such an analytical procedure.

Chromatography makes possible the selective determination of microimpurities at virtually any level, which is especially important in the solution of ecological problems. As a result of the chromatography of a mixture, the separated individual components pass to the instrument for their determination (mass spectrometer, IR Fourier spectrometer, etc.) and are then identified by spectroscopic methods. At the present time, all the leading and the majority of ordinary analytical laboratories abroad, engaged in the analysis of objects in the environment, are equipped with chromatograph-linked mass spectrometers and a large number of gas and liquid chromatographs.

The state of organic analysis in our country is extremely unsatisfactory: thus only one of each ten sanitary-epidemiological stations, i.e. the principal organ for the monitoring of the environment, is at present equipped with gas chromatographs and the number of liquid chromatographs is even smaller. We lag behind the USA by a factor of 5–6 as regards the manufacture of gas chromatographs and by a factor of 50–60 as regards liquid chromatographs. Chromatograph-linked mass spectrometers of modern design are not manufactured in the USSR and, according to our information, IR Fourier spectrometers, which might be used in combination with chromatographs, are not being developed either.

The foregoing shows that, for the successful solution of ecological problems, it is necessary to develop analysis and especially organic analysis on the basis of primarily chromatographic methods combined with mass spectrometry. For a rapid rectification of the existing situation, it is desirable to organise a methodological centre and regional analytical centres provided with modern equipment purchased abroad.

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Electrochemistry and protection of the environment

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There are many electrochemical aspects of the solution of ecological problems. In the first place, these include the creation of new industrial technologies, procedures for the purification of waste waters, and the development of sensors for the monitoring of the environment. Electrochemistry can also make a serious contribution to the creation of ecologically clean transport and power engineering.

A series of studies designed to protect the environment has been carried out in recent years at the Institute of Electrochemistry of the USSR Academy of Sciences. A procedure has been developed for the ultilisation of gas-absorption hydrochloric acid, which is a waste product of the large scale organochlorine synthesis in the electrochemical chlorination of ethylene to dichloroethane. This procedure is protected by patents. An experimental-industrial 5 kA apparatus has been constructed and tested jointly with the undertakings of the Ministry of Chemical Industry at the "Orgsintz" factory in Sumgaite. A technical requisition for a plan of an experimental works designed to produce 10000 tonnes of dichloroethane annually has been made. Unfortunately, the works has not so far been constructed and the contamination of the Caspian Sea continues.