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Analysis of Atmospheric Pollutants by Gas Chromatography

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Chromatographic methods for the analysis of atmospheric pollutants, including the principal stages of the determination, from the sampling procedure to the evaluation of the results of the analysis, have been examined. The difficulties and limitations frequently encountered in the examination of the separate stages of the analysis and the various methods have been analysed. The review is based on work published in the period 1965-1978. The bibliography contains 398 references.

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I. INTRODUCTION

The contamination of the environment, particularly the atmosphere, which in many countries has become a serious international problem, is posing analytical chemistry important and complex problems in the analysis of many-component mixtures of various atmospheric pollutants, the components of which are present in trace concentrations. Practically the whole arsenal of physical and chemical methods available to analytical chemistry is now being used for the analysis of atmospheric pollutants[1]. Its high sensitivity and extremely high selectivity have made gas chromatography one of the basic methods of analysis in the chemistry of industrial hygiene and the chemistry of the atmosphere.

The importance of the problem of analysing the atmosphere is to a large extent responsible for the large number of publications on this subject, and the number is increasing continuously[2,3]. In 1968, a detailed review[4] analysed the achievements of gas chromatography during ten years of application in the chemistry of the atmosphere. A number of later reviews and monographs deal with the gas-chromatographic analysis of atmospheric pollutants[5,6] and the chromatographic determination of harmful substances in the air of industrial plants (industrial atmosphere).[7] The present review includes material published in the period from 1965 to 1978.

At the present time, the problem of separating complex mixtures of substances by gas chromatography often presents no special difficulties. The use of stationary phases of high selectivity (particularly in micro-packed capillary columns) and capillary columns with a separation efficiency of > 200000 theoretical plates makes it possible to separate and analyse complex mixtures of organic and inorganic compounds consisting of several hundred components. Another important advantage of this method is its extremely high sensitivity, which makes it possible to determine micro-concentrations of a substance at a level of 10^{-10}%†.

Nevertheless, the gas-chromatographic method also encounters certain difficulties in the analysis of micro-quantities of various toxic substances in air. Since the maximum permissible concentrations (MPC) for most toxic chemical compounds in the air of industrial plants is 0.01-0.001 mg m^{-3}, that is about 10^{-7}-10^{-8}%, the specimen of air for analysis, with a volume of 1-10 ml, should contain not more than 10^{-10}-10^{-12} g of the substance. This quantity lies at the limits of many chromatographic detectors used for the analysis of air[8]. The MPC of harmful substances in atmospheric air is lower by a factor of approximately 10. If in addition account is taken of the losses of the substance being analysed during sampling, the treatment of the sample and its introduction into the chromatograph, and the chromatographic separation, the problem of inadequate analytical sensitivity becomes particularly acute.

Another important problem is the qualitative analysis of many-component mixtures, since polluted air generally contains complex mixtures of chemical con pounds of different classes. The chromatographic analysis is also complicated considerably by rapid change in the composition of the air being analysed (particularly atmospheric air) under the influence of meteorological conditions and photochemical reactions taking place in the atmosphere between compounds present in the air, under the influence of solar radiation.

The gas-chromatographic analysis of micro-quantities of substances includes the following stages.

1. Sampling. Storage of the sample.
2. Concentrating the components.
3. Treatment of the sample and its introduction into the chromatograph.
4. Chromatographic separation of the components of the sample.
5. Detection, and also, at intervals,
   a) calibration of the chromatograph (detector);
   b) qualitative and quantitative analysis of micro-quantities of substances.

II. AIR SAMPLING PROCEDURE

Sampling (and the concentrating of micro-quantities of substances) presents one of the principal problems in the analysis of polluted air, because of the insufficient sensitivity of detectors and the existence of active sites, capable

†Here and subsequently, concentrations are given in wt.%.

of sorbing traces of material in the chromatographic apparatus (chromatograph connections, columns) and in the sorbents used. Concentrating the sample with micro-component concentrations at a level of 10^{-4}–10^{-5}% is often also carried out in work with highly sensitive ionisation detectors. In these cases it is usually sufficient to concentrate the components from one litre of the air being analysed. This technique is also used when it is impossible to carry out the direct analysis of the gaseous sample on capillary columns and in certain other cases.

Existing methods for sampling air can be divided into four groups: 1) sampling into various containers; 2) aspiration of the air through a solvent which retains the impurities; 3) absorption of harmful substances from the air by sorbents; and 4) freezing the impurities in a cooled trap on an inert packing or sorbent. The methods of the last three groups are techniques for concentration.

The simplest method is the direct introduction of the sample into the chromatograph. In this case the air is sampled with a glass or plastic syringe, and also into gas pipettes, steel or glass bottles, bags made of polymer film, and other containers. With this method, satisfactory results are obtained only in the analysis of gaseous samples containing traces of substances which are not too polar (light hydrocarbons, oxides of carbon, nitrous oxide, etc.). The accuracy of these determinations is low because in practice it is very difficult to take account of the losses of the substances being analysed, which in some cases (the analysis of reactive gases and vapours) may reach 40%[9]. Not only reactive compounds, but also hydrocarbons, are adsorbed on the walls of containers[4].

The sampling of components for analysis by absorption in a suitable solvent is also a method for the equilibrium concentrating of these compounds. In contrast to the case of sampling into containers, there is practically no limit to the range of substances that can be analysed by this method. In addition, the aspiration of the sample through a solvent makes possible the selective removal of substances of different classes from the air. Nevertheless, sampling into a solvent is not often used in chromatographic analysis, since it is not possible to achieve a very high sensitivity in the determination. This is because, despite the high degree of enrichment of the substances of the sample in the solution being analysed, only a small fraction of the absorbing liquid is taken for analysis (1–10 μl), that is 0.1–0.2% of the original volume of the solution, which should not be less than 3–5 ml. It is true that the sensitivity can be increased by repeating the concentration procedure, for example by evaporating the solution after sampling. This introduces an additional error into the determination, however, due to the volatility of the dissolved compounds of the sample. To avoid possible errors in the analysis of trace quantities, it is also necessary to take account of the volatility of the solvent itself and the rate of aspiration of the air through the absorber. To increase the sensitivity it may be more promising to extract the substances dissolved in the absorbing liquid by a much smaller volume of a selective solvent, that is by a repeated concentration. This is because the extracting agents used are solvents for which the distribution coefficient of the trace component is much greater than that of the main component[10].

A method particularly widely used in the gas-chromatographic analysis of atmospheric pollutants is frontal non-equilibrium concentration, based on the complete absorption of heavy impurities by sorbents with a highly developed surface. The substances being analysed are collected in traps (columns) filled with a small quantity of sorbent (silica gel, active carbon, polymeric sorbents)[4,11]. These are then desorbed and separated in a chromatographic column. The calculation of the minimum length of the trap, that is the length in which all the heavy trace components being analysed are completely retained, has been described in a monograph[10]; the equations given make it possible to formulate the principal requirements to be satisfied by the parameters of the concentration process and to carry out different versions of the analysis. An advantage of the frontal method of concentration is that it is possible to absorb large quantities of trace components quantitatively from the air (high degree of enrichment). In addition, sampling is usually carried out at the temperature of the surrounding medium (rarely with cooling). Moisture does not interfere in the determination for most sorbents (active carbon, graphitised carbon black, Porapak-S), since these sorbents are hydrophobic. By concentrating the substances in the sample on adsorbents, it is possible to achieve a very high sensitivity of the determination; it is often not necessary to pass large volumes of air through the trap, particularly when a sensitive detector is used. In this case the trap acts as a sampler rather than a concentrator.

A disadvantage of the frontal method of concentrating trace quantities is the difficulty of desorbing the substances absorbed by the trap, particularly when the trap is heated (that is in thermal desorption). A high desorption temperature for the trace components may lead to various undesirable side reactions, for example in the determination of unstable compounds. It is often therefore preferable to use displacement (extraction) of the trace components by a suitable solvent[10].

An adsorbent used particularly frequently in the frontal concentration of trace components is active carbon, which at a temperature from −60°C to +20°C can be used successfully for sampling and concentrating pollutants in atmospheric[4] and industrial[12] air. It should be noted that a concentrator containing active carbon has a very high adsorption capacity and retains micro-components strongly, making their thermal desorption difficult. Moreover, carbon reacts with various sulphur-containing compounds, and to trap effectively substances with a low molecular weight (ethylene, methylene chloride), extensive cooling of the trap is required[4]. Nevertheless, according to data obtained by American workers, the best method for the chromatographic determination of micro-quantities of organic substances in air involves the passage of large quantities of the contaminated air (about 10 litres) through active carbon[13] with subsequent desorption of the sorbed trace components by carbon disulphide and analysis of the extract obtained[14]. The efficiency of the adsorption of most organic substances on active carbon is almost 100%, and is not influenced by the volume of the sample nor the rate of sampling. The efficiency of the desorption of organic substances from carbon using carbon disulphide is on the average greater than 90%[15] (according to the data of the National Institute for Occupational Safety and Health (USA)[16] it varies for different substances in the range 81–100%).

The trapping of micro-components from air in a column containing silica gel at ordinary or more particularly at low temperatures is very effective. Silica gel is widely used to concentrate light and heavy hydrocarbons[4], and also organic substances of other classes and inorganic substances[17]. An unsatisfactory feature of silica gel is its highly hydrophilic nature and the incomplete trapping of light hydrocarbons (up to C_3). Thus ethylene is not completely sorbed on silica gel even when the trap is cooled to

−78°C.[4] In this case it is necessary to use more effective sorbents, for example molecular sieves, which are also among the best adsorbents for carbon dioxide[18]. The selectivity of zeolites with respect to various classes of compound and individual substances makes it possible to use them for the directed control and identification of micro-components[10]. A serious disadvantage of these adsorbents is the difficulty of desorbing the trace components, particularly heavy components.

Thermal graphitised carbon black, treated with hydrogen at a high temperature, is also used to concentrate trace components. At low temperatures this non-specific adsorbent makes it possible to trap micro-quantities of organic and inorganic substances, including reactive compounds, from the surrounding air[9].

To extract readily volatile organic substances from air, use is also made of carbon molecular sieves, consisting of highly pure porous carbon, obtained by the thermal decomposition of polyvinylidene chloride[11]. The high adsorption capacity (specific surface approximately 1000 m^2/g), ease of desorption of trace components, and high thermal stability (the adsorbent is stable up to 400°C) make carbon sieves (Carbopacks) valuable materials for filling sampling adsorption tubes. In addition, Carbopacks are extremely hydrophobic.

Other materials which do not absorb moisture include polymeric sorbents, which together with active carbon are most frequently employed to concentrate harmful substances from air in gas-chromatographic analysis[19]. Porous polymeric sorbents are fairly stable to heat, have a high adsorption capacity, and make it possible to sample air at a high rate; the nature of the polymer influences the selectivity of the absorption of micro-components belonging to different classes. Recently, a new highly effective sorbent, "Tenax GC", has been used to concentrate traces of toxic substances from air. This is a polymer of 2,6-diphenyl-*p*-phenylene oxide, which is now often preferred to other adsorbents[20], is less polar than Porapak-S and Chromosorbs, has a very high thermal stability, and is characterised by a non-specific type of adsorption; this is important for the desorption of high-boiling organic compounds. Tenax is used at temperatures up to 400°C; it does not react with most organic substances, and the efficiency of the adsorption and desorption of micro-quantities of organic compounds of different classes is greater than 90%. Another advantage of this polymer, which is used for the analysis of the most varied trace components in air, is the possibility of high-speed sampling (a sample can be taken in 10–20 s)[21] and the high adsorption capacity for compounds of different molecular weight.

Good results in the chromatographic analysis of air have been obtained using sampling devices filled with hydrophobic packing or surface-modified adsorbents or modified (for example by polyethylene) solid carriers[22], which have been used to analyse substances with different boiling points, including polyaromatic hydrocarbons.

One method for concentrating micro-components from air on sorbents involves the removal of a sample on to a moving sorbent (a so-called fluidised bed). This method ensures more uniform distribution of the substances being analysed throughout the volume of the sorbent and also a high rate of sampling (up to 16 litre min^{-1}).[10] The method is a version of the equilibrium concentrating method.

The methods for the absorption of trace components in a concentrating trap, described above, are based on the complete absorption of heavy trace components. A fundamentally new method was proposed by Novak and coworkers[23]. The gas sample was passed through a small concentrator column containing a suitable stationary phase at the temperature of the surrounding medium, until "breakthrough" of the trace components being analysed. Under these conditions, the concentration of heavy trace components in the sorbent along the entire length of the column is in equilibrium with their concentration in the original mixture. In the frontal method of concentration, only part of the layer of sorbent is treated, whereas in the equilibrium concentrating of trace components, the entire volume of sorbent in the trap is used, so that the total quantity of trace components absorbed in the concentrator is greater in this method. From the analytical viewpoint, the equilibrium concentrating method has the following advantages: 1) it is not necessary to measure accurately the volume of gas passed through the trap; it is necessary only to use an excess of gas and to know accurately the temperature of the concentrator; 2) the method makes it possible to increase selectively the sensitivity of the determination of trace components and to avoid the sorption of components which interfere in the determination, by selecting a suitable filler; 3) it is possible to "equalise" the quantities of individual components in the trap, since the distribution coefficients increase in proportion to the increase in molecular weight and the decrease in vapour pressure. The unsatisfactory features of this method include the need to keep the trap and sorbent at a constant temperature, and the possibly incomplete thermal desorption of the specimen.

A method has been proposed[24] for the gas-chromatographic analysis of atmospheric pollutants by saturating a volatile liquid with the air being studied until the equilibrium distribution of the trace components being determined between the two phases (gas–liquid) is achieved, followed by the chromatographic determination of the equilibrium concentration of trace components in the liquid. This method has the following advantages over the equilibrium concentrating of micro-components in non-volatile liquids with subsequent thermal desorption: it does not require a knowledge of the exact quantity of absorbing liquid, it allows repeated analysis from one sample of the concentrator, and it uses volatile solvents of low molecular weight. In some cases it is appropriate to use a non-volatile liquid as solvent.

The chromatographic analysis is sometimes preceded by a concentration based on the condensation (freezing) of trace components. After sampling, the trap is heated, and the trace components are displaced into the chromatographic column by a stream of carrier gas. To increase the efficiency of the condensation of the trace components, it is necessary to increase the cooled surface area of the trap. This can be achieved by increasing the length of the concentrating tube or by filling it with metal or glass spheres or a column sorbent or adsorbent. Since subsequent thermal desorption of the sample is necessary, thermally stable liquids are used as stationary phases for these sorbents[25]. If extensive cooling of the trap is used, micro-quantities of hydrocarbons in air at a level of 10^{-8}% can be determined using a flame ionisation detector[26]. At the temperature of liquid nitrogen, the stationary phase acts not as a solvent but as an absorbent with a low specific surface. The liquid phase is sometimes applied directly to the walls of the concentrator tube, and the impurities concentrated on it are desorbed by heating and collected again in a trap containing molecular sieves, with cooling by liquid nitrogen[27]. This two-stage concentration makes it possible to determine very low concentrations of trace components in air, for example in the study of various biological substrates. The original method provides for direct sampling into the chromatographic

column, the initial section of which is cooled to −78°C.[28] Here, the three stages of the chromatographic analysis of the trace components (sampling, concentration, and introduction of the sample into the chromatographic column) are replaced by a single operation.

A serious disadvantage of concentration methods involving extensive cooling of the concentrator trap is the condensation of water in the traps, leading to a sharp decrease in the adsorption capacity of the sorbent. Thus in the concentration of trace components, a column containing a reagent for the selective absorption of water vapour is placed in front of the trap. The selection of a drying agent is made difficult by the fact that it must retain only water vapour and readily allow the passage of the other components of the mixture being analysed[10]. Heated calcium chloride and magnesium perchlorate are often used to dry specimens of air for analysis[29]. It must be remembered, that Anhydrone irreversibly absorbs nitro-compounds, ethers, nitriles, and unsaturated hydrocarbons. Anhydrous potassium carbonate is a universal and readily accessible drying agent for organic compounds. Hydrocarbons, aldehydes, ketones, alcohols, esters, and many other organic compounds pass practically unchanged through absorbing columns containing potassium carbonate[30].

The temperature of the cooling mixture must be 150–180 K lower than the boiling points of the compounds being trapped from the air. If the temperature is too low, however, aerosols which are not held in the trap may be formed. Thus liquid nitrogen is suitable as a cooling agent only to trap the vapours of compounds which boil at temperatures not exceeding 100°C.[10]

The removal of aerosols and solid particles from air has its own specific features, associated with the fact that they are not absorbed by the usual sorbents. The sampling of aerosols, which represent the form in which most high-boiling hydrocarbons are present in air, and also solid particles (dust, soot) is carried out on fine-fibre filters of glass, plastic, or ceramic[31]. The compounds of the sample collected on the filter are usually extracted in a Soxhlet apparatus, and the resulting solution analysed. Specimens of solid particles carrying various chemical compounds on their surface in the adsorbed state are treated similarly. Aerosols of metals and various inorganic compounds (oxides, salts) are collected on filters of glass fibre or on highly-dispersed fibrous filters of polymeric materials (AFA-V-10 polyvinyl chloride filters).

An important contribution to the theory and development of methods for the analysis of micro-components‡ has been made by the work of Soviet scientists. The methods of chromatography without a carrier gas, many of which were first proposed and developed by Zhukhovitskii and coworkers[32], and which are also called high-concentration gas chromatography, make it possible, under isothermal conditions, to obtain a concentrated zone of both light and heavy trace components at the column outlet. The use of chromatography without a carrier gas, proposed by Zhukhovitskii and Turkel'taub[33], makes it possible to improve and simplify many methods for the analysis of trace components. The method of vacancy chromatography[34] is of considerable importance for the determination of trace components in air and other gases. A high degree of enrichment of the sample in the micro-components being analysed can be achieved by a thermal dynamic method of concentration[35] based on the use of a heater with a negative temperature gradient, moving at intervals along the chromatographic column; the principal component of the mixture being analysed is used as carrier gas. Under the influence of the thermal field, the trace components, which are sorbed more effectively than the principal component, are concentrated, move along the column, and are eluted from it at intervals. The trace component zones become narrower, and sharp separation of the zones takes place. These studies have made it possible to design several forms of chromatograph specially for the analysis of micro-components; these are now produced regularly by Soviet industry, in particular the "Luch" chromatograph, which uses enrichment of the micro-components for analysis on previously evacuated columns[36].

An interesting development of the method of chemical concentration was proposed by Sakharov and coworkers[37], who increased the sensitivity by chemical concentration of the micro-components being analysed, by means of a series of successive chemical reactions.

Since the analysis of micro-components exhibits a whole series of characteristic features, and the determination of trace quantities of harmful substances in air encounters various difficulties, these questions must be examined in more detail. Even in its present form, chromatography represents a method for determining traces (10^{-1}–10^{-7}%) and micro-quantities (below 10^{-7}%) of substances, that is it deals with specimens in the region of 10^{-8} g. At the same time, in some cases it is necessary to detect the compounds being analysed in quantities of 10^{-15} g. In quantitative analysis, the range of concentrations extends from 99.9999% to 10^{-10}%, and in the near future it may be necessary to work at even lower concentrations[5].

The limit of detection of the compounds being analysed is determined by a number of restrictions, namely:
1) non-representative removal of an average sample;
2) the inclusion of new components (contaminants) in the mixture being analysed, at different stages of the analysis (from the sampling device to detection) from foreign sources, and by consequent reactions of the components being analysed; 3) loss of material by selective adsorption during the analysis, and also by chemical reaction; and
4) a decrease in the maximum concentration of a substance during separation.

The problems of the removal of a representative sample are general for all analytical methods and are not examined in the present review. Selective sorption must be examined in more detail. This restriction is associated with the removal of the sample, and a number of factors—temperature, the polarity of the surface and the substances in the sample, their concentration, the degree of turbulence of the flow, and the ratio of the volume to the surface—all influence the results of the analysis. It is particularly difficult to determine traces of non-polar substances present in polar compounds, and also traces of polar substances present in non-polar compounds. The determination of traces of substances at concentrations lower than 3×10^{-6}% depends on the sorptive activity of the surface of the sampling device, which may lead to systematic errors. In this concentration range, therefore, the sampling should be dynamic[5]. In the analysis of micro-components, it is necessary to use special sampling methods, preferably of the continuous type, and special materials for the construction of the containers and connecting tubes; the roughness coefficient of the surface should be close to unity[5,38].

‡The theory of the analysis and chromatographic separation of micro-components is not discussed in the present work, since it has been examined in detail in a number of papers and in a monograph[10].

Kaiser[5,39] lists the following difficulties in the analysis of trace quantities.

1. The number of individual chemical compounds which may be present in small quantities is extremely large. At concentrations in the region of 10^{-4}%, in addition to the principal component (for example with air) with a concentration of 99%, the maximum possible number of components present in trace quantities is 10000, and in many cases only several hundred can be detected individually. At concentrations in the region of 10^{-7}%, in addition to a principal component at a concentration of 99.9%, the possible number of components present in trace quantities reaches 10^6. All this complicates considerably the analysis and particularly the individual identification of micro-quantities of harmful substances present in air, after their chromatographic separation.

2. The chemical reactivity of a number of components present in trace quantities is extremely high. Many facts indicate that some substances present in concentrations of $\sim 10^{-7}$% cannot be concentrated to 10^{-4}%, since they tend to decompose at these concentrations. This introduces a considerable restriction on the possibility of concentrating micro-quantities of various substances from air.

3. The concentration of stable substances present in a sample in trace quantities may be so low, and the concentration of reactive unstable substances so high, that many attempts to manipulate the sample will systematically lead to a false result.

These difficulties in the analysis of micro-quantities of harmful substances in air cannot always be overcome, but there is now a fairly large number of chromatographic methods which make it possible to analyse atmospheric pollutants with a relative error of not more than 15–20%.

III. DETECTORS. CALIBRATION

Although more than fifty detectors of different types are now used in gas-chromatographic analysis, very few of these have found extensive application for the analysis of atmospheric pollutants. This is due chiefly to the inadequate sensitivity of many detectors, which makes it impossible to carry out the direct determination of ultra-small quantities of substances in air samples. The detailed characteristics and applications of chromatographic detectors for the analysis of micro-components have been described in monographs[40,41] and in a large number of reviews devoted to detectors of different types[42,43] and problems of specific detection[44].

1. Universal Detectors

Of the gas-chromatographic detectors known at present, the flame ionisation detector (FID) is most frequently used in atmospheric and industrial chemistry; the FID is an almost ideal detector for the analysis of micro-quantities of hydrocarbons and most organic compounds. It makes it possible to analyse hydrocarbons at a concentration in air of $\sim 10^{-7}$–10^{-8}%, and when combined with preliminary concentration of the sample, even from small volumes of air, the sensitivity of the determination is increased by an order of magnitude[4]. The FID, which was previously regarded as insensitive to most inorganic compounds[40], also reacts to the presence, in the sample being analysed, of oxygen, nitric oxide, nitrous oxide[45,46], ammonia, phosphine, other oxides of nitrogen and cyanogen[47], oxides of carbon[48], and perfluoroalkanes[49]; it can also be used to determine low concentrations in air of sulphur dioxide, hydrogen sulphide, carbon disulphide, and carbonyl sulphide, mixed with thiols[50]. For example, it is convenient to use the flame ionisation detector, the sensitivity of which for carbon disulphide depends on the rate of flow of hydrogen and the carrier gas, the flame temperature, and other factors, for determining carbon disulphide vapour at concentrations ≤ 0.01%. In this concentration range, the magnitude of the FID signal is directly proportional to the concentration; the formation of ions apparently takes place via the formation, from carbon disulphide, of a small number of $CH^{\cdot}$ radicals, followed by the ionisation reaction $CH^{\cdot} + O = CHO^{+} + e$, characteristic of the operation of the FID.[40,51] By using perfluoromethane (Freon 116) as carrier gas, it is possible to detect sulphur dioxide and carbon dioxide, and also nitrogen and inert gases[52]. The use of ammonia as carrier gas has made it possible to increase considerably the sensitivity of the FID towards chlorinated hydrocarbons[53].

An even more universal detector than the FID is the argon ionisation detector, used for the analysis of many organic and inorganic compounds[40]. The sensitivity of the argon detector towards inorganic compounds of sulphur lies in the range 10^{-6}–10^{-3}%;[54] for phosphine the value is $\sim 10^{-4}$%.[55] The threshold sensitivity of this detector for oxygen, nitrogen, hydrogen, methane, oxides of nitrogen and carbon, and sulphur dioxide is $\sim 10^{-5}$%,[40] although for organic compounds it lies at the sensitivity level of the FID.

Recently, micro-components in air have been analysed using a pyroelectric katharometer, the sensitivity of which is 500 times that of an ordinary thermistor katharometer[50].

2. Selective Detectors

The analysis of atmospheric pollutants is made particularly effective by using selective highly sensitive detectors--electron capture (ECD), thermo-ionic (TID), flame photometric (FPD), and coulometric (COULD) detectors—which make it possible to carry out the qualitative and quantitative analysis of micro-concentrations of pollutants in complex many-component mixtures of substances of different classes. Comparison of the chromatograms obtained using universal detectors (reacting to all components) and selective detectors (reacting to molecules with definite hetero-atoms and functional groups) provides a reliable means of identifying trace components in complex mixtures in atmospheric and industrial air. This method makes it possible, against a background of the hydrocarbons most frequently encountered in polluted air, to determine halogens (ECD), sulphur (FPD), phosphorus (TID), etc. Combinations of FID and ECD, FID and FPD, and FID and COULD are particularly effective. The mass-spectral detector[40] has a unique selectivity.

The most sensitive detector in gas chromatography (see Table) is the electron capture detector[57], which, in spite of its short linear range, is widely used to determine halogens, sulphur-, nitrogen-, and halogen-containing organic compounds, and also metal aerosols (as chelate or organometallic compounds) in air[58,59]. This is one of the few detectors which can be used to determine nitrogen dioxide[60], inorganic compounds of sulphur[61], and other reactive substances by the direct method at concentrations of $\sim 10^{-7}$–10^{-4}%.[62] The ECD can be used to detect micro-quantities of polyaromatic hydrocarbons[63]; in the determination of meteorological tracers, for example sulphur hexafluoride, in the atmosphere, the sensitivity of the analysis reaches the phenomenal value of 2×10^{-10}%.[64]

The very high sensitivity of the ECD towards compounds of the halogens (which increases with increased number of halogen atoms in the molecule), and in particular to pesticides[65], has made this detector irreplaceable in the analysis of residual quantities of pesticides in the environment.

Sensitivity and selectivity of the detectors most frequently used for the analysis of pollutants in air.

Detector	Selectivity*							Threshold sensitivity, wt.%	Refs.
	N	S	Hal	O	P	hydrocarbons	OMC		
FID	–	–	–	–	–	–	–	10^{-8}	40, 41
Mass spectrometer	–	–	–	–	–	–	–	10^{-8}	40
ECD	+	+	+	+	+	PAH	+	10^{-9}	58, 63
TID	+	–	+	–	+	–	–	$5\cdot10^{-9}$	63, 74
FPD	–	+	+	–	+	–	+	10^{-8}	71, 72
COULD	+	+	+	–	+	–	–	10^{-7}	76
Detector with microwave radiation	–	+	+	–	+	+	+	10^{-8}	63, 80
Spectrofluorimetric detector	–	–	–	–	–	AH PAH	–	10^{-5}	40, 63

*Symbols: PAH = polyaromatic hydrocarbons; AH = aromatic hydrocarbons; OMC = organometallic compounds. The "plus" symbol indicates the class of compound to which the given detector is most sensitive.

The FPD is also frequently used for this purpose. The FPD has a high selectivity and is used for the analysis of such atmospheric pollutants as sulphur-, phosphorus-, nitrogen-, and halogen-derivatives of hydrocarbons, oxides of nitrogen and sulphur, hydrogen fluoride, nitrogen fluorides, carbon disulphide, and metals (as chelate compounds)[40,63,66]. The FPD has been used to determine nanogram quantities of the halogens and alkyl halides[67,68] and 10^{-1}–10^{-8}% of volatile compounds of sulphur and phosphorus[60,70], and a combination of an FPD and an FID makes it possible to analyse separately, in atmospheric air, micro-quantities of sulphur-, chlorine-, phosphorus-, and nitrogen-containing compounds[71]. The chief characteristic of the FPD and its use for the analysis of volatile compounds of sulphur in air have been described[72]. This detector makes it possible to determine, in polluted air, ~ 10^{-7}% of sulphur dioxide, hydrogen sulphide, carbon disulphide, carbon oxide sulphide, sulphides, and thiols[73].

Ultra-small quantities of substances containing phosphorus, nitrogen, and halogens can be detected using the TID, the threshold sensitivity of which is 2×10^{-6}% for chlorine, 10^{-8}% for nitrogen, and 5×10^{-9}% for phosphorus[40,74]. Thus the TID, together with the ECD, is used for the analysis of residual quantities of pesticides, and also to determine toxic organic compounds of nitrogen and chlorine in air[41,75].

The COULD has a high sensitivity towards compounds of sulphur, nitrogen, the halogens, and phosphorus[63]. It has been used to determine micro-quantities of the halogens, sulphur dioxide, and hydrogen sulphide (10^{-5}%) in air[76]. The COULD, like other selective detectors (ECD, FPD, TID), has an extremely low sensitivity towards hydrocarbons (lower by 3–5 orders of magnitude than that for heteroatoms).

Among the other detectors used to determine traces of harmful substances in air, the helium ionisation detector has a high sensitivity. It makes it possible to analyse the permanent gases, various light compounds of sulphur, and light hydrocarbons (~ 10^{-7}%)[77], and also to determine low concentrations of chlorine and Freons in air[78].

In the analysis of air, increasing use is being made of sensitive spectral detectors, the selectivity of which may vary over a wide range; for example, the emission spectrometer[79], a detector using microwave radiation[80], and a spectrofluorimetric detector, selective towards aromatic compounds[63]. A very valuable detector for the gas-chromatographic analysis of micro-components is the mass spectrometer, the sensitivity of which is comparable to that of the FID.[40] A combination of gas chromatography and mass spectrometry makes it possible to determine very low concentrations of toxic substances in air, and this method is now preferred to all other methods for identifying traces of a substance leaving a chromatographic column[81].

3. Preparation of Standard Mixtures and Calibration

The magnitude of the signal of differential detectors depends to a considerable extent on the nature of the compounds being analysed. Thus to carry out accurate quantitative determinations it is necessary to know the individual sensitivity of the detecting assembly with respect to the substances being analysed. For the calibration, that is for the determination of the quantitative relationship between the instrument signal and the absolute concentration of a component, it is necessary to have mixtures of the compounds being analysed with known concentrations, that is standard mixtures. The basic principles, methods, and characteristic features of the calibration of chromatographic detectors has been examined in detail[40,41,43] and are well known.

Static methods for preparing these mixtures are simple and most convenient for gaseous and volatile substances. The simplest involves the use of gas-measuring devices of known volume, glass bottles, and other containers, into which an accurately known quantity of the substance or mixture of substances being analysed is introduced[82,83]. Static methods of calibration are characterised by a large number of possible sources of error, and are therefore less reliable than dynamic methods; the chief disadvantage of static methods of preparing standard mixtures is the adsorption of micro-components on the walls of the containers (in some cases the losses may reach 50%[10]).

The dynamic method of calibration, which does not have these disadvantages, is used much more frequently in analysis. The simplest version of this method involves the dilution (sometimes in several stages) of pure cylinder gases, which are not always available, however. Here it is necessary to have a special measuring apparatus which makes it possible to control the gas flow rate very accurately[84]. The National Bureau of Standards (USA) has developed an apparatus for creating micro-concentrations of hydrogen fluoride, arsine, and phosgene by dilution[85]. The method makes it possible to obtain mixtures with a concentration of substances in the range 0.5–5 times the MPC. The method of exponential dilution[86], previously proposed by Lovelock[10], makes it possible to decrease considerably adsorption on the walls of the container and to prepare very low concentrations of several substances simultaneously. For the production of ultra-low concentrations in a stream or in a closed volume, a method based on the electrochemical preparation of the components of

the mixture being produced[87] is of interest. A significant advantage of this method is the absence of parts subject to friction and the ease of control of the rate of liberation of the gas being calibrated, by changing the current strength through the electrolyte.

The method of preparing standard mixtures of micro-quantities of different substances, based on the diffusion of the gases or vapours of liquids into the stream of diluent gas (carrier gas), is most widely used. The diffusion may take place through a tube, a porous surface (glass or ceramic), or a polymer film; in diffusion methods, sorption on the walls of the vessels is not significant. The use of diffusion cells makes it possible to calculate the concentration of the mixture, but the accuracy of the dosage and the reproducibility of the method are not always satisfactory[88].

The ability of micro-components to diffuse through the walls of plastic tubing has aroused considerable interest among analytical chemists[89]. It has been found that the stationary rate of diffusion of gases through the walls of tubes of ethylene and propylene Fluoroplasts at a constant temperature is practically constant, depending to slight extent on the composition and pressure of the gas. The rate of diffusion (and hence the concentration of micro-components obtained) is determined from the decrease in the weight of the tube containing the liquefied gas. The method of preparing standard mixtures of micro-concentrations of different substances based on this phenomenon has been widely used. The permeability of polymer tubes to different substances has been studied[89,90]. Diffusion through Teflon has been used to prepare standard mixtures of hydrogen sulphide, carbon disulphide, hydrogen fluoride, chlorine, ammonia, phosgene, propane, and methanethiol in air[91,92]. The method of preparing the filling the diffusion tubes has been described[93]. Diffusion through a Teflon tube may be constant for several years, and the total error of this dosage method does not exceed 1–2%.[94] The preparation of mixtures of moist air containing oxides of carbon, sulphur, nitrogen, ammonia, chlorine, hydrogen chloride, and other gases has been described[95]. The construction of an apparatus for the accurately controlled dilution of a gas specimen using semi-permeable polymer membranes has been discussed[96]. For this purpose, use has also been made of silicone rubber, which passes the vapours of organic substances at a rate directly proportional to the surface area of the tube and inversely proportional to its wall thickness[97].

A simple method for preparing micro-concentrations of chlorine and nitrogen dioxide involves the saturation, by these gases, of BAU active carbon, from which the gases can be desorbed to give concentrations of the gases at the level of the MPC, which remain constant for a prolonged period[98]. Various experimental problems in the preparation of standard mixtures and the calibration of chromatographs have been discussed in various papers[99,100] and a monograph[13]. An interesting review of methods for preparing standard mixtures at ultramicro-concentrations has been published[101]. The theory of the principal methods for calibrating instruments for gas analysis (in particular chromatographs) has been described in detail[102].

IV. CHARACTERISTIC FEATURES OF THE QUALITATIVE AND QUANTITATIVE ANALYSIS OF MICRO-QUANTITIES OF HARMFUL SUBSTANCES IN AIR

The principal methods for identifying micro-concentrations of harmful substances in complex mixtures in polluted air, used in conjunction with gas chromatography, have been examined in detail[63]. The most promising method for the qualitative analysis of micro-components in complex mixtures of organic and inorganic compounds of different classes is undoubtedly the combination of gas-chromatographic separation with mass-spectral analysis of the individual components of the sample, leaving the chromatographic column (GC-MS). This method of identification gives the most reliable results and is widely used in the analysis of atmospheric air and the air in living quarters and in industrial plants (gas liberation from polymers, rubber, plastics, etc.). After sampling and preliminary treatment, the sample is introduced into the gas chromatograph–mass spectrometer system[103], and the results of the analysis are processed on a computer[104]. The method is expensive and complex, but is being used on an increasing scale for the control of pollutants in the environment, particularly in those cases where the polluted air contains many-component mixtures of toxic substances.

Simpler methods are now being used for the same purposes, and these methods, taken together, may give more or less identical information on the composition of complex mixtures of chemical substances. One such method is the chromatographic-distribution method of identifying volatile organic compounds[105]. This method makes it possible to carry out the qualitative and quantitative analysis of organic substances (dissolved in an absorbing liquid) from the relative distribution coefficients in a liquid–liquid system (K_{rel}). The value of K_{rel} is determined by gas chromatography from the results of the analysis of aliquot portions of both liquid phases.

Various methods for the qualitative analysis of micro-components after chromatographic separation of the compounds in the sample have been described[63,106]. For this purpose it is also possible to use purely chromatographic methods, identifying the substances in the sample from their retention characteristics[107–109] and from their logarithmic relationships[63,110] or by reaction gas chromatography[63,111–113] and various other methods of analysis[114].

Sometimes, the components leaving a chromatographic column are identified using colour reactions for individual functional groups in organic compounds[63], but their sensitivity (0.1–1.0 μg)[115] is often insufficient (in analysis on capillary columns and in various other cases when small samples are being analysed). The infrared spectrum of a substance provides a reliable method for its identification. The successful use of this method to characterise individual substances after chromatographic separation is difficult, however, in the case of micro-components, and is fairly infrequently encountered in the analysis of air, due to the difficulty of accumulating a sufficient quantity of substance (20–30 mg) to obtain infrared spectra[63]. A spectrometer can also be used directly as a gas-chromatographic detector, but this requires a special analytical technique (spectrometer connected to the chromatograph, special cells, etc.)[116].

The successful identification of micro-quantities of harmful substances in complex mixtures in polluted air depends largely on the completeness of the separation of the compounds being analysed in the sample. Thus the chromatographic separation of toxic substances in air samples is carried out using capillary packed columns containing selective liquid phases[117] or highly efficient capillary columns[118]. The characteristic features of the identification and quantitative analysis of micro-components in air have been examined[10,119,120].

It has been shown[121] that the analysis of various aromatic hydrocarbons at a concentration of 10^{-7}% from one litre of air can be carried out with an accuracy of ±25%.

The accuracy of the analysis depends on the complexity of the system used for sampling, concentrating, preparation of the sample for chromatographic separation, and the chosen method of calibration. The use of even a moderately complex concentrating system may in itself introduce an additional source of errors in all analytical operations[4]. To increase the accuracy of the chromatographic analysis of atmospheric pollutants, it is necessary to use special vapour–gas mixtures as standards, and also to measure the rate of flow of air by means of additional flow-meters in the dosage systems[99,101]. The methods of calculation used in chromatography and the question of the accuracy of chromatographic analysis have been discussed[122,123].

V. ANALYSIS OF INORGANIC SUBSTANCES

The principal inorganic atmospheric pollutants are the oxides of carbon, nitrogen, and sulphur, hydrogen sulphide, and the halogens, the main sources of which are industrial emission and automobile exhaust. In addition, atmospheric dust contains highly toxic oxides and aerosols of metals (lead, mercury, beryllium, etc.). The compositions of inorganic industrial poisons are determined by the specific features of the production process (inorganic synthesis, metallurgy, textile production, etc.). Various problems of the chromatographic analysis of micro-quantities of harmful inorganic substances in air have been discussed[4,124].

1. Halogens and Their Compounds

The determination in air of micro-concentrations of the halogens and their derivatives, which exhibit an appreciable toxicity, involves familiar difficulties, associated chiefly with the high reactivity of these substances: they react with the material of the traps, the chromatographic packing, the connecting tubes of the chromatographs, and the detectors used. This can be partly avoided by using apparatus constructed from corrosion-resistant materials and by using inert sorbents and stationary phases stable towards reactive compounds. Nevertheless, an unavoidable feature of the analysis of traces of corrosive and reactive substances is the prolonged conditioning of the chromatographic apparatus and sorbents in contact with the gases being analysed[9]. All these problems in the chromatographic analysis of air have been discussed in detail[9,124–127].

The gas-chromatographic determination in air of the extremely reactive fluorine and most of its compounds is carried out using completely inert sorbents and liquid phases (chlorofluorohydrocarbons and polymers based on them), and the parts of the chromatographic apparatus (columns, connecting tubes, detectors) are made of Teflon and pure nickel and its alloys[124]. The methods of sampling air contaminated by fluorine-containing inorganic compounds have been examined[128], but there is very little published information on the gas-chromatographic determination of fluorine in air, and this generally relates to the analysis of not fluorine, but its derivatives, for example triethylfluorosilane[129]. The very reactive chlorine trifluoride, which is liberated from liquid oxidants in the transport of rocket fuel, has been determined (at a concentration of $5 \times 10^{-6}\%$) on a chromatograph with an ECD on a packing containing a methylsilicone oil after separation from air and halogens[130]. Analyses of this kind cannot be carried out on columns with halogen-containing stationary liquid phases, since the ECD is very sensitive to halogens.

The analysis of chlorine and hydrogen chloride does not require such rigorous conditions. These substances are separated on ordinary stationary phases[124], but particular care is necessary with the very unstable chlorine dioxide, particularly during its concentration[9]. The quantitative determination of the MPC of chlorine and nitrogen dioxide in the presence of other reactive gases has been described[131].

The conditions for the gas-chromatographic determination of various reactive gases in air have been examined in detail[132]. It was established that by using an ECD it is possible to analyse 10^{-4}–$10^{-5}\%$ of chlorine and oxides of sulphur and nitrogen with a relative error of ~ 10%, although for nitrogen dioxide the error may reach 50%.

The chromatographic analysis of phosgene presents no particular difficulty, and the use of an ECD makes it possible to analyse this gas in mixtures with chlorinated hydrocarbons in concentrations of ~ 10^{-6}–$10^{-7}\%$[133]. The high sensitivity of the ECD makes it possible to analyse air for ultramicroconcentrations of sulphur hexafluoride and various other tracers used to study the propagation of air currents in the atmosphere and various pollutants in the troposphere (lower atmosphere)[64].

2. Compounds of Nitrogen

Among many methods for the analysis of oxides of nitrogen[134,135], their gas-chromatographic determination in air has recently been widely used[136], but at present this method is not preferred, because the chromatographic analysis of micro-quantities of oxides of nitrogen, particularly nitrogen dioxide, encounters a whole series of difficulties, associated with the high reactivity of these compounds. For the analysis of micro-concentrations of nitrogen dioxide, it is best to use glass columns and inert stationary phases based on chlorofluorohydrocarbons[137]. However, prolonged conditioning of the chromatographic packing in the presence of oxides of nitrogen makes it possible to analyse these and other reactive gases on ordinary stationary phases, for example diethyl phthalate[131]. Various chromatographic columns and detectors used for this purpose have been discussed[138]. The detection of nitrogen dioxide by a katharometer after preliminary concentration of the sample makes it possible to determine ~ $10^{-4}\%$ of this gas in air[131]. A similar result is obtained in the direct determination of oxides of nitrogen using an ECD[139].

In view of the difficulties of the direct analysis of micro-quantities of nitrogen dioxide, the methods of reaction gas chromatography have been increasingly used in recent years for this purpose. By using an ECD, it is possible to determine with a high sensitivity the products of the reaction of oxides of nitrogen with phosphines or phosphites[140], styrene, or xylenes[141]. The conversion of nitrogen dioxide into nitrobenzene and the determination of the latter (10^{-12} g) using an ECD has been described[142].

The analysis of oxides of nitrogen in the atmosphere is further complicated by the fact that, under the influence of sunlight, they react with hydrocarbons, forming in the smog an even more reactive mixture of ozone, peroxyacetyl nitrate, and peroxybenzoyl nitrate. Methods for sampling air and for the chromatographic analysis of

oxides of nitrogen in the atmosphere in the presence of oxides of sulphur and carbon, oxidants, and hydrocarbons have been described[143,144].

Equal difficulties are encountered in the chromatographic analysis of nitric oxide, which is usually present in air mixed with other oxides of nitrogen[140]. The accuracy of the analysis can be improved by the quantitative removal of nitrogen dioxide in a special column using 2,2',2''-nitrilotri(ethanol) on a diatomite carrier[145]; to increase the sensitivity, the products of the reaction of nitric oxide with sodium butoxide are detected using an FID.[146]

The determination of nitrous oxide in atmospheric air presents no difficulties, and is generally carried out by gas-adsorption chromatography[147]. An interesting feature is that with increase in temperature from 20°C to 400°C the sensitivity of the ECD towards nitrous oxide increases by a factor of 1000. This phenomenon can be used to monitor low concentrations of nitrous oxide in the atmosphere[147].

The electron-capture detector makes it possible to determine 10^{-7}% of nitrates and nitrites in air and in biological media after conversion to nitrobenzene[148]. The direct chromatographic analysis of ammonia, particularly in the presence of moisture, is complicated by the spreading of the peak corresponding to this substance on most available packings[149]. The determination of ammonia in cigarette smoke has been described[150]; ammonia has been detected together with other gases in the products of the combustion of plastics[151].

Similar mixtures of inorganic gases, also containing cyanide vapours, are encountered in industrial air contaminated by the products of the combustion of polyurethanes[152]. Micro-quantities of hydrogen cyanide and cyanogen (~ 10^{-4}%) have been determined in air using an FID after the separation of hydrogen cyanide from other gases on a column containing Carbopacks on Teflon[153]. A method has been described for removing cyanide vapours on silica gel with subsequent extraction of the sample by methanol and chromatographic analysis of the resulting solution at room temperature on a column containing adiponitrile on celite[154]. Traces of cyanogen chloride in air have been determined using an ECD[155].

3. Compounds of Sulphur and Phosphorus

Inorganic compounds of sulphur are sampled and concentrated using cooled traps containing column packings[156] or concentration columns containing 13X molecular sieves[157] or active carbon[158] as adsorbents. In the last case, the sample is extracted from the column using benzene, and analysed on a chromatograph with a flame photometric detector.

In the analysis of compounds of sulphur, glass or Teflon columns are used[159], and Porapak-S is successfully used as sorbent for the chromatographic separation. Columns containing different packings, previously conditioned by the gases being analysed, are also used. The best solid carriers are Chromosorb W and porous polymeric sorbents, on which various liquid phases (chiefly polar phases) are deposited[160]. In the opinion of some authors[161], the separation of organic compounds of sulphur, hydrogen sulphide, sulphur dioxide, and carbonyl sulphide present in air in very low concentrations is best carried out using chromatographic columns containing Carbopacks, treated with a solution of phosphoric acid and nitrylsilicone XE-60.

Gas-chromatographic methods for determining micro-quantities of carbon disulphide and carbon oxide sulphide[158] and hydrogen sulphide[162], and the analysis of complex mixtures of inorganic compounds of sulphur in the atmosphere[163], in the neighbourhood of a cellulose and paper plant[164], in the effluent gases from plants producing starch[165], and in sulphuric acid manufacture[166] have been described.

Cryogenic gas chromatography has recently been used for the analysis of atmospheric pollutants. Traces of the oxides of nitrogen, carbon, and sulphur, hydrogen sulphide, carbonyl sulphide, and light hydrocarbons are much more effectively separated on ordinary chromatographic packing at low temperatures[167].

Elemental phosphorus in air is determined by trapping it in an absorber containing xylene and analysing an aliquot portion of the solution on a chromatograph with an FPD[168]. Phosphine can be determined in air at a concentration of 10^{-7}% using ionisation detectors[169].

4. Permanent Gases

The permanent gases and other low-boiling gases are generally analysed by gas-adsorption chromatography, since the solubility of these gases in the liquids used as stationary phases in gas-liquid chromatography is usually too low. Most work on the chromatography of the permanent gases has been devoted to the determination of the oxides of carbon, liberated into the atmosphere in various processes of fuel combustion and in forest fires.

The chromatographic separation of micro-quantities of the permanent gases is usually carried out using active carbon, molecular sieves, and porous polymers as adsorbents[124]. For the analysis of mixtures of substances having a wide range of boiling points (permanent and inert gases and hydrocarbons), 2–3 columns with different adsorbents are used[170].

In recent years, several detectors have been described, which make it possible to determine with a high sensitivity (10^{-4}–10^{-5}%) the oxides of carbon and other permanent gases in the atmosphere and in industrial air. These include discharge detectors[171], ultrasonic detectors[172], and the pyroelectric katharometer[173]. The last detector can be used to detect reliably 5×10^{-5} vol.% of carbon monoxide with a relative error of not more than 5%. A high sensitivity in the determination of CO can also be achieved using a detector of low sensitivity. In this case the carbon monoxide present in a sample of several litres of air is concentrated by extensive cooling on a column containing CaA zeolite[174]. By concentrating the CO in stages, it is possible to determine less than 10^{-6}% of carbon monoxide[175]. Nevertheless, the analysis of micro-concentrations of carbon monoxide (and sometimes also carbon dioxide) is most frequently carried out by catalytic hydrogenation of CO to methane with subsequent detection of the CH_4 on an FID.[176] The sensitivity of this method is ~ 10^{-5}%; an unsatisfactory feature is the low accuracy and the time taken for the conversion.

The chromatographic determination of micro-quantities of carbon dioxide is carried out using columns containing silica gel and other adsorbents[177]. In addition to the analysis of atmospheric air[178], gas chromatography is used to determine CO,[179] CO and CH_4,[180] and CO and light hydrocarbons[181] in respirator gases, and also to analyse air in sealed isolated compartments[182] and mines[183].

Gas chromatography can also be used to determine traces of ozone, separated from air and chlorine on silica gel at low temperatures, and detected using an ECD ($\sim 5 \times 10^{-3}\%$) [184] §.

5. Metal Aerosols

The ability of various metals to form volatile complex compounds with organic ligands, particularly chelate compounds [185], has made it possible to use gas chromatography to determine the aerosols of various toxic metals and their compounds in air.

Only a few minutes are required for the chromatographic analysis of picogram quantities of aluminium and chromium as their chelate compounds with trifluoroacetylacetone (TFA) [186]. The methods of sampling and the conditions for the separation and chromatographic analysis of highly toxic aerosols of metallic beryllium and its compounds have been described [187]. The air being analysed was passed through a filter, the aerosols retained were ashed with the filter and dissolved, and a solution of TFA in benzene was added. An aliquot portion of the benzene solution of the resulting $Be(TFA)_2$ was analysed on a chromatograph using an ECD, which makes it possible to determine metal chelate compounds with a very high sensitivity (10^{-10} g aluminium, 10^{-12} g chromium, and 10^{-13} g beryllium) [188].

VI. ANALYSIS OF ORGANIC SUBSTANCES

1. Readily Volatile Hydrocarbons

Methods for the gas-chromatographic analysis of micro-quantities of hydrocarbons in air have been fairly well developed and described in detail [4,189,190]. The substances present in a sample of polluted air are usually concentrated on a suitable adsorbent (silica gel, active carbon, polymeric sorbents) at the temperature of the surrounding medium (or with cooling), or trapped in a concentrator containing an inert packing at low temperatures, and the separation and analysis are carried out using various sorbents and a flame ionisation detector. For the overall determination of hydrocarbons and other organic substances in air [191], the sample being analysed is introduced directly into the FID. For the separate determination of the light hydrocarbons (C_1–C_4), gas-adsorption chromatography is used, with active carbon, silica gel [192], molecular sieves [193], or Porapak-S [194] as adsorbents. Micro-quantities of heavier hydrocarbons (beginning from $\sim C_5$–C_6) are analysed by gas-liquid chromatography, and several dozen liquids of different polarity are used as stationary phases.

Gas chromatography can be successfully used to analyse samples of polluted air of complex composition containing, in addition to hydrocarbons, their derivatives containing atoms of oxygen, nitrogen, sulphur, and halogens. Mixtures of industrial poisons of this kind are liberated into the air of industrial plants in the preparation, processing, and storage of polymers and technical compositions based on them, and also in the pyrolysis of these materials under different conditions [195,196]. A combination of chromatographic columns with stationary phases of different polarity has made it possible to separate and identify the components of the gases liberated in the vulcanisation of rubber [197] and in rubber mixing [198], and the combination of gas chromatography and mass spectrometry has given detailed information on the composition of the volatile products polluting air when various rubbers are heated [199].

The possibilities provided by gas chromatography in the study of toxic products in atmospheric and industrial air have been extended considerably by the use of highly efficient capillary columns. Approximately 100 paraffinic, naphthenic, and aromatic hydrocarbons have been determined in the air of industrial plants containing white-spirit vapour. The analysis was carried out on a chromatograph with a 70-metre capillary column containing squalane at 100°C [200-202]. A mixture of alkylbenzenes liberated into the air by plants producing polystyrene has been studied similarly [203]. Complex mixtures of hydrocarbons and their derivatives, polluting the air in the production of rubber footwear, have been separated on capillary columns and identified by various physicochemical methods [204]. The use of temperature programming on capillary columns containing silicones has made it possible to separate and identify up to 200 C_3–C_{12} hydrocarbons present in the gases emitted from automobile and diesel engines [205]. The absolute quantity of soot in treated automobile gases has also been determined by gas chromatography after trapping the soot by means of a sitall (glass ceramic) filter and pyrolysis of the sample [206], and the highly toxic tetra-ethyl-lead has been determined in air at a concentration of 1 mg m^{-3} using an ECD [207].

Particularly valuable information on the composition of atmospheric pollutants is given by the combination of gas chromatography and mass spectrometry. This method has been used to determine the concentration of organic pollutants in industrial and city air [208,209]. The sample of air being analysed was passed through a drying agent and a cooled trap containing Tenax GC [210] or Chromosorb W, impregnated with a silicone [211]; the concentrated components were displaced from the trap by heating, into a capillary column connected to the mass spectrometer.

2. Vapours and Aerosols of Hydrocarbons with a Low Volatility

The chromatographic analysis of hydrocarbons with a high molecular weight encounters certain difficulties associated with the sampling, separation, and detection of high-boiling compounds. Organic pollutants of high molecular weight in the form of aerosols, and also adsorbed on dust particles suspended in air, are trapped by mechanical or electrostatic filters and fractionated by extraction or thin-layer chromatography. Methods for isolating organic substances from aerosols and dust, and apparatus and procedures for the analysis of atmospheric pollutants of this kind have been described [212,213].

More than 100 organic substances (C_6–C_{20}) have been identified in city air after passing the sample through a cigarette filter of active carbon or through a column containing graphitised carbon black, with subsequent extraction of the sorbed compounds by carbon disulphide and chromatographic analysis of the substances liberated on a capillary column with a silicone liquid phase [214]. The components of these complex mixtures are identified by the usual chromatographic–mass-spectrometric method [214,215].

Gas chromatography has been used increasingly in recent years to solve the important problem of determining the concentration in air of polycyclic aromatic hydrocarbons (PAH), many of which are carcinogenic. The PAH

§ See also Ref. 340.

present in air, which are usually adsorbed on dust particles, are concentrated on active carbon[216] or collected on a glass fibre filter[217]; they are then extracted by benzene, cyclohexane, or nitromethane, and subsequently analysed by gas chromatography. A simple apparatus for the effective collection of samples of this kind, consisting of a condenser coil containing Tenax GC, has been described[218]. Micro-concentrations of PAH are now successfully separated using modified sorbents. A short column containing celite-545, the surface of which is covered by linear polyethylene, with temperature programming from 70°C to 290°C, can be used to separate 16 polyaromatic hydrocarbons[219], and even to separate such pairs as phenanthrene and anthracene, chrysene and benzanthracene, and perylene and 3,4-benzpyrene. Equally effective results were obtained using a column containing graphitised carbon black[220], and also carbon black impregnated with a small quantity of a polyphenyl ester[221]. This packing makes it possible to separate 3,4- and 1,2-benzpyrenes in 30 min, and anthracene and phenanthrene in 2–3 min (at 320°C).

The combination of gas-chromatographic separation with spectrofluorimetric detection has a high selectivity in the analysis of PAH[222]. The fluorimetric detector, the sensitivity of which with respect to fluorene is not less than 5 ng, can be used to detect selectively even PAH peaks which overlap on the chromatograms[223]. An even greater increase in the selectivity of this analysis can be achieved by preliminary separation of the PAH from the air sample by thin-layer chromatography[224]. Approximately 40 new PAH have been identified in air after separating an extract of the sample by liquid chromatography on a column containing silica gel, with subsequent gas-chromatographic analysis on a capillary column using a mass spectrometer[225]. This method has been used particularly frequently in recent years, and the polyaromatic compounds have been identified by a combination of gas chromatography, mass spectrometry, nuclear magnetic resonance, and computer calculations[226].

Progress in the gas-chromatographic analysis of polynuclear hydrocarbons in recent years has been discussed[227], and it has been pointed out that the extraction of the PAH sample from glass fibre filters, carried out in a Soxhlet apparatus, takes a long time and has a low reproducibility, and liquid-phase extraction using ultrasonics, or the even more effective gas-phase extraction, have been recommended for this purpose.

3. Oxygen-containing Organic Compounds

One of the most toxic atmospheric pollutants is peroxyacetyl nitrate (PAN), which is formed together with other compounds in the photolysis of automobile exhaust gases or as a result of atmospheric photochemical reactions involving hydrocarbons and oxides of nitrogen. Reactive PAN and alkyl nitrates are analysed using a glass or Teflon column with a packing of polyethylene glycol on Chromosorb W, and an ECD, which selectively detects PAN in mixtures with hydrocarbons[228,229]. The same methods are used to analyse toxic nitroalkenes[230], peroxypropionyl nitrate, and peroxybenzoyl nitrate[231].

Micro-quantities of polar aldehydes, ketones, and alcohols have been separated from hydrocarbons using a sectional chromatographic column containing OP-7 detergent and the highly polar cyanoethoxypropane, which are also present in the packing of the enriching column[232]. The determination of aldehydes and ketones in air by gas chromatography has been described[233,234]. In the analysis of alcohols and esters, a liquid absorber containing an alcohol or n-paraffinic hydrocarbons, or a column containing active carbon or silica gel, are used as concentrators[235]. The use of water for the selective extraction of C_1–C_4 alcohols adsorbed on carbon makes it possible to separate them from other compounds in the sample[236]. Chromatographic methods have been developed for the analysis of phenols in air; the phenols are separated on capillary and packed columns[237,238]. For the separate determination and identification of carboxylic acids, the air is passed through a glass fibre filter impregnated with alkali, or through a column containing silica gel; alternatively, the acids are absorbed by a solution of sodium hydroxide[239]. Capillary columns containing squalane and XE-60 cyanosilicone have been used to determine the composition of a complex mixture of oxygen-containing volatile substances (aldehydes, alcohols, carboxylic acids), contaminating air as a result of the decomposition of resin[240].

4. Organic Compounds of Sulphur and Phosphorus. Pesticides

Gas-chromatographic methods for determining volatile organic and inorganic compounds of sulphur using different detectors and different packing have been reviewed[241]. The sulphur compounds are trapped from the air in concentration tubes containing silica gel, active carbon, or Tenax GC[242,243]. Micro-quantities of organic compounds of sulphur are generally separated using the same packing as in the analysis of hydrocarbons, and the preferred detector is the FPD, which has a high sensitivity and selectivity to volatile compounds of sulphur[244]. Gas chromatography has been used to analyse sulphur-containing odourants and to determine other pollutants with a strong odour in air[245], and also for the analysis of traces of the highly toxic dimethyl sulphate[246].

The chromatographic analysis of organic compounds of phosphorus has been reviewed[247]. Gas chromatography is now the most sensitive and most convenient method for analysing the environment for pesticides, most of which are organic compounds of phosphorus and chlorine[248]. Most organic pesticides are fairly volatile, so that they can be separated in the vapour phase at temperatures up to 250°C. The methods of air sampling and the quantitative chromatographic analysis of pesticides have been discussed[249,250]. Micro-quantities of pesticides are analysed on glass columns (to avoid the decomposition of complex halogen-containing molecules) containing different packing, usually with silicone stationary phases[251,252]; glass capillary columns combined with an ECD are also used[253]. After enrichment of the sample, the sensitivity of the determination of pesticides using an ECD may reach 1 ng m^{-3} air[251]. The TID is extremely selective and sensitive to phosphorus-containing pesticides, and is now being used successfully to determine these substances in air[254].

5. Halogen-containing Organic Compounds

Fluorinated hydrocarbons[255], chlorofluorohydrocarbons[256], and fluoro-organic acids[257] in air are determined by gas chromatography using an ECD. In addition, a large number of recently published papers describe the chromatographic analysis of chlorinated hydrocarbons, particularly the determination of the highly toxic vinyl

chloride. Methods for determining chlorinated hydrocarbons, proposed as standard methods, have been described[258]. Organic chlorine-containing compounds are most frequently concentrated in short columns containing active carbon[259], from which they are desorbed by heating or extracted by an organic solvent; silicones, hydrocarbons, and phthalates are generally used as stationary phases for the separation of these compounds.

Micro-quantities of halogenated hydrocarbons are usually detected using the COULD and ECD[260,261], and the latter is an almost ideal detector for the analysis of halogen-containing substances. It is practically insensitive to hydrocarbons, whereas its sensitivity towards various organic compounds of chlorine may reach 8.5×10^{-11}%.[262] At the same time, the FID is most frequently used for the analysis of vinyl chloride (one chlorine atom in the molecule)[263]. Samples of air contaminated by vinyl chloride are obtained using Tenax GC or other adsorbents, the best of which is active carbon. If carbon disulphide is used as extracting agent, the efficiency of the desorption of vinyl chloride from carbon is greater than 90%.[264]

Gas chromatography has been used to analyse chlorine-containing pesticides[265], complex mixtures of Freons[266], polychlorobiphenyls[267], and other chlorine-containing organic pollutants of atmospheric and industrial air[268].

6. Nitrogen-containing Organic Substances

1 mg m^{-3} of the isomers of nitrotoluene can be determined by passing 20 litres of air through an absorber containing ethanol[269]. The gas-chromatographic analysis of air contaminated by benzene, chlorobenzene, nitrobenzene[270], and volatile N-nitroso-compounds has been described[271]. Nitriles, to which the ECD and FID are equally sensitive, are determined using the second of these detectors, by means of which it has been possible to detect 5×10^{-5}% of acrylonitrile in 1 ml of sample[272,273]. Micro-concentrations of 2,4-toluenedi-isocyanate have been determined in air using an ECD[274]. The accuracy of the chromatographic determination of mono-, di-, and trimethylamines in air using the FID is not less than 15%, and the sensitivity of the analysis is ~ 0.2 mg m^{-3}.[275,276] Good results are obtained by concentrating and separating amines on columns containing Tenax GC[277]. The flame ionisation detector has also been used to determine micro-quantities of aniline[278], pyridine, picolines, lutidines, and other pyrimidine bases, which contaminate the air in the production of tar and pitch[279]. The analysis of complex mixtures of polycyclic quinones in the atmosphere has been described[280].

VII. SUMMARY

Methods for the gas-chromatographic analysis of pollutants in the environment are being intensively developed. Among recently published studies, the following are noteworthy.

Sources of atmospheric pollution have been discussed[284], and the problems of analysis in the control of the pollution of the environment have been reviewed[285]. A detailed review of methods for the analysis of polluted air has been published[286]. Special reviews have recently been devoted to the gas-chromatographic analysis of air[287-289].

The general principles and methods of sampling air have been reviewed[290,291], and the criteria for evaluating methods for trapping traces of harmful substances in air on solid sorbents have been discussed[292]; active carbon[293] or polymeric sorbents[294] are most frequently used for this purpose. A promising sorbent is polyurethane foam, which has been found to be an effective material in traps for concentrating traces of phthalates[295], pesticides[296,297], polychlorobiphenyls[297], and PAH[298]. Polysorbimide-1[299] and the new carbon-containing sorbents Carbochrome-5 and Ambersorb XE-340[299,300] have proved to be very effective sorbents for micro-quantities of various chemical substances. Different types of apparatus and filters for trapping solid particles and aerosols have been described[301-303]. Selective sorbents for carbon monoxide have been found. These include silver-containing[304,305] and copper-containing[305] zeolites.

The electron-capture micro-detector, used in work with glass capillary columns, is being increasingly employed in the analysis of air[306]. The principles of the detection of traces of harmful substances in air using the COULD[307], conductometric[308], ultrasonic[309], and piezo-electric[310] detectors, the pyroelectric katharometer[311], and photometric[312] and electrochemical[313] detectors have been further developed. The combination of gas-chromatographic separation with detecting systems such as atomic-absorption[314] and atomic-fluorescence[315] spectrometers appears extremely promising for the analysis of micro-quantities of metals. The semiconducting detector[316] has an exceptionally high sensitivity towards organic substances with a large number of carbon atoms. A promising detector for the analysis of many inorganic compounds is the aerosol detector[317], and the neon ionisation detector can be used to determine approximately 10^{-5} vol.% of carbon monoxide in air without preliminary concentration[318]. A whole series of new methods based on reaction gas chromatography have been proposed for increasing the sensitivity of detection, and have been used to analyse air for micro-quantities of hydrogen fluoride[319], halogen compounds[320], styrene[321], carboxylic acids[322], and bischloromethyl ether[323]. The general principles of the chemical concentration of trace components using reaction gas chromatography has been described[324].

New versions have been developed for various methods of preparing standard mixtures of substances for calibrating detectors[325-327]; permeable polymer membranes are used particularly frequently for this purpose[328,329]. New methods of preparing effective glass capillary columns[330] and methods of using capillary columns for the highly sensitive quantitative analysis of micro-components[331] have been described. Micro-quantities of harmful substances in complex mixtures in polluted air are most frequently identified by the GC-MS method[332,333]. Other systems successfully used for this purpose include the microwave helium detector[334], a combination of gas chromatography with infrared and NMR spectroscopy[335], and the identification of the components of complex mixtures of hydrocarbons using the retention indices[336].

Gas chromatography has been used to analyse air for micro-quantities of phosgene[337], oxides of nitrogen[338], hydrogen cyanide[339], ozone[340], inorganic compounds of sulphur[341,342], carbon monoxide[343,344], the permanent gases[345], organometallic compounds[346], and metals in the form of chelate compounds[347]. Two recently published detailed reviews deal with the gas-chromatographic determination of metals, including the volatile complexes of metals with organic ligands[348,349].

A large number of papers have dealt with the determination of traces of organic substances in air. Methods for the analysis of hydrocarbons and other organic compounds

in solid dust particles and aerosols have been described[350-356]. Complex mixtures of atmospheric pollutants liberated from polymers and elastomers have been analysed[357,358] and the determination of a large number of organic substances in town and country air by GC-MS has been described[299,300]. Automobile exhaust gases contaminating the atmosphere have been analysed[359]. The gas-chromatographic method for determining traces of PAH in air has been further developed[360-362]; steel and glass capillary columns have been used to separate these carcinogenic substances. The analysis of air for phthalates[363], formic acid[364], phenols[365], acetone[366], acrolein and isoprene[367], biphenyl[368], peroxyacetyl nitrate[369], and various solvents[370] and odourants[371] has been described.

Gas chromatography has been used successfully for the analysis of amines[372], nitro-compounds[373], and the carcinogenic nitrosamines[374,375]. Odourants containing organic and inorganic compounds of sulphur[376-378], toxic low-molecular-weight chlorohydrocarbons[379-382], and very low concentrations of the carcinogenic vinyl chloride[383-385] and trichloroethylene[386] have been analysed. The ECD has been successfully used to analyse air for traces of pesticides[387,388], polychlorobiphenyls[389], and bischloromethyl ether[390].

A large number of automatic gas analysers have recently been developed for the operational control of the state of the atmosphere (in cities, industrial centres, factories, etc.), and the use of these analysers has been reviewed[391]. Gas-chromatographic analysers have been specially produced for analysing air for traces of carbon monoxide[392] and reactive hydrocarbons[393], for the analysis of solvent vapours[394], the determination of vinyl chloride[395], and the control of the concentration of sulphur dioxide[396], pesticide vapours[397], and bischloromethyl ether[398] in the atmosphere.

The present problems in the chemistry of the atmosphere and industrial hygiene relate chiefly to the accurate and sensitive determination of the concentration, in the troposphere, of hydrogen sulphide, sulphur dioxide, compounds of the halogens, and various acidic gases, and the identification and determination of a whole series of substances which irritate the eyes and have unpleasant odours. Gas chromatography, and particularly chromatographic–mass-spectral analysis with computer processing of the results, can obviously be of considerable assistance in the study of the qualitative composition of even very complex mixtures in polluted air, consisting of several hundred chemical compounds, and also for the accurate quantitative estimation of the level of contamination of air.

In recent years there has been a marked increase in interest in the standardisation of analytical methods for the study of polluted air[3]. It is now urgently necessary to unify methods for the analysis of photochemical oxidants, oxides of nitrogen, sulphur, and carbon, and solid particles suspended in air. The need to develop standard gas-chromatographic methods for the analysis of hydrocarbons in the atmosphere has been justified[281].

Methods of this kind have also been developed for other organic compounds[3,16,282,283].

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In conclusion it should be noted that gas chromatography has become the chief method for the analysis of polluted air, and it is now used to determine traces of practically all organic and many inorganic substances, and also metal aerosols and organometallic compounds entering the atmosphere. A whole series of problems remains unsolved in this field of the analysis of micro-components, however, associated with obtaining representative samples of the air, the concentrating of the trace components, the sensitive and specific detection of the substances being analysed against a background of interfering components, and also the reliable identification of trace components after chromatographic separation.

The solution of the problem of sampling air, which is essentially the problem of concentrating the trace components, depends to a large extent on the development of polymeric sorbents of the "Tenax" type, which make it possible to trap various chemical compounds effectively from contaminated air. On the other hand, a no less effective method involves the selective trapping of the trace components using reactive sorption columns placed in front of the trace component concentrator. This method of sampling appears more promising, since it facilitates considerably the subsequent identification of the substances being analysed and increases the speed of analysis. Methods of sampling (concentrating) trace components by bubbling the air through an active liquid also deserve attention.

Approximately ten selective and sensitive detectors (ECD, FPD, COULD, etc.) are used for the chromatographic analysis of trace components in air, but there is still no suitable detector for the selective detection of microquantities of inorganic substances (particularly carbon monoxide) against a background of the interfering organic trace components of the sample. The development of detectors selective towards the principal classes of atmospheric pollutant has made it necessary in some cases to detect only particular components (usually the most toxic) of the sample against a background of all other substances contaminating the air.

The most reliable information on the composition of complex mixtures of atmospheric pollutants is obtained by the GC-MS method, but the extensive application of this method is restricted by the high cost of the analyses. This has made it necessary to develop simpler methods for identifying trace components, based, for example, on the use of reaction gas chromatography or the chromatographic–distribution method of analysis.

REFERENCES

1. P. Chovin, Bull. soc. chim. France, 2655 (1974).
2. A. P. Altshuller, Anal. Chem., 37, 11 (1965).
3. B. E. Saltzman and J. E. Cuddeback, Anal. Chem., 47, 1 (1975).
4. A. P. Altshuller, "Advances in Chromatography", Vol. 5, London–New York, Marcel Dekker, 1968, p. 229.
5. R. Kaiser, in "Uspekhi Khromatografii" (Progress in Chromatography), Izd. Nauka, Moscow, 1972.
6. T. A. Gosink, Environ. Sci. Technol., 9, 630 (1975).
7. W. Leithe, Die Analyse der Luft und ihrer Verunreinigungen in der freien Atmosphäre und am Arbeitsplatz, XV, Wiss. Verlagsges, Stuttgart, 1974.
8. C. J. O. R. Morris, Lab. Pract., 23, 513 (1974).
9. Yu. S. Drugov, Candidate's Thesis, Scientific Research Institute of Work Hygiene and Occupational Diseases, Academy of Medican Sciences of the USSR, Moscow, 1969.
10. V. G. Berezkin and V. S. Tatarinskii, "Gazo-khromatograficheskie Metody Analiza Primesei" (Gas-Chromatographic Methods for the Analysis of Trace Components), Izd. Nauka, Moscow, 1970.

11. A. Zlatkis, H. A. Lichtenstein, and A. Tishbee, Chromatographia, 6, 67 (1973).
12. C. L. Fraust, Amer. Ind. Hyg. Assoc. J., 36, 278 (1975).
13. Amer. Ind. Hyg. Assoc. J., 32, 404 (1971).
14. J. E. Cuddeback, W. R. Burg, and S. R. Birch, Environ. Sci. Technol., 9, 1168 (1975).
15. L. D. White, D. G. Taylor, P. A. Mauer, and R. E. Kupel, Amer. Ind. Hyg. Assoc. J., 31, 245 (1970).
16. NIOSH Manual of Analytical Methods, U.S. Department of Health, Education and Weeface, Cincinnati, Ohio, 1974.
17. H. Bartels and B. Prijs, in "Advances in Chromatography", (edited by J. C. Giddings and R. A. Keller), Vol. 11, New York, Marcel Dekker, 1974, p. 196.
18. L. Dubois and J. L. Monkman, Microchim. Acta, No. 2, 313 (1970).
19. J. W. Russell, Environ. Sci. Technol., 9, 1175 (1975).
20. A. Zlatkis, W. Bertsch, D. A. Bafus, and H. M. Liebich, J. Chromatogr., 91, 379 (1974).
21. J. S. Parsons and S. Mitzner, Environ. Sci. Technol., 9, 1053 (1975).
22. W. A. Aue and D. R. Younker, J. Chromatogr., 88, 7 (1974).
23. J. Novak, V. Vasak, and J. Janak, Anal. Chem., 37, 660 (1965).
24. V. N. Borisov, B. V. Ioffe, and A. G. Vitenberg, Zhur. Anal. Khim., 30, 1289 (1975).
25. C. Nicotra, A. Cornu, R. Massot, and P. Perilhon, Gas Chromatography 1972, (edited by E. G. Perry), Appl. Sci. Publ., London, 1973, p. 9.
26. E. V. Vagin, in "Gazovaya Khromatografiya, Trudy III Vsesoyuznoi Konferentsii, Dzerzhinsk, 1966" (Proceedings of the Third All Union Conference on Gas Chromatography, Dzerzhinsk, 1966), p. 467.
27. A. Dravnieks and B. K. Krotoszynski, J. Gas Chromatogr., 4, 367 (1966).
28. H. Binder, J. Chromatogr., 25, 189 (1966).
29. G. Mueller and G. Gnauck, "Reinste Gase (Physikalisch-chemische Trenn- und Messmethoden)" (Translated into Russian), Izd. Mir, Moscow, 1968.
30. I. H. Williams, Anal. Chem., 37, 1723 (1965).
31. W. W. Bunn, E. R. Deane, D. W. Klein, and R. D. Kleopfer, Water, Air and Soil Pollut., 4, 367 (1975).
32. A. A. Zhukhovitskii, V. V. Naumova, M. S. Selenkina, N. M. Turkel'taub, V. P. Shvartsman, and A. F. Shlyakhov, see Ref. 26, p. 74.
33. A. A. Zhukhovitskii, N. M. Turkel'taub, and T. V. Georgievskaya, Dokl. Akad. Nauk SSSR, 92, 987 (1953).
34. A. A. Zhukhovitskii and N. M. Turkel'taub, Dokl. Akad. Nauk SSSR, 143, 646 (1962).
35. A. A. Zhukhovitskii, N. M. Turkel'taub, L. A. Malyasov, A. F. Shlyakhov, V. V. Naumova, and T. I. Pogrebnaya, Zavod. Lab., 29, 1162 (1963).
36. B. K. Krylov and V. I. Kalmanovskii, Zavod. Lab., 35, 152 (1969).
37. V. M. Sakharov, G. S. Beskova, and A. I. Butusova, J. Chromatogr., 69, 71 (1972).
38. R. E. Kaiser, Chromatographia, 2, 453 (1969).
39. R. E. Kaiser, Chromatographia, 5, 281 (1972).
40. V. V. Brazhnikov, "Differentsial'nye Detektory dlya Gazovoi Khromatografii" (Differential Detectors for Gas Chromatography), Izd. Nauka, Moscow, 1974.
41. D. Jentzsch and E. Otte, Detektoren in Gas Chromatography, Bd. 14, Akad. Verlag, Frankfurt-am-Main, 1970.
42. E. R. Adlard, Crit. Revs Anal. Chem., 5, 1 (1975).
43. D. A. Leathard, in "Advances in Chromatography", (edited by J. C. Giddings, R. A. Keller, and J. Cazes) New York, Marcel Dekker, Vol. 13, 1975, p. 324.
44. M. Krejci and M. Dressler, Chem. listy, 65, 574 (1971).
45. V. S. Mirzayanov, V. G. Berezkin, and V. A. Nikol'skii, Zhur. Anal. Khim., 21, 1239 (1966).
46. B. A. Schaefer, J. Chromatogr. Sci., 10, 110 (1972).
47. A. T. Blades, J. Chromatogr. Sci., 10, 693 (1972).
48. B. A. Schaefer and D. M. Douglas, J. Chromatogr. Sci., 9, 612 (1971).
49. W. C. Askew and K. D. Maduskar, J. Chromatogr. Sci., 9, 702 (1971).
50. C. H. Hartmann, AIAA Paper, No. 1046, 6 (1971).
51. A. T. Blades, J. Chromatogr. Sci., 8, 414 (1970).
52. W. C. Askew, Anal. Chem., 44, 633 (1972).
53. V. G. Berezkin and L. A. Shkolina, J. Chromatogr., 119, 33 (1976).
54. J. Lasa, A. Korus, and M. Kilarska, Rept. Inst. fiz. jadr. Krakowie, No. 738, 16 (1970).
55. H. Hein, Chem. Lab. und Betr., 25, 241 (1974).
56. F. A. Perner and J. B. Angel, 24th Electron. Compan. Conf., Statler Hilton, Washington, 1974, p. 162.
57. P. G. Simmonds, A. J. Lovelock, and J. E. Lovelock, J. Chromatogr., 126, 3 (1976).
58. J. E. Lovelock, J. Chromatogr., 99, 3 (1974).
59. E. D. Pellizzari, J. Chromatogr., 98, 323 (1974).
60. M. E. Morrison, R. G. Rinker, and W. H. Corcoran, Anal. Chem., 36, 2256 (1964).
61. M. Kilarska, Chem. anal. (PNR), 15, 953 (1970).
62. V. V. Brazhnikov and K. I. Sakodynski, J. Chromatogr. 66, 361 (1972).
63. V. G. Berezkin (Editor), "Metody-sputniki v Gazovoi Khromatografii" (Auxiliary Methods in Gas Chromatography), Izd. Mir, Moscow, 1972.
64. P. G. Simmonds, G. R. Shoemake, J. E. Lovelock, and H. C. Lord, Anal. Chem., 44, 860 (1972).
65. D. B. Girenko and M. A. Klisenko, Ukrain. Khim. Zhur., 41, 422 (1975).
66. P. R. Roberts and S. K. Sood, Atmos. Environ., 10, 403 (1976).
67. B. Gutsche, R. Herrmann, and K. Rüdiger, Z. anal. Chem., 258, 273 (1972).
68. M. C. Bowman, M. Beroza, and K. R. Hill, J. Chromatogr. Sci., 9, 162 (1971).
69. R. Jeltes, E. Burghardt, R. J. Koch, J. G. Koen, and P. H. Tomassen, Proc. III Int. Clean. Air Congr., Düsseldorf, 1973, S. 42.
70. R. F. Addison and R. G. Ackman, J. Chromatogr., 47, 421 (1970).
71. J. Sevcik, Chromatographia, 4, 195 (1971).
72. D. G. Greer and T. J. Bydalek, Environ. Sci. Technol., 7, 153 (1953).
73. R. K. Stevens, J. D. Mulik, A. E. O'Keeffe, and K. J. Krost, Anal. Chem., 43, 827 (1971).
74. B. Kolb and J. Bischoff, J. Chromatogr. Sci., 12, 625 (1974).
75. W. A. Aue, K. O. Gerhardt, and S. Lakota, J. Chromatogr., 63, 237 (1971).
76. T. E. Applebury and M. J. Schaer, J. Air Pollut. Contr. Assoc., 20, 83 (1970).
77. G. Castello and S. Munari, Chem. e Ind., 51, 469 (1969).

78. A.V. Markevich, S.L. Dobychin, B.A. Gerasimov, A.A. Gnitetskaya, and V.M. Partispanyan, in collected papers "Gazovaya Khromatografiya" (Collected Papers on Gas Chromatography), No. 4, NIITEKhIM, Moscow, 1966, p. 61.
79. J.E. Longbottom, Anal. Chem., 44, 1111 (1972).
80. F.A. Serravallo and T.H. Risby, J. Chromatogr. Sci., 12, 585 (1974).
81. B. Versino, H. Knöppel, M. deGroot, A. Peil, J. Poelman, H. Schauenburg, H. Vissers, and F. Geiss, J. Chromatogr., 122, 373 (1976).
82. Yu.S. Drugov, in collected papers "Okhrana Truda i Tekhnika Bezopasnosti, Ochistka Stochnykh Vod i Otkhodyashchikh Gazov v Khimicheskoi Promyshlennosti" (Collected Papers on Labour Protection and Safety Techniques and the Purification of Effluent Liquids and Gases in the Chemical Industry), No. 1, NIITEKhIM, Moscow, 1969, p. 26.
83. J. May, Staub, 25, 153 (1965).
84. M. Benarie and D. Bodin, Atmos. Environ., 8, 193 (1974).
85. P.A. Pella, E.E. Hughes, and J.K. Taylor, Amer. Ind. Hyg. Assoc. J., 36, 755 (1975).
86. V. Svojanovsky, M. Krejci, K. Tesarik, and J. Janak, Chrom. Rev., 8, 90 (1966).
87. M. Pribyl, Z. anal. Chem., 217, 7 (1966).
88. D.K. Kollerov and K.D. Mgaloblishvili, Izmerit. Tekhnika, No. 7, 50 (1968).
89. A.E. O'Keeffe and G.C. Ortman, Anal. Chem., 38, 760 (1966).
90. H. Kettner, Staub., 29, 153 (1969).
91. R.K. Stevens, A.E. O'Keeffe, and G. C. Ortman, Environ. Sci. Technol., 3, 652 (1969).
92. L. De Maio, Instrum. Technol., 19, 37 (1972).
93. F. Lindqvist and R.W. Lanting, Atmos. Environ., 6, 943 (1972).
94. J.R. McNesby, R. Byerly, J. Taylor, and E. Hughes, Nat. Bur. Stand. U.S. Tech. Note, No. 711, 68 (1972).
95. G.O. Nelson, L.E. Swisher, R.D. Taylor, and B.E. Bigler, Amer. Ind. Hyg. Assoc. J., 36, 49 (1975).
96. D.P. Lucero, J.D. Barden, and J.W. Paljug, US P. 3 833 016 (1974); Ref. Zhur. Khim., 13 I 722 (1975).
97. D.F. Meigh, Chem. e Ind., 35, 1487 (1967).
98. Yu.S. Drugov, in collected papers, "Okhrana Truda i Tekhnika Bezopasnosti, Ochistka Stochnykh Vod i Otkhodyashchikh Gazov v Khimicheskoi Promyshlennosti" (Collected Papers on Labour Protection and Safety Techniques and the Purification of Effluent Liquids and Gases in the Chemical Industry), No. 8, NIITEKhIM, Moscow, 1972, p. 3.
99. V.A. Popov, Gigiena i Sanitariya, No. 2, 80 (1973).
100. J.C. Hilborn and J.L. Monkman, Sci. Total Environ., 4, 97 (1975).
101. V.A. Popov and K.V. Pechennikova, Zavod. Lab., 40, 1 (1974).
102. D.K. Kollerov, "Metrologicheskie Osnovy Gazoanaliticheskikh Izmerenii" (Metrological Principles of Gas-analytical Measurements), Izd. Komiteta Standartov, Mer, i Izmeritel'nykh Priborov, Moscow, 1967.
103. W. Cautreels and K. Van Cauwenberge, Atmos. Environ., 10, 447 (1976).
104. H. Atanus, West. Elc. Eng., 18, 39 (1974).
105. V.G. Berezkin, V.D. Loshchilova, A.G. Pankov, and V.D. Yagodovskii, "Khromato-raspredelitel'nyi Metod" (The Chromatographic-Distribution Method), Izd. Nauka, Moscow, 1976.
106. New Methods in Environmental Chemistry and Toxicology, Research Conference on New Methodology in Ecological Chemistry, November 23–25, 1973, Japan, Tokyo, 1973.
107. Compilation Gas Chromatographic Data, (edited by O.E. Schupp and J.S. Lewis), Philadelphia, ASTM Data Series Publ., No. DS25-A, 1967.
108. S.T. Preston, "A Guide to the Analysis of Hydrocarbons by Gas Chromatography", Evanston, Polyscience Corp., 1969.
109. Gas Chromatographic Data Compilation, Suppl. 1, (Edited by O.E. Schupp and J.S. Lewis), Philadelphia, ASTM AMD 25 AS-1, 1971.
110. R.C. Crippen, Identification of Organic Compounds with the Aid of Gas Chromatography, McGraw-Hill, New York, 1973.
111. V.G. Berezkin, "Analiticheskaya Reaktsionnaya Gazovaya Khromatografiya" (Analytical Reaction Gas Chromatography), Izd. Nauka, Moscow, 1966.
112. L. Peyron, Chim. anal., 52, 1384 (1970).
113. D.A. Leathard and B.C. Shurlock, "Identification Techniques in Gas Chromatography", Wiley Intersci. London, 1970, p. 66.
114. L. Peyron, Riv. ital. essenze. profumi, piante offic., aromi, saponi, cosmet. aerosol., 57, 561 (1975).
115. D.A. Cronin and J. Gilbert, J. Chromatogr., 71, 251 (1972).
116. L. Grupinski, Staub-Reinhalt. Luft., 25, 484 (1965).
117. L.A. Shkolina, E.E. Kugucheva, V.G. Berezkin, and O.A. Artemova, Zavod. Lab., 41, 787 (1975).
118. Yu.S. Drugov, in collected papers "Proizvodstvo Shin, RTI, i ATI" (Collected Papers on the Production of Tyres and Rubber and Asbestos Technical Materials), No. 6, TsNIITEneftekhim, Moscow, 1972, p. 33.
119. K.H. Bergert and V. Betz, Chromatographia, 7, 681 (1974).
120. Yu.G. Shirokov, Yu.S. Drugov, G.V. Murav'eva, and G.A. Letunovskaya, Gigiena i Sanitariya, No. 1, 50 (1976).
121. R.E. Neligan, M.J. Leonard, and R.J. Bryan, 150th American Chemical Society Meetings, Atlantic City, 1965, Proceed, New York, 1965.
122. L.A. Kogan, "Kolichestvennaya Gazovaya Khromatografiya" (Quantitative Gas Chromatography), Izd. Khimiya, Moscow, 1975.
123. C.A. Young Irving, Amer. Lab., 7, 27 (1975).
124. B.I. Anvaer and Yu.S. Drugov, "Gazovaya Khromatografiya Neorganicheskikh Veshchestv" (The Gas Chromatography of Inorganic Substances), Izd. Khimiya, Moscow, 1976.
125. G. Guiochon and C. Pommier, La chromatographie en phase gaseuse en chimie inorganique, Ganthier-Villars, Paris, 1971.
126. B.I. Anvaer and Yu.S. Drugov, Zhur. Anal. Khim., 26, 1180 (1971).
127. F.D. Huillet and P. Urone, J. Gas Chromatogr., 4, 249 (1966).
128. P. Hermann, Proc. III Int. Clean Air Congress, Dusseldorf, 1973, p. 16.
129. K. Ranfft, Z. anal. Chem., 269, 18 (1974).
130. S. Zolty and M.J. Prager, J. Gas Chromatography, 5, 533 (1967).
131. Yu.S. Drugov and S.F. Yavorovskaya, in collected papers "Gazovaya Khromatografiya" (Collected Papers on Gas Chromatography), No. 14, NIITEKhIM, 1970, p. 65.

132. R. M. Bethea and M. C. Meador, J. Chromatogr. Sci., 7, 655 (1969).
133. R. Jeltes, E. Burghardt, and J. Breman, Brit. J. Ind. Med., 28, 96 (1971).
134. J. D. Allen, J. Inst. Fuel, 46, 123 (1973).
135. H. Peperstraete, Ingenieursblad, 43, 337 (1974).
136. L. M. Beddows and A. White, J. Brit. Soc. Sci. Glassblowers, 12, 60 (1974).
137. C. E. Döring, R. Geyer, and P. Röske, Acta chim. Acad. Sci. hung., 73, 399 (1972).
138. J. M. Trowell, Anal. Chem., 37, 1152 (1965).
139. A. Lawson and H. G. McAdie, J. Chromatogr. Sci., 8, 731 (1970).
140. C. E. Döring, R. Geyer, and P. Röske, Acta chim. Acad. sci. hung., 75, 89 (1973).
141. O. Grubner and A. S. Goldin, Anal. Chem., 45, 944 (1973).
142. W. D. Ross, G. W. Buttler, T. G. Duffy, W. R. Rehg, M. T. Wininger, and R. E. Sievers, J. Chromatogr., 112, 719 (1975).
143. E. D. Palmes, A. F. Gunnison, J. Dimattio, J. Gunnison, and C. Tomczyk, Amer. Ind. Hyg. Assoc. J., 36, 15 (1975).
144. R. Villalobos and R. L. Chapman, ISA Trans., 10, 356 (1971); Ref. Zhur. Khim., 19I620 (1972).
145. D. A. Levaggi, W. Siu, M. Feldstein, and E. L. Kothny, Environ. Sci. Technol., 6, 250 (1972).
146. G. S. Beskova, A. I. Butusova, and V. S. Filippov, Zavod. Lab., 42, 394 (1976).
147. W. E. Wentworth and R. R. Freeman, J. Chromatogr., 79, 322 (1973).
148. J. W. Tesch, W. R. Rehg, and R. E. Sievers, J. Chromatogr., 126, 743 (1976).
149. L. G. Berezkina, S. V. Mel'nikova, and V. I. Sukhodolova, Zhur. Anal. Khim., 28, 177 (1973).
150. K. D. Brunnemann and D. Hoffmann, J. Chromatogr. Sci., 13, 159 (1975).
151. K. Takeyama, T. Morimoto, and F. Konishi, Nat. Techn. Rept., 20, 562 (1974).
152. D. R. Paulson and G. F. Moran, Environ. Sci. Technol., 8, 1116 (1974).
153. A. L. Myerson and J. J. Chludzinski, J. Chromatogr. Sci., 13, 554 (1975).
154. W. Leithe, "The Analysis of Air Pollutants", Ann Arbour Science Publ., 1971.
155. J. Fogl and M. Fortelny, Chem. Prumysl., 17, 42 (1967).
156. R. Sarteur and J. C. Fayard, Pollut. atmos., 17, 14 (1975).
157. R. Staszewski, J. Chromatogr., 65, 217 (1972).
158. C. S. McCammon, P. M. Quinn, and R. E. Kupel, Amer. Ind. Hyg. Assoc. J., 36, 618 (1975).
159. E. Tosiaki, Anal. Instrum., 14, 83 (1976).
160. D. A. Tourres, Chromatographia, 5, 441 (1972).
161. F. Bruner, P. Ciccioli, and C. Bertoni, J. Chromatogr., 120, 200 (1976).
162. J. A. Barynin and M. J. Wilson, Atmos. Environ., 6, 197 (1972).
163. X. Yasujuki, Anal. Instrum., 13, 211 (1975).
164. X. Yasujuki, K. Satoshi, K. Ichiro, K. Kazumi, and Y. Kenji, Pollut. Contr., 9, 284 (1974).
165. X. Yasujuki, K. Ishiro, K. Kazumi, and Y. Kenji, J. Japan. Oil. Chem. Soc., 24, 317 (1975).
166. N. A. Elefterova, Candidate's Thesis, Research Institute for Fertilisers and Insectofungicides, Moscow, 1975.
167. J. A. Giannovario, R. L. Grob, and P. W. Rulon, J. Chromatogr., 121, 285 (1976).
168. C. D. Bohl and E. F. Kaelble, Amer. Ind. Hyg. Assoc. J. 34, 306 (1973).
169. B. Berck, W. E. Westlake, and F. A. Gunther, J. Agr. Food Chem., 18, 143 (1970).
170. L. Giry and M. Chaigneau, Analysis, 2, 163 (1973).
171. N. Harrison, Ann. Occup. Hyg., 18, 37 (1975).
172. H. W. Grice and D. J. David, J. Chromatogr., 7, 247 (1969).
173. V. G. Guglya, V. E. Shepelev, and A. A. Zhukhovitskii, Zhur. Anal. Khim., 28, 1223 (1973).
174. S. A. Volkov, E. G. Rastyannikov, and L. N. Tarasova, Gigiena i Sanitariya, No. 10, 62 (1973).
175. A. K. Ghosh, D. P. Rajwar, and P. K. Bandopadnyay, J. Chromatogr., 117, 29 (1976).
176. L. DuBois, A. Zdrojewski, and J. L. Monkman, J. Air Pollut. Contr. Assoc., 16, 135 (1966).
177. J. F. Clarke and R. B. Faoro, J. Air Pollut. Contr. Assoc., 16, 212 (1966).
178. H. Nagai and H. Utiki, Hitachi hydron., 53, 499 (1971); Ref. Zhur. Khim., 23G230 (1971).
179. K. Greider and H. Buser, Beitr. Tabakforsch., 6, 36 (1971).
180. J. D. O'Neel, F. L. Rodkey, and H. A. Collison, U.S. Gov. Res. Develop., Rep., 70, 54 (1970).
181. E. E. Sotnikov, V. N. Blinov, and S. A. Filippova, Gigiena i Sanitariya, No. 8, 66 (1973).
182. E. E. Sotnikov and G. A. Gaziev, Zhur. Anal. Khim., 30, 48 (1975).
183. H. W. Lang and R. W. Freedman, S. Afr. Mining Eng. J., 85, 59 (1973).
184. Yu. S. Drugov, in collected papers "Okhrana Truda i Tekhnika Bezopasnosti, Ochistka Stochnykh Vod i Otkhodyashchikh Gazov v Khimicheskoi Promyshlennosti" (Collected Papers on Labour Protection and Safety Techniques and the Purification of Effluent Liquids and Gases in the Chemical Industry), No. 8, NIITEKhIM, Moscow, 1971, p. 5.
185. R. W. Moshier and R. E. Sievers, "Gas Chromatography of Metal Chelates" (Translated into Russian), Izd. Mir, Moscow, 1967.
186. T. A. Gosink, Anal. Chem., 47, 165 (1975).
187. W. D. Ross and R. E. Sievers, Talanta, 15, 87 (1968).
188. Yu. S. Drugov, G. V. Murav'eva, K. M. Grinberg, G. N. Nesterenko, and D. N. Sokolov, Zavod. Lab., 38, 1305 (1972).
189. W. Bertsch, R. C. Chang, and A. Zliatkis, J. Chromatogr. Sci., 12, 175 (1974).
190. P. Ciccioli, G. Bertoni, E. Brancaleoni, R. Fratarcangeli, and F. Bruner, J. Chromatogr., 126, 757 (1976).
191. M. T. Dmitriev, L. N. Tarasova, and L. D. Pribytkov, Gigiena i Sanitariya, No. 8, 66 (1972).
192. T. A. Bellar and J. E. Sigsby, Environ. Sci. Technol., 1, 242 (1967).
193. A. Zlatkis, H. R. Kaufman, and D. E. Durbin, J. Chromatogr. Sci., 8, 416 (1970).
194. J. A. De Greef, M. De Proft, and F. De Winter, Anal. Chem., 48, 38 (1976).
195. N. S. Novikova, I. V. Pervuzina, and E. V. Terent'eva, Zhur. Anal. Khim., 31, 1747 (1976).
196. N. M. Luk'yanova, R. A. Malysheva, and R. A. Sivkova, in collected papers "Promyshlennost' Sinteticheskogo Kauchuka" (Collected Papers on the Synthetic Rubber Industry), No. 8, TsNIITEneftekhim, Moscow, 1974, p. 11.

197. Yu.S. Drugov and G.V. Murav'eva, in collected papers "Proizvodstva Shin, RTI, i ATI" (Collected Papers on the Production of Tyres and Rubber and Asbestos Technical Materials), No. 6, TsNIITE-neftekhim, Moscow, 1971, p. 18.
198. A.G. Pankov, B.B. Shugaev, A.V. Bitkina, V.V. Afanas'eva, and V.D. Loshchilova, in collected papers "Toksikologiya i Gigiena Produktov Neftekhimii i Neftekhimicheskikh Proizvodstv" (Collected Papers on the Toxicology and Hygiene of the Products of Petroleum Chemistry and Petrochemical Products), Yaroslavl', 1972, p. 163.
199. S.M. Rappaport and D.A. Fraser, Anal. Chem., 48, 476 (1976).
200. S.A. Leont'eva, Yu.S. Drugov, N.I. Lulova, and N.M. Koroleva, Zhur. Anal. Khim., 32, 1638 (1977).
201. S.A. Leont'eva, Yu.S. Drugov, and N.I. Lulova, Zavod. Lab., 40, 653 (1974).
202. S.A. Leont'eva, Yu.S. Drugov, and N.I. Lulova, Zavod. Lab., 42, 790 (1976).
203. Yu.S. Drugov and G.A. Letunovskaya, in collected papers "Ochistka Promyshlennykh Vybrosov i Tekhnika Bezopasnosti na Khimicheskikh Predpriyatiyakh" (Collected Papers on the Purification of Industrial Waste Products and Safety Techniques in the Chemical Industry), No. 1, NIITEKhIM, Moscow, 1975, p. 22.
204. Yu.S. Drugov and G.V. Murav'eva, in collected papers "Proizvodstvo Shin, RTI, i ATI" (Collected Papers on the Production of Tyres and Rubber and Asbestos Technical Articles), No. 9, TsNIITEneftekhim, Moscow, 1976, p. 28.
205. L.J. Papa, D.L. Dinsel, and W.C. Harris, J. Gas Chromatogr., 6, 270 (1968).
206. T.A. Mironova, M.V. Nikolaeva, and D.A. Vyakhirev, Zavod. Lab., 40, 942 (1974).
207. V. Cantuti and G. Cartoni, J. Chromatogr., 32, 641 (1968).
208. A. Cornu, R. Massot, C. Nicotra, P. Perilhon, R. Faivre-Pierret, A. Tregoures, and M.C. Lopez, Informs. Chem., No. 142, 127 (1975).
209. V.A. Isidorov, I.G. Zenkevich, and B.V. Ioffe, "Primenenie Molekulyarnoi Khromatografii dlya Analiza Okruzhayushchei Sredy i Issledovaniya Biokhimicheskikh Protsessov, Samarkand, 1976; Tezisy Dokladov Simpoziuma" (Summaries of Papers Presented at the Symposium on the Use of Molecular Chromatography for the Analysis of the Environment and the Study of Biochemical Processes, Samarkand, 1976), Moscow, 1976, p. 11.
210. J.P. Mieure and M.W. Dietrich, J. Chromatogr. Sci., 11, 559 (1973).
211. K.H. Bergert, V. Betz, and D. Pruggmayer, Chromatographia, 7, 115 (1974).
212. G. Ketseridis and J. Hahn, Z. anal. Chem., 273, 257 (1975).
213. H. Matsushita, K. Arashidani, and H. Hayashi, Japan. Anal., 25, 412 (1976).
214. K. Grob and G. Grob, J. Chromatogr., 62, 1 (1971).
215. A. Raymond and G. Guiochon, Environ. Sci. Technol., 8, 143 (1974).
216. A. Stefanescu and L. Stanescu, Rev. Chim., 17, 307 (1966).
217. H. Utaka, Hitachi hyoron, 52, 708 (1970); Ref. Zhur. Khim., 6G204 (1971).
218. Process Eng., No. 2, 89 (1976).
219. W.A. Aue, C.R. Hastings, and K.O. Gerhardt, J. Chromatogr., 99, 45 (1974).
220. A. Liberti and L. Zoccolillo, Proc. of TECOMAP, 1973, Helsinki; WMO, Geneva, 1974, p. 89.
221. F. Bruner, P. Ciccioli, and F. DiNardo, J. Chromatogr., 99, 661 (1974).
222. M.C. Bowman and M. Beroza, Anal. Chem., 40, 535 (1968).
223. Fluorescence News, 5, 6 (1970).
224. L. E. Strömberg and G. Widmark, J. Chromatogr., 49, 334 (1970).
225. R.C. Lao, R.S. Thomas, H. Oja, and L. Dubois, Anal. Chem., 45, 908 (1973).
226. R.C. Lao, R.S. Thomas, and J.L. Monkman, Advances in Chromatography 1975, (edited by A. Zlatkis), X Chromatogr. Symp., Houston, Texas, 1975, p. 681.
227. H.P. Burchfield, E.E. Green, R.J. Wheeler, and S.M. Billedeau, J. Chromatogr., 99, 697 (1974).
228. S.A. Penkett, F.J. Sandalls, and J.E. Lovelock, Atmos. Environ, 9, 139 (1975).
229. B. Dimitriades, J. Air Pollut. Contr. Assoc., 17, 460 (1967).
230. E.R. Stephens and M.A. Price, J. Chem. Educ., 50, 351 (1973).
231. J.M. Heuss and W.A. Glasson, Environ. Sci. Technol., 2, 1109 (1968).
232. M.T. Dmitriev and L.D. Pribytkov, Gigiena i Sanitariya, No. 2, 67 (1975).
233. D.A. Levaggi and M. Feldstein, J. Air Pollut. Contr. Assoc., 20, 312 (1970).
234. J. Hovorka, Chem. prum., 26, 75 (1976).
235. R. Jeltes, J. Chromatogr., 24, 402 (1966).
236. L.A. Ruslanova, V.S. Tatarinskii, G.I. Volkova, V.G. Berezkin, and A.K. Zhomov, in collected papers "Nauchnye Raboty NII Okhrany Truda" (Collected Papers on the Research Work of the Scientific Research Institute for Labour Protection), No. 51, Moscow, 1968, p. 66.
237. W.A. Dietz, J. Chromatogr. Sci., 10, 423 (1972).
238. A.K. Aunap and V.Kh. Tikhane, in collected papers "Issledovaniya po Professional'noi Meditsine v Est. SSR" (Collected Papers on Studies in Occupational Medicine in the Estonian SSR), Tallin, 1975, p. 17.
239. M. Okabayashi, T. Ishiguro, and T. Hasegawa, Japan Anal., 25, 436 (1976).
240. Yu.S. Drugov and G.V. Murav'eva, Zhur. Anal. Khim., 31, 2205 (1976).
241. P. Ronkainen, J. Denslow, and O. Leppänen, J. Chromatogr. Sci., 11, 384 (1973).
242. R.V. Carter and B. Linsky, Atmos. Environ., 8, 57 (1974).
243. W. Bertsch, F. Hsu, and A. Zlatkis, Anal. Chem., 48, 928 (1976).
244. S. Hasinski, Chem. anal. (PRL), 20, 1135 (1975).
245. H. Maarse and M.C.T.N. De Brauw, Chem. e Ind., No. 1, 36 (1974).
246. D. Ellgehausen, Z. anal. Chem., 272, 284 (1974).
247. F. Eisenberg, Anal. Chem. Phosphor Compounds, New York, 1972, p. 69.
248. "Environmental Pollution by Pesticides" (edited by C.A. Edwards), Plenum Press, London, 1973.
249. J.W. Miles, L.E. Fetzer, and G.W. Pearce, Environ. Sci. Technol., 4, 420 (1970).
250. L.F. Fishbein, "Chromatography of Environmental Hazards", Vol. 3, Pesticides, Elsevier, Amsterdam, 1975.
251. T. Wakimoto, R. Tatsukawa, T. Ogawa, and I. Watanabe, Japan Anal., 23, 790 (1974).

252. K. Beyermann and W. Eckrich, Z. anal. Chem., **269**, 279 (1974).
253. J. J. Franken and H. L. Vader, Chromatographia, 6, 22 (1973).
254. J. Sherma and T. M. Shafik, Arch. Environ. Contam. Toxicol., 3, 55 (1975).
255. L. Zafonte, N. E. Hester, E. R. Stephens, and O. C. Taylor, Atmos. Environ., 9, 1007 (1975).
256. P. G. Simmonds, S. L. Kerrin, J. E. Lovelock, and F. H. Shair, Atmos. Environ., 8, 209 (1974).
257. M. H. Yu and G. W. Miller, Environ. Sci. Technol., 4, 492 (1970).
258. Anal. Chim. Acta, **82**, 1 (1976).
259. A. J. Murray and J. P. Riley, Nature, **242**, 37 (1973).
260. D. Lillian and H. B. Singh, Anal. Chem., 46, 1060 (1974).
261. G. McConnell, D. M. Ferguson, and C. R. Pearson, Endeavour, **34**, 13 (1975).
262. J. E. Lovelock, Nature, **256**, 193 (1975).
263. R. C. Lao, R. S. Thomas, and J. L. Monkman, Amer. Ind. Hyg. Assoc. J., 37, 1 (1976).
264. R. H. Hill, C. S. McCammon, A. T. Saalwaechter, A. W. Teass, and W. J. Woodfin, Anal. Chem., 48, 1395 (1976).
265. S. Spiro and G. R. Trevisani, Boll. lab. chim. provinc., **24**, 179 (1973).
266. D. Lillian, H. B. Singh, and A. Appleby, J. Air Pollut. Contr. Assoc., **26**, 141 (1976).
267. J. Sherma, in "Advances in Chromatography", Vol. 12 (edited by J. C. Giddings, E. Grushke, R. A. Keller, and J. Cazec), New York, Marcel Dekker, 1975.
268. B. Zimmerli, J. Chromatogr., 88, 66 (1974).
269. E. G. Ivanyuk and Yu. A. Kolievskaya, Gigiena i Sanitariya, No. 6, 45 (1975).
270. R. Fahuort, Z. gesamte, Hyg., 16, 497 (1970).
271. D. H. Fine and D. P. Rounbehler, J. Chromatogr., 109, 271 (1975).
272. Amer. Ind. Hyg. Assoc. J., 31, 517 (1970).
273. M. T. Dmitriev and N. A. Kitrosskii, Gigiena i Sanitariya, No. 8, 63 (1970).
274. G. W. Schanche and E. R. Hermann, Amer. Ind. Hyg. Assoc. J., 35, 47 (1974).
275. T. Okita, Bull. Inst. Public Health, 16, 59 (1967).
276. A. N. Ivanov and G. A. Gaziev, in collected papers "Mediko-tekhnicheskie Problemy Individual'noi Zashchity Cheloveka" (Collected Papers on Medical and Technical Problems of the Individual Protection of People), No. 13, Izd. Meditsina, Moscow, 1973, p. 77.
277. B. E. Bowen, Anal. Chem., 48, 1584 (1976).
278. G. O. Wood and R. G. Anderson, Amer. Ind. Hyg. Assoc. J., 36, 538 (1975).
279. V. Masek and J. Neiser, Bitum. Teere, Asph., Peche, **24**, 306 (1973).
280. R. C. Pierse and M. Katz, Environ. Sci. Technol., 10, 45 (1976).
281. R. A. Rasmussen, H. H. Westberg, and M. Holdren, J. Chromatogr. Sci., **12**, 80 (1974).
282. "Tekhnicheskie Usloviya na Metody Opredeleniya Vrednykh Veshchestv v Vozdukhe" (Technical Conditions for Methods of Determining Harmful Substances in Air), No. 9, Institute of Labour Protection of the All Union Central Council of Trade Unions, Moscow, 1973.
283. "Metodicheskie Ukazaniya na Metody Opredeleniya Vrednykh Veshchestv v Vozdukhe" (Methodological Notes on Methods of Determining Harmful Substances in Air), No. 12, Scientific Research Institute of Water Transport Hygiene, Moscow, 1977.
284. K. D. Anil and K. P. Bata, J. Ind. Chem. Soc., 3, 265 (1977).
285. F. Ya. Rovinskii and N. K. Gasilina, Zhur. Anal. Khim., 33, 160 (1978).
286. B. E. Saltzman and W. R. Burg, Anal. Chem., 49, 1 (1977).
287. R. L. Grob, in "Contemporary Topics in Analytical and Clinical Chemistry", Vol. 1 (edited by M. Hercules), Plenum Press, New York, 1977, p. 160.
288. B. A. Rudenko and G. I. Smirnova, Zhur. Anal. Khim., **32**, 367 (1977).
289. S. P. Gram and T. H. Risby, Anal. Chem., 50, 213 (1978).
290. M. Neuray, W. De Craecker, and J. Stevens, Ann. mines Belg., 389 (1976).
291. M. K. Molineux, Safety Surv., 5, 9 (1977).
292. R. G. Melcher, R. R. Langner, and R. O. Kagel, Amer. Ind. Hyg. Assoc. J., 39, 349 (1978).
293. A. T. Saalwaechter, C. S. McCammon, I. C. Roper, and K. C. Carlberg, Amer. Ind. Hyg. Assoc. J., 38, 476 (1977).
294. M. W. Dietrich, L. M. Chapmen, and J. P. Mieure, Amer. Ind. Hyg. Assoc. J., 39, 385 (1978).
295. H. Yamasaki and K. Kuwata, Japan Analyst, **26**, 1 (1977).
296. B. C. Turner and D. E. Glotfelty, Anal. Chem., 49, 7 (1977).
297. R. G. Lewis, A. R. Brown, and M. D. Jackson, Anal. Chem., 49, 1668 (1977).
298. A. M. Krstulovic, D. M. Rosie, and P. R. Brown, Pittsburg Conf. on Analytical Chemistry and Applied, Spectroscopy, Cleveland, Ohio, 1977, Abstracts, Pittsburg, 1977, p. 414.
299. B. V. Ioffe, V. A. Isidorov, and I. G. Zenkevich, J. Chromatogr., **142**, 787 (1977).
300. J. Holzer, H. Shanfield, A. Zlatkis, W. Bertch, P. Juarez, H. Mayfield, and H. M. Liebich, J. Chromatogr., **142**, 755 (1977).
301. H. Mohrmann and A. Biermann, Staub-Reinhalt. Luft, 37, 431 (1977).
302. K. Spurny, Chem.-Techn., 6, 69 (1977).
303. N. A. Fuchs, Atmos. Environ., 9, 697 (1975).
304. G. V. Tsitsishvili, T. G. Andronikashvili, O. S. Banakh, and L. V. Stril'chuk, Izv. Akad. Nauk SSSR, Ser. Khim., 3, 22 (1977).
305. R. J. Anthony, F. G. Nelson, and A. C. Leslie, US P. 4 019 879, 4 019 880 (1977); Ref. Zhur. Khim., 6I576, 6I577 (1978).
306. B. Brechbüchler, L. Gay, and H. Jeager, Chromatographia, 10, 478 (1977).
307. S. I. Krichmar, Zh. B. Levchenko, and A. E. Stepanenko, Zhur. Anal. Khim., **32**, 1703 (1977).
308. R. G. Schiler and R. B. Bronsky, J. Chromatogr. Sci., 15, 541 (1977).
309. H. W. Dürbeck and R. Niehaus, Chromatographia, 11, 14 (1978).
310. L. M. Webber, K. H. Karmarkar, and G. G. Guilbault, Anal. Chim. Acta, 97, 29 (1978).
311. V. G. Guglya, V. I. Kalmanovskii, and V. V. Shevchenko, Zavod. Lab., 44, 283 (1978).
312. W. A. Aue and C. G. Flinn, J. Chromatogr., **142**, 145 (1977).

313. J.R.Stetter, J.M.Sedlak, and K.F.Blurton, J.Chromatogr.Sci., 15, 125 (1977).
314. W.R.Wolf, J.Chromatogr., 134, 159 (1977).
315. J.C.VanLoon, Proc.22th Colloq.Spectrosc.Int.and 7th Int.Conf.Atom.Spectrosc., Praha, 1977, p.125; Ref.Zhur.Khim., 12G52 (1978).
316. V.G.Guglya, G.S.Korobeinik, and A.A.Zhukhovitskii, Zavod.Lab., 44, 539 (1978).
317. P.Popp, H.G.Grosse, and G.Oppermann, J.Chromatogr., 147, 47 (1978).
318. B.P.Okhotnikov, V.A.Rotin, V.N.Khokhlov, and V.S.Yusfin, in collected papers "Khromatografiya" (Collected Papers on Chromatography), Vol.II, VINITI, Moscow, 1978, p.28.
319. M.Re and G.Cellerino, Ann.Chim., 66, 325 (1976).
320. K.Bächmann, H.M.Biehl, W.Emig, and J.Rudolph, Int.Symp.Microchem.Techn., Davos, 1977, Abstr., p.180.
321. Y.Hoshika, J.Chromatogr., 136, 95 (1977).
322. J.E.Greving, J.H.Jonkman, and R.A.De Zeeuwn, J.Chromatogr., 148, 389 (1978).
323. E.F.Ault and R.A.Solomon, Austral.P.483 368 (1977); Ref.Zhur.Khim., 18G341 (1978).
324. A.I.Butusova, Candidate's Thesis, GIAP, Moscow, 1978.
325. D.J.Freed and A.M.Mujsce, Anal.Chem., 49, 139 (1977).
326. E.Kebbekus and F.Scornavacca, Amer.Lab., 9, 51 (1977).
327. A.G.Vitenberg and B.V.Ioffe, Dokl.Akad.Nauk SSSR, 238, 352 (1978).
328. W.R.Burg, S.R.Birch, J.E.Cuddeback, and B.E.Saltzman, Environ.Sci.Technol., 10, 1233 (1976).
329. T.Ibusuki, M.Sakuma, H.Hirasawa, and K.Imagami, Pollut.Contr., 13, 101 (1978).
330. K.Grob and G.Grob, Wiss,Z.Karl-Marx-Univ. Leipzig, Math.-naturwiss.R., 26, 379 (1977).
331. G.Schomburg, H.Benlau, R.Dielmann, E.Weeke, and H.Husmann, J.Chromatogr., 142, 87 (1977).
332. M.Iwanaga, Chimadzu Rev., 34, 127 (1977).
333. J.T.Bursey, D.Smith, J.E.Bunch, R.N.Williams, R.E.Berkley, and E.D.Pellizzari, Int.Lab., 11 (1978).
334. J.Bonnekessel and M.Klier, Anal.Chim.Acta, 103, 29 (1978).
335. R.H.Shaps, W.Simons, and A.Varano, Amer.Lab., 9, 95 (1977).
336. S.A.Leont'eva, Yu.S.Drugov, N.I.Dulova, and N.M.Koroleva, Zhur.Anal.Khim., 32, 1638 (1977).
337. G.G.Esposito, D.Lillian, G.E.Podolak, and R.M.Tuggle, Anal.Chem., 49, 1774 (1977).
338. J.Amouroux, D.Rapakoulias, and A.Saint-Yrieix, Analysis, 5, 372 (1977).
339. E.Urbas and E.Küllik, J.Chromatogr., 137, 210 (1977).
340. P.Lepsi, Chem.prum., 27, 411 (1977).
341. C.D.Pearson and W.J.Hines, Anal.Chem., 49, 123 (1977).
342. J.J.Richard and R.D.Vick, Environ.Sci.Technol., 11, 1084 (1977).
343. P.Popp and G.Opperman, J.Chromatogr., 148, 265 (1978).
344. O.S.Banakh, I.P.Fedorovich, B.A.Plastunov, I.A.Datsenko, T.G.Andronikashvili, L.A.Tiunov, M.P.Shlemkevich, and T.N.Gladyshevskaya, Gigiena i Sanitariya, No.11, 75 (1978).
345. A.A.Zhukhovitskii, L.G.Novikova, S.M.Yanovskii, E.V.Kanunnikova, and V.P.Shvartsman, Zhur.Anal. Khim., 30, 2251 (1975).
346. J.W.Robinson, E.L.Kiesel, J.P.Goodbread, R.Bliss, and R.Marshall, Anal.Chim.Acta, 92, 321 (1977).
347. N.Hasegawa, Bunseki, No.34, 639 (1977); Ref. Zhur.Khim., 9G210 (1978).
348. D.N.Sokolov, Uspekhi Khim., 46, 740 (1977) [Russ. Chem.Rev., No.4 (1977)].
349. P.C.Uden, Analyst., 102, 889 (1977).
350. G.G.Esposito and B.W.Jacobs, Amer.Ind.Hyg. Assoc.J., 38, 401 (1977).
351. W.Cautreels and K.Van Cauwenberge, J.Chromatogr., 131, 253 (1977).
352. R.Jeltes, E.Burghardt, T.R.Thijsse, and W.A.M.De Tonkelaar, Chromatographia, 10, 430 (1977).
353. H.H.Hill, K.W.Chan, and F.W.Karasek, J.Chromatogr., 131, 245 (1977).
354. F.W.Karasek, D.W.Denney, K.W.Chan, and R.E.Clement, Anal.Chem., 50, 82 (1978).
355. G.Ketseridis, J.Hahn, R.Jaenicke, and C.Junge, Atmos.Environ., 10, 603 (1976).
356. W.E.May, S.N.Chesler, H.S.Hertz, and S.A.Wise, Anal.Chem., 50, 428 (1978).
357. H.Ariton and R.Soda, Ann.Occup.Hyg., 20, 247 (1977).
358. Yu.S.Drugov, G.V.Murav'eva, and G.A.Letunovskaya, in collected papers "Proizvodstvo Shin, Rezinotekhnicheskikh i Asbestotekhnicheskikh Izdelii" (Collected Papers on the Production of Tyres and Rubber and Asbestos Technical Articles), No.4, TsNIITEneftekhim, Moscow, 1978, p.36.
359. M.S.Black, W.R.Rehg, R.E.Sievers, and J.J.Brooks, J.Chromatogr., 142, 809 (1977).
360. G.Grimmer, H.Boehnke, and K.W.Naujack, Z.anal.Chem., 290, 147 (1978).
361. W.Giger and C.Schaffner, Anal.Chem., 50, 243 (1978).
362. A.Ya.Khesina, G.A.Smirnov, E.A.Ermakov, A.A.Knyazeva, and Ya.I.Yashin, Zhur.Anal.Khim., 33, 2032 (1978).
363. M.T.Dmitriev and V.A.Mishchikhin, Gigiena i Sanitariya, No.5, 59 (1978).
364. A.W.Smallwood, Amer.Ind.Hyg.Assoc.J., 39, 151 (1978).
365. A.A.Grote and R.E.Kupel, Amer.Ind.Hyg.Assoc. J., 39, 78 (1978).
366. J.E.Scott, Analyst., 102, 614 (1977).
367. S.G.Zeldes and A.D.Horton, Anal.Chem., 50, 779 (1978).
368. V.Rimatori, G.Carell, B.Sperduto, and R.Marsili, Ann.Ist.Super.sanita., 13, 257 (1977); Ref.Zhur. Khim., 16I554 (1978).
369. W.A.Lonneman, J.J.Bufalini, and R.L.Siela, Environ.Sci.Technol., 10, 374 (1976).
370. J.Remen, M.Revus, and J.Hrivnak, Ropa u uhile, 20, 83 (1978).
371. J.Bernet, Gesunh-Ing., 98, 318 (1977).
372. E.Volpi, Inquinamento, 19, 81 (1977).
373. E.G.Ivanyuk and Yu.A.Kolievskaya, Zavod.Lab., 43, 157 (1977).
374. K.Bretschneider, K.Horn, and J.Matz, Gigiena i Sanitariya, No.7, 86 (1977).
375. R.L.Fisher and R.W.Reiser, Anal.Chem., 49, 1821 (1977).
376. M.Hangartner and H.U.Wanner, Wasser, Energ., Luft, 70, 3 (1978).

377. V.V.Tsibul'skii, A.G.Vitenberg, and I.A.Khripun, Zhur.Anal.Khim., 33, 1184 (1978).
378. D.S.Walker, Analyst, 103, 397 (1978).
379. V.V.Zykova and L.I.Volokhova, in "Sbornik Nauchnykh Trudov Instituta Obshchei i Kommunal'noi Gigieny" (Collected Papers of the Institute of General and Communal Hygiene), No. 5, 58 (1977).
380. S.K.Yasuda and E.D.Loughran, J.Chromatogr., 137, 283 (1977).
381. Yu.S.Drugov, G.V.Murav'eva, and G.A.Letunovskaya, in collected papers "Proizvodstvo Shin, Rezinotekhnicheskikh i Asbestotekhnicheskikh Izdelii" (Collected Papers on the Production of Tyres and Rubber and Asbestos Technical Articles), No. 6, TsNIITEneftekhim, Moscow, 1977, p.27.
382. R.Tatsukawa, Japan Analyst, 27, 164 (1978).
383. Wasser, Luft und Betr., 21, 184 (1977).
384. I.A.Murdoch and A.R.Hammond, Ann.Occup.Hyg., 20, 55 (1977).
385. Yu.S.Drugov, G.V.Murav'eva, and G.A.Letunovskaya, in collected papers "Proizvodstvo Shin, Rezinotekhnicheskikh i Asbestotekhnicheskikh Izdelii" (Collected Papers on the Production of Tyres and Rubber and Asbestos Technical Articles), No. 9, TsNIITEneftekhim, Moscow, 1978, p.25.
386. J.C.Gage, V.Laggesson, and A.Tunek, Ann.Occup.Hyg., 20, 127 (1977).
387. R.G.Melcher, W.L.Garner, L.W.Severs, and J.R.Vaccaro, Anal.Chem., 50, 251 (1978).
388. M.A.Klisenko, in collected papers "Sovremennye Metody Sanitarno-gigienicheskikh Issledovanii i Primenenie ikh v Praktike Sanitarnogo Kontrolya, Materialy Simpoziuma, Tartu, 1978" (Proceedings of the Symposium on Modern Methods in Health and Hygiene Studies and Their Application in Health Control Practice, Tartu, 1978), p.69.
389. B.Bush and R.Narang, Pittsburgh Conf. on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, Abstracts, Pittsburgh, 1977, p.302.
390. Y.Bara and T.Tanaka, Bull.Chem.Soc.Japan, 51, 317 (1978).
391. N.A.Vasil'eva and N.A.Gozhenko, in collected papers "Khimicheskaya Tekhnologiya" (Collected Papers on Chemical Technology), No. 6, Moscow, 1977, p.10.
392. V.O.Pikhl, Ya.O.Penchuk, K.A.Il'mov, L.I.Margna, and I.P.Orav, see Ref. 388, p.121.
393. B.E.Saltzman, R.B.William, and J.E.Cuddeback, J.Air Pollut.Contr.Assoc., 27, 63 (1977).
394. G.Gazzaniga and E.Crovato, Boll.chim.Unione ital. lab.prov., 28, 57 (1977).
395. G.L.Baker and R.E.Reiter, Amer.Ind.Hyg.Assoc. J., 38, 24 (1977).
396. G.Maffiolo, Y.Leriquer, M.C.Naudy, and J.Dubois, Nuisan.et environ., 25 (1977); Ref.Zhur. Khim., 7I577 (1978).
397. L.Elias, J.Chromatogr.Sci., 13, 178 (1975).
398. L.S.Frankel and R.F.Black, Anal.Chem., 48, 732 (1976).

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