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Gas-chromatographic Analysis of Unstable Inorganic and Organoelement Compounds

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The present state of the gas-chromatographic analysis of unstable and reactive substances if reviewed and described systematically in terms of the characteristic reactions of such compounds, such as hydrolysis, oxidation, thermal and catalytic degradation, and isomerisation. The requirements which must be met by the carrier gas, the solid carrier, and the stationary phase in the analysis of these compounds are discussed together with the characteristics of the qualitative analyses, as well as the apparatus employed.
The bibliography includes 218 references.

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I. INTRODUCTION

Gas-chromatography is the most universal method for the solution of various analytical problems. However, the application of the usual version of gas chromatography in the analysis of unstable substances is impossible owing to the high reactivity of the compounds analysed. In the analysis of such substances, it is therefore necessary to carry out methodological modifications involving the elimination of the causes responsible for these reactions or the latter must be carried out either before injection into the column or in the column.

One of the trends in the development of gas chromatography is the development of special methods whereby gas chromatography can be used to analyse unstable compounds.

Several reviews have been published on chromatographic analysis, which include, in particular, data on the analysis of relatively unstable compounds[1-4]. However, they mainly describe isolated data for specific classes of substances combined because of the similarity of their molecular structures. We thought it most useful to give a systematic account of the gas-chromatographic analysis of unstable compounds on the basis of their characteristic reactions, such as hydrolysis, oxidation, thermal and catalytic degradation, and isomerisation.

In order to prevent the above reactions in chromatographic analysis, it is necessary to take special precautions in the preparation of the carrier gas and in the selection of the solid carrier, the stationary phase, the apparatus, etc. In the first place, more stringent requirements must be met by the carrier gas as regards its nature and purity, in particular its content of oxygen and moisture. In the analysis of unstable compounds, much attention is devoted to the selection of the solid carrier on the basis of diatomite and polytetrafluoroethylene. The structures and properties of solid carriers have been described in detail[5]. On the other hand, the choice of the carrier in the analysis of readily hydrolysable, oxidisable, and thermally and catalytically active compounds has its own characteristic features. Important properties of the carrier are its specific surface, mechanical strength, surface pH, and adsorption and catalytic activities. Its chemical properties (acidity or alkalinity) to a large extent determine the error in qualitative or quantitative analysis. In order to eliminate the chemical, catalytic, or adsorption activity of the carrier, it is modified by thermal, acid, or alkaline treatment, by coating the surface with a continuous film of an inert material, by deactivating the adsorption-active centres as a result of the introduction of small amounts of adsorption-active additives, and by chemical conversion of the polar hydroxy-groups into non-polar groups. Inert polymeric sorbents based on Teflon are used successfully.

In the first place, the mobile phase should be incapable of dissolving oxygen, should be chemically inert, with respect to the substances analysed, and should be hydrophobic. Specific requirements in the analysis of compounds of the type under consideration must be met by the material of the column, the metering device, and the detector, and the conditions during analysis. In order to prevent the decomposition of thermally unstable compounds, the percentage impregnation of the mobile phase is low and use is made of solid carriers with small surface areas, vacuum, low temperature, short columns, and high carrier gas flow rates. In many cases the instability of certain compounds makes it possible to analyse them on the basis of the stable products of their characteristic reactions; the reactions are carried out in the column or before injection into the latter (the method of reaction chromatography). Stable compounds in unstable products are analysed by the same method involving a preliminary reaction with the unstable compound in order to remove it and subsequent separation of the stable compounds.

The gas-chromatographic study of the reactions of unstable substances (hydrolysis, oxidation, isomerisation, etc.) constitutes a separate problem and is not discussed in this review.

II. ANALYSIS OF READILY HYDROLYSABLE SUBSTANCES

One of the large groups of substances which are analysed by gas chromatography are those which can be hydrolysed. These include metal chlorides, chlorosilanes and organochlorosilanes, boron, hydrides, chlorine, bromine, and iodine fluorides, and alkylated derivatives of boron, aluminium, beryllium, and gallium. The following reactions may be quoted as examples of hydrolysis:

$$BCl_3 + 3H_2O \rightarrow 3HCl + H_3BO_3,$$
$$BHCl_2 + 3H_2O \rightarrow 2HCl + H_2 + H_3BO_3,$$
$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl.$$

Evidently hydrolysis results in the evolution of gaseous substances (such as HCl and H_2) and solid products (silicon dioxide and boric acid). The occurrence of such reactions cannot be allowed in gas-chromatographic analysis, because, on the one hand, it distorts the quantitative result and, on the other hand, leads to corrosion of the apparatus (HCl) and the formation of a solid deposit which blocks the metering device, the detector, and the connecting capillaries. Furthermore, the formation of a solid deposit on the stationary phase impairs the separation and alters the chromatographic characteristics of the substances analysed.

Numerous studies have been devoted to the direct gas-chromatographic analysis of readily hydrolysable substances. The first publications on this problem appeared in 1957–1960[6,7] and subsequently their number greatly increased[8–45]. Table 1 presents the fundamental groups of substances which are readily hydrolysable. Direct gas-chromatographic quantitative analysis of compounds of this type requires careful drying of the carrier gas until its water content is such that it does not affect the analytical results. The drying agents employed in gas chromatography are listed in Table 2, which shows that the best drying effect is achieved in the presence of phosphorus pentoxide. Furthermore, moisture is removed by condensing water vapour at the temperature of liquid nitrogen. In the majority of studies involving the analysis of readily hydrolysable substances, drying is achieved with a combination of drying systems. Thus, in the analysis of inorganic hydrides[46,47], the carrier gas (nitrogen) was dried by being passed through a system of five series-connected columns filled with granulated copper, KSK silica gel, activated granulated alumina, type 5 Å molecular sieve, and a liquid eutectic mixture of sodium and potassium. After passage through the system, up to 8×10^{-5}% of water remained in the nitrogen. However, in another investigation[7] oxygen-free nitrogen for the analysis of boron hydrides was dried with magnesium perchlorate alone, the drying effect being regarded as sufficient.

In the analysis of inorganic corrosive gases, the drying agents employed were 5 Å molecular sieve (nickel column 12.5 mm in diameter and 107 cm long) subjected to preliminary activation by heat treatment (at 300–325°C, and a residual pressure less than 1 mmHg) for 2 h. The authors[48] claim that such activation makes it possible to employ the drying agent without reactivation for several months, and that the water content in the gas is reduced to $< 5 \times 10^{-4}$%. A gas-chromatographic method has also been proposed for the determination of residual moisture in the carrier gas by condensing water at −78°C and then removing it by reaction with calcium hydride with determination of the oxygen formed. The drying capacities of KSK silica gel, Anhydrone, 5 Å and 4 Å molecular sieves, and phosphorus pentoxide have been tested[49]. The maximum attainable drying effect has been achieved, for example, in the drying of chlorosilanes with the aid of phosphorus pentoxide (5×10^{-3} mg litre^{-1}). In order to increase the period during which the P_2O_5 column is serviceable (the P_2O_5 is deposited on lumps of pumice), some other drying agent must be placed before this column: molecular sieves, Anhydrone, or silica gel. In some investigations[50,51], three columns (100 cm long and 40 mm in diameter), made of glass and filled with 5 Å molecular sieve, were used as the drying train. The moisture content in the nitrogen emerging from the chromatographic column was less than 5×10^{-4} mole %, which is permissible for the analysis of germanium tetrachloride and trichlorosilane.

Table 1. Conditions in the gas-chromatographic analysis of readily hydrolysable substances.

Substance analysed	Carriers and stationary phases	Carrier gas and requirements which it must meet	Detector	Refs.
Boron hydrides	Celite 545, Chromosorb W, Chromaton N, Embacel, liquid paraffin, tricresyl phosphate, Octoyl S, silicone oil 702, OV-17, SE-30, E-301, OV-1, Apiezon L	helium and nitrogen: oxygen content not more than 1×10^{-3} mg litre^{-1}	katharometer, flame-photometric detector	6-13
Metal chlorides, BCl_3, $SiCl_4$, $SnCl_4$, $TiCl_4$, PCl_3, $TaCl_5$, $NbCl_5$	Celite 545, Teflon, Chromosorb AW-HMDS, graphite heated in a stream of Cl_2, Sterchamol, silicone oils, DC-703, DC-550, XE-60, Kel-F, Apiezon L, saturated n-alkanes, paraffin, $BiCl_2$–$PbCl_2$ eutectic mixture	helium, nitrogen, and hydrogen with a water content up to 1×10^{-3} mg litre^{-1}	katharometer, thermionic detector, electron capture detector	
Chlorosilanes and organochlorosilanes	infusorial earth, tiles, Celite 545, INZ-600, Sterchamol, treated DMDXC, Spherochrome, Chromaton NWA, nitrobenzene, benzophenone, liquid paraffin, diethyl- and dibutyl phthalates, tricresyl phosphate, silicone oils NF-M50150, DC-703, PFMS-4, F-169, FS-16, OE-4178, SF-96, DC-LS, K-3-0295, SKTFT-50, and E-301	helium and nitrogen, argon with a water content up to 1×10^{-3} mg litre^{-1}	electrical conductivity detection, katharometer, flame-ionisation detector	23-36
Corrosive inorganic gases	PTFE, solid Kel-F polymer, silica gel, NaF, LiF, liquid Kel-F, oil. dimethyl galcarbonic ether of triethylene glycol, chlorofluorohydrocarbons	helium, nitrogen, and argon	nickel katharometer, thermistors coated with Teflon	37-45

Thus specially activated 5 Å molecular sieve and phosphorus pentoxide may be regarded as the most effective drying agents in the analysis of readily hydrolysable compounds. The degree of drying of the carrier gas can be usefully inferred from the chromatograms of readily hydrolysable products, for example trichlorosilane.[52] When moisture is present in amounts exceeding 5×10^{-4} mole %, two peaks due to trichlorosilane and its hydrolysis product (hydrogen chloride) appear on the chromatogram. When the degree of drying was inadequate, the sorbent was additionally dried by passing trichlorosilane vapour through the column.

In the drying of the carrier gas, account must be taken of the tendency for the moisture content in the carrier gas–sorbent system to reach equilibrium. The dew point in the carrier gas does not therefore characterise the moisture content of the system as a whole, which is the most important parameter.

We shall now consider a number of drying procedures. Thus, in order to prevent the decomposition of boron trichlorides in the chromatograph, the sample injection system is coated with Teflon and the connections between the latter, the column, and the detector are made of Teflon tubes [15]. The carrier gas is carefully dried by means of a molecular sieve and a trap cooled with a mixture of acetone and ice and is treated with 1% of boron trichloride†.

Table 2. Comparison of the drying capacities of various substances.

Drying agent	Residual concentration of water vapour at 25°C, mg litre^{-1}
Fused $CaCl_2$	0.36
Granulated $CaCl_2$	0.14–0.25
Al_2O_3	0.03
$Mg(ClO_4)_2.3H_2O$	0.002
Anhydrous $Mg(ClO_4)_2$	0.0005
Molecular sieves	0.0005
Phosphorus pentoxide	0.000025

In many cases the gas system of the chromatograph is dried by substances more readily hydrolysable than the compound analysed. For example, before the analysis of dichloro-(β-cyanoethyl)methylsilane, trichlorosilane or silicon tetrachloride are introduced several times into the apparatus after the column has been flushed with dry helium [35]. Alkylated boron derivatives are analysed after the entire system has been flushed with the carrier gas at 150°C and above, with subsequent repeated passage of boranes through the column [53]. On the other hand, in the analysis of readily hydrolysable compounds, for example, boron trichloride, the final drying is carried out using the compound analysed [54,55].

A scheme with circulation of the carrier gas [56] is of interest. The authors showed that the passage of 1.5 litres of the carrier gas (containing water at a concentration of 1×10^{-4}%) through the column at a rate of 50 ml min^{-1} causes the decomposition of 0.002 ml of the bisisopropyl benzenechromium specimen. On the other hand, circulation of the carrier gas makes it possible to reduce its moisture content by its interaction with the first portion of the substance chromatographed. The employment of stepwise chromatography in the analysis of readily hydrolysable substances is also of considerable interest. In this case, hydrolysis does not affect the results of the quantitative analysis [52].

†We believe that the cooling of the carrier gas described above is not a rational procedure, because the drying capacity of molecular sieves is extremely high and there is a possibility of the formation of a mist in the trap, which would prevent the complete drying of the carrier gas.

As already mentioned, special requirements must be met by the solid carrier in the analysis of readily hydrolysable and corrosive compounds. In the first place, it is necessary to remove physically adsorbed moisture, which leads to the instantaneous hydrolysis of the substances analysed. However, drying should not remove the water which is used to deactivate the active centres of the carrier [57]. Thus it has been noted‡ that, in the analysis of boron trichloride on Celite (Chromaton) subjected to preliminary vacuum drying at 300°C, boron trichloride undergoes complete irreversible adsorption. The HCl peak is not then observed, which indicates the absence of moisture from both the system and the solid carrier. On the other hand, partial removal of water from the active centres of the solid carrier led to a sharp increase of the retention time of boron trichloride (the peak remained asymmetric). In the drying of the solid carrier, it is therefore necessary to select optimum conditions.

Various methods are used to eliminate the adsorption activity of the carrier. Together with the generally accepted procedures described above, the most effective method for modifying the solid carrier involves its treatment with the substances analysed. In the analysis of primary amines, the preliminary steps involve the repeated admission of the mixture analysed, after which quantitative analysis becomes possible [58]. A study of the influence of irreversible adsorption on the analysis of 1-butanol showed that the error in the determination of 1-butanol decreases appreciably with the increase of the number of successive analyses. If the strongly adsorbed compounds are then desorbed by heating the solid carrier in a stream of carrier gas, saturation is again necessary in the subsequent analyses [59].

The INZ-600 carrier modified by chloromethylsilanes has been used in the analysis of readily hydrolysable chlorosilanes and organochlorosilanes. It was shown that the best modifying agent is dichlorodimethylsilane. [52,60–62] Boron trichloride has been analysed on non-modified Celite 545. [55] In subsequent studies, additional treatment of the solid carrier with boron trichloride proved to be necessary in order to obtain reproducible quantitative results. The method of treatment was as follows: the solid carrier was dried *in vacuo* at 200°C for 3 h, after which it was treated with boron trichloride vapour for 1 h, freed from the trichloride which failed to be adsorbed on the surface by a stream of dry carrier gas, and the stationary phase was deposited (avoiding contact with air). Fig. 1 presents two chromatograms for boron trichloride obtained on untreated and treated carriers.

The solid carrier is also modified when substances of a similar type are introduced into the carrier gas. It is recommended that, in the analysis of amines, a volatile amine or ammonia be added to the carrier gas [63]. In another investigation [15], 1% of boron trichloride was added to the carrier gas in order to achieve additional drying. In this case, boron trichloride probably also behaves as a modifying agent in relation to the carrier surface.

It is claimed [64] that diatomite carriers such as Celite 545 and Chromosorb are unsuitable for the analysis of hydrogen chloride and chlorine even after they have been washed with acid. Further studies showed that this view is

‡N. I. Ivanova, L. D. Prigozhina, S. V. Syavtsillo, G. V. Avdonin, and L. A. Frangulyan, "Protsessy v Khromatograficheskikh Konokakh" (Processes in Chromatographic Columns), Karpov Physicochemical Institute, Moscow, 1975, No. 26, p. 65.

invalid[65-69]. However, the usual silanised diatomite carriers do not always permit the separation of corrosive mixtures. Carriers based on polymeric materials, a major proportion of which have a hydrophobic surface and low adsorption and catalytic activities, are used to separate such mixtures. Carriers based on polytetrafluoroethylene[5], which is manufactured in the USSR under the names Ftoroplast, Polykhrom-1, and Polykhrom-2, have found extensive applications. Outside the USSR, analogous materials are manufactured under the names Teflon (USA), Fluon (England), Algoflon (Italy), Hostaflon (German Federal Republic), and Soreflon (France). Methods have been described[70] for the preparation of an effective Teflon carrier (Polykhrom-1 and Polykhrom-2) and it has been shown that they can be used for the separation of phosphorus, silicon, germanium, strontium, titanium, and arsenic halides and oxide halides. PTFE type carriers are also used for the analysis of corrosive inorganic gases (chlorine fluorides, chlorine oxide fluoride, hydrogen fluoride, hydrogen chloride, and chlorine)[71-75].

Mainly gas–liquid chromatography is used for the analysis of readily hydrolysable compounds. Gas–adsorption chromatography (GAC) has been applied in only a few studies. Graphite, heated beforehand in a stream of chlorine and then evacuated, is used in the analysis of metal chlorides[18]. Studies have shown[76-78] that GAC employing Carbochromes and Silochromes is the best method for the separation of structural and steric isomers of organic derivatives of Group IVB elements. Studies have been made on the analysis of reactive substances on a graphitised carbon black[79]. Furthermore, artificial diamond has been used as the solid carrier for the analysis of hydrogen fluoride, hydrogen chloride, fluorine, and chlorine trifluoride [80], while the alkali metal fluorides KF, RbF, and CsF have been used for the separation of SF_4, SOF_2, COF_2, and SO_2F_2.[81]

In the analysis of readily hydrolysable unstable substances, the stationary phase must not be hygroscopic and must not contain hydroxy-groups; it must be thermally stable under the conditions of the gas-chromatographic experiment and must not react with the compounds analysed. Before being deposited on the solid carrier, the stationary phase is dried. In the analysis of chloromethylsilanes, the stationary phase was subjected to preliminary distillation from phosphorus pentoxide and stored over anhydrous sodium sulphate[82]. The high-boiling liquids employed as stationary phases are dried by evacuation at appropriate temperatures. Nitrobenzene was used as the stationary phase in early studies on the analysis of chlorosilanes and organochlorosilanes[23-29,81-83]. However, despite the satisfactory selectivity of this phase in relation to chlorosilanes, it is highly volatile (b.p. 210°C); it can be used only at room temperature and for a short time, since the separating capacity of the column is impaired as the stationary phase is carried away.

Stationary phases based on organosilicon liquids, which are hydrophobic, thermally stable, and exhibit different polarities depending on the nature of their organic group, began to be used to an increasing extent[25-35,84,85]. Alkyl-, aryl-, and fluorine-containing liquid polysiloxanes were tested as stationary phases for the analysis of organochlorosilanes. It was shown that the separating capacity in relation to chromomethylsilanes increases with the polarity of the stationary phase. Liquids containing fluorinated groups, for example the FS-16 liquid, exhibit a high selectivity. In terms of selectivity, the FS-16 liquid is close to organic stationary phases such as diethyl and dibutyl phthalates. The PFMS-4 and PFMS-6 liquids as well as silicone rubbers and elastomers are used in the analysis of more high-boiling organochlorosilanes. Silicone oil 703 has been employed to analyse boron trichloride, diborane, dichloroborane, and monochlorodiborane, while glycols, the Apiezon grease, phthalates, sulphides, and phosphates reacted with these compounds[54].

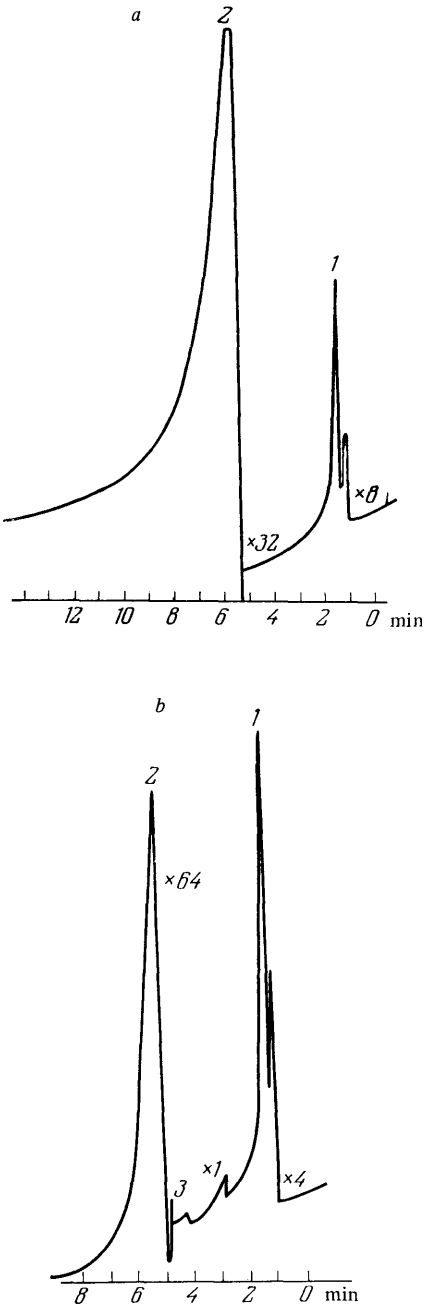


Figure 1. The chromatogram of BCl_3 on untreated (*a*) and BCl_3-treated (*b*) Chromaton N: 1) HCl; 2) BCl_3; 3) $COCl_2$.

Table 3. The interaction of hydrides with water and oxygen.

Group in Periodic System	Element	Interaction with water		Interaction with oxygen	
		nature of interaction	example of reaction	nature of interaction	example of reaction
III, IV	B, Si	decomposition with evolution of H_2	$SiH_4 + 4H_2O \rightarrow 4H_2 + Si(OH)_4$	explosive decomposition	$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$
IV, V	Sn, Sb, P, As, Ge	does not react	—	quiet oxidation	$4AsH_3 + 6O_2 \rightarrow 2As_2O_3 + 6H_2O$
V	N	addition of H^+ ions	$NH_3 + H_2O \rightleftarrows H_4^+ + OH^-$	—	—
VI	O, S, Se, Te	weak oxidative dissociation	$H_2S \rightleftarrows H^+ + HS^-$	weak interaction	$2H_2Se + 3O_2 \rightarrow 2SeO_2 + 2H_2O$
VII	F, Cl, Br, I	vigorous acid dissociation	$HCl \rightleftarrows H^+ + Cl^-$	—	—

Only a few studies have been made on the analysis of the very readily hydrolysable boron trichloride and extremely contradictory results have been obtained.

Some authors believe [86] that boron trichloride is bound in an involatile complex with PMS-100 which conflicts with the results of other investigations [54,87,88] where liquid polyorganosiloxanes were used as the stationary phases in the analysis of this compound. The authors of this review showed that the hydrophobic properties and lack of reactivity of liquid silicones permitted the employment of these compounds, such as VKZh-94, PMS-100, and E-301, for the analysis of boron trichloride, boron hydrides, and alkylated boron derivatives§. Readily hydrolysable boron hydrides have been analysed in most cases on silicone stationary phases [6-13]. It has been shown that liquids containing unsaturated compounds and hydroxy-compounds cannot be used as stationary phases.

However, despite the careful selection of the stationary phase and its preparation, analysis cannot be achieved immediately. The above procedure, involving the drying of the system by passing the most readily hydrolysable component through it before analysis, is applicable also in the final drying of the stationary phase. Apart from the generally adopted silicone stationary phases [22,87,88], the $BiCl_3$–$PbCl_2$ eutectic mixture, melting at 217°C, has been used in the analysis of metal chlorides and for the separation of titanium tetrachloride and antimony trichloride.

Thus the assortment of stationary phases for the analysis of readily hydrolysable substances is limited. For this reason, their selection for the analysis of various groups of substances is highly specific.

III. THE USE OF HYDROLYTIC REACTIONS FOR ANALYTICAL PURPOSES

Hydrolytic reactions can be used in the analysis of readily hydrolysable compounds for the following purposes: (1) when a direct determination is impossible; (2) in the detection of non-hydrolysable substances which do not exhibit corrosion activity; (3) in order to increase sensitivity by employing detectors selective in relation to the hydrolysis products.

The hydrolytic reaction is employed in the analysis of organometallic derivatives of Group I–IV elements (organolithium, organosodium, organopotassium, organomagnesium, organocalcium, and organoaluminium compounds) in order to convert these substances into stable volatile compounds, which are then subjected to gas-chromatographic analysis. Thus vinyl-lithium was determined on the basis of its hydrolysis product—ethylene [89]. The hydrolytic reaction has been used for the analysis of organopotassium, organolithium, and organosodium compounds [90-95]. In the analysis of complexes of phenylcalcium and *m*-tolylcalcium iodides with dioxan and of phenylcalcium in tetrahydrofuran (THF) solution, their hydrolysis products (C_6H_6 and $C_6H_5CH_3$) were analysed by gas–liquid chromatography [96]. Ethylmagnesium iodide was hydrolysed by phosphoric acid in the reactor and the gaseous reaction products were then injected into the chromatographic column [97].

Different versions of the analysis of trialkylaluminium compounds, based on their reaction with hydroxy-compounds, which leads to the formation of the corresponding hydrocarbons, have been described [98]. Rapid analysis of C_1–C_5 aluminium and zinc alkyls has been achieved on the basis of their gaseous hydrolysis product [99,100]. A method has been proposed for the determination of (iso-OC_4H_9)Al (iso-C_4H_9)$_2$ and (iso-OC_4H_9)$_2$Al (iso-C_4H_9) in tri-isobutylaluminium on the basis of the hydrolysis product—the alcohol [101]. Alkylaluminium derivatives have also been analysed using their hydrolysis products [102,103].

Since substances containing active hydrogen are hydrolysed, quantitative gas-chromatographic determination of, for example, B–H and Si–H bonds is possible on this basis. A rapid method for the quantitative determination of the total content of B–H bonds in chloroboranes and boron hydrides, based on the hydrolysis of these substances followed by the detection of hydrogen with a thermistor-based thermal conductivity detector, has been developed [104]:

$$BHCl_2 + 3H_2O \rightarrow B(OH)_3 + 2HCl + H_2,$$
$$B_2H_5Cl + 6H_2O \rightarrow 2B(OH)_3 + HCl + 5H_2,$$
$$B_2H_6 + 3HOH \rightarrow 2B(OH)_3 + 3H_2 \quad \text{etc.}$$

A method has been described for the determination of hydride hydrogen in boron compounds and of hydroxyl hydrogen in alcohols [105]. Si–H bonds are determined by the gas-chromatographic estimation of hydrogen after the hydrolysis of the substances in the presence of KOH. [106]

Diborane and dichloroborane have been determined in hydrogen, nitrogen, and boron trichloride using hydrolytic reactions [107]. The same report [107] describes the apparatus and experimental technique. Furthermore, there is a possibility of reactions with the HCl hydrolysis products. Hydrogen chloride mixed with acetylene and methylene chloride was determined on the basis of the CO_2 formed via the reaction [108]

$$HCl + NaHCO_3 \rightarrow NaCl + H_2O + CO_2.$$

§N. T. Ivanova, L. D. Prigozhina, S. V. Syavtsillo, G. V. Avdonin, and P. A. Frangulyan, Symposium, "Uspekhi Gazovoi Khromatografii" (Advances in Gas Chromatography), Kazan, 1975, No. IV, Part 1, p. 75.

The same reaction can be carried out with the hydrogen chloride evolved after the hydrolysis of the corresponding compounds and the reaction mechanism can be represented as follows:

$$CO_2 \xrightarrow[\text{catalyst}]{H_2,\ T} CH_4.$$

This makes it possible to improve the sensitivity of the determination by using the more sensitive flame-ionisation detector [109].

In the analysis of readily hydrolysable reactive substances, the problem arises of the determination of stable organic and inorganic impurities. The determination of the impurities requires the employment of highly sensitive detectors, or concentration of the impurities, or reactions must be carried out with the impurities in order to improve the sensitivity of the analysis. When highly sensitive ionisation detectors such as the thermionic detector (TID), the electron capture detector (ECD), and the flame-ionisation detector (FID) are used, the entry of the main organoelement derivative into the detector is prevented, since this puts it out of order. Thus microimpurities consisting of chlorinated hydrocarbons of the methane series have been determined in boron trichloride using a thermionic detector after binding BCl_3 into a complex with diphenylamine, which was deposited (in an amount corresponding to 20%) on the INZ-600 carrier. [110] Certain organic chloroderivatives and inorganic substances have been determined in boron trichloride with the aid of a thermionic detector also after their binding into involatile complexes [86]. Using the ability of arsenic trichloride to form a complex with tricresyl phosphate, its organic impurities were determined with the aid of a flame-ionisation detector. Chromosorb W with 15% of tricresyl phosphate was placed in the initial section of the column, while the rest of the column was filled with Chromosorb, containing 10% of PEG-400. [111] In addition, a method is used where the main substance is removed after emerging from the column and before reaching the detector. CCl_4, C_6Cl_6, C_2H_5Cl, and $C_2H_4Cl_2$ impurities in arsenic trichloride have been determined with the aid of a flame-ionisation detector, $AsCl_3$ being removed before reaching the detector [112].

IV. ANALYSIS OF READILY OXIDISABLE SUBSTANCES

The next group of substances which must be analysed by gas chromatography comprises those which are oxidised by atmospheric oxygen. They include boron, silicon, phosphorus, arsenic, tellurium, and selenium hydrides as well as alkyl derivatives of boron, aluminium, gallium, and silicon. However, the majority of oxidisable substances are also capable of interacting with water to some extent. Table 3 presents examples of the interaction of hydrides with water and oxygen.

The oxidation reaction proceeds with formation of water and the solid metal oxide, i.e. with decomposition of the substance. Special precautions are therefore necessary in the chromatographic analysis of certain substances in order to prevent the oxidation reaction. In gas-chromatographic analysis, the products may be oxidised by the oxygen contained in the carrier gas, adsorbed on the solid carrier, and dissolved in the stationary phase. Furthermore, the products may also be oxidised outside the chromatograph at the instant of the removal and injection of the sample. The gases produced by the USSR industry and used as carrier gases, namely helium, nitrogen, and argon, contain the oxygen impurity in amounts of 0.001 to 0.003, 0.1–1, and 0.003–0.4% respectively. For a valid analysis, one must therefore select a carrier gas with the minimum oxygen content and, when necessary, additional elimination of oxygen must be carried out.

In the analysis of silicon, germanium, arsenic, and phosphorus hydrides, the carrier gas was freed from moisture and oxygen by means of a system [46] comprising granulated copper, KSK silica gel, active granulated alumina, 5 Å molecular sieves, and the sodium-potassium eutectic mixture. This made it possible to eliminate oxygen from nitrogen down to 1×10^{-3}%. It is noteworthy that in most instances substances with a tendency towards being oxidised are also hydrolysed. For this reason, a system of drying and oxygen-removing columns is used as a rule. In another study [47], the authors thought that the elimination of oxygen in a granulated copper column alone was sufficient for the analysis of silicon, germanium, phosphorus, and arsenic hydrides.

It has been shown that the removal of the oxygen impurity from technical helium is necessary, since the presence of oxygen (0.003%) lowers the sensitivity of the determination of phosphine approximately by an order of magnitude. Oxygen must be removed from helium at 300°C on a column 1 m long and 3 cm in diameter and filled with a granulated chromium–nickel catalyst. The catalyst was reduced beforehand in a stream of hydrogen until the complete elimination of the water evolved. Table 4 presents the results of the calibration of the chromatograph by Lovelock's method against phosphine with and without the removal of oxygen from helium. It is seen that the area of the peak corresponding to the same concentration of phosphine (0.08%) is almost ten times greater when helium is additionally freed from oxygen. Evidently the lower the concentration of the substance, the more harmful the presence of oxygen in the carrier gas; this is particularly the case in the analysis of impurities. With the aid of such purification, it has been possible to achieve a sensitivity in relation to arsine (by the direct method) of 5×10^{-3}%.

Furthermore, it has been suggested that MnO, obtained from manganese acetate, be used for the absorption of oxygen from the gas stream [113]. According to the authors, this makes it possible to reduce the concentration of oxygen in nitrogen to 10^{-7}%.

Table 4. The influence of the elimination of oxygen from the carrier gas on the analytical results.

Calc. concn. of phosphine, %	Phosphine peak areas, cm²	
	with elimination of O_2	without elemination
3.87	38.4	28.6
2.38	23.8	15.5
1.51	15.2	8.6
0.77	7.6	2.38
0.28	2.88	0.35
0.16	1.54	0.16
0.08	0.81	0.08

However, the carrier gas always contains some residual oxygen. In order to prevent the reaction or reduce the percentage decomposition of the substance analysed, the method involving a decrease of contact time is used. Thus nitrogen freed from oxygen and moisture, a column 50 cm long at 34.5°C, and Celite 545 with 30% of silicone 702 were used in the separation of boron hydrides ranging from B_2 to B_5. [7] By passing the separated

components through the chromatographic column again, it was established that the compounds B_2H_6, B_4H_{10}, and B_5H_9 are not decomposed at all under the conditions of the analysis, while B_5H_{11} decomposes to the extent of 10% during each pass through the column. We believe that drying with Anhydrone, suggested in the above investigation for the analysis of boron hydrides, is inadequate, and this may be the reason for the decomposition of B_5H_{11}.

The scheme involving the circulation of the carrier gas discussed in the preceding section is of undoubted interest also for the elimination of oxygen from the carrier gas [56]. The carrier gas is freed from oxygen following the injection of the first samples containing the readily oxidisable compounds to be analysed. The reactivities of such substances are not the same and an individual approach to the selection of drying agents and of the oxygen-elimination system is therefore necessary [114,115].

In the analysis of boron trialkyls, attention was drawn to their extremely high reactivity in relation to moisture and oxygen, which necessitated the "complete" absence of the latter [114,115]. However, it is known that trimethylboron is resistant to water and is not oxidised in air and that triethylboron and tripropylboron are less steadily hydrolysed than boron hydrides and triethyl aluminium [116]. One of the authors of the present review [117] tested the influence of the removal of oxygen from the carrier gas by the chromium–nickel catalyst on the decomposition of triethylboron. The experiments demonstrated a slight change in the results of the analysis for the main product (97.0% with elimination of oxygen and 96.9% without). The "complete absence" of oxygen and moisture is therefore not obligatory in the analysis of boron alkyls. The use of technical helium dried over phosphorus pentoxide without additional elimination of oxygen is quite feasible.

Table 5. Conditions in the chromatographic analysis of oxidisable substances.

Substances analysed	Carriers and stationary phases	Carrier gas and requirements which it must meet	Detector	References
Boron, silicon, germanium, phosphorus, arsenic, selenium, tellurium, and tin hydrides	Celite, Chromosorb W, Embacel, liquid silicones Apiezones, BAU charcoal, Polysorb-1	helium, nitrogen, and argon freed from H_2O and O_2 to within 1×10^{-3}%	katharometer, FID PPD	6,10,13,46,47,53, 79,113,117,118, 121–124
Alkylated boron, aluminium, gallium, tin, and silicon derivatives	refractory brick, Polychrom-1, Kieselguhr, Sterchamol, Celite, liquid silicones	ditto	katharometer	113–116

The requirements which must be met by the solid carrier in the analysis of substances showing a tendency towards both hydrolysis and oxidation (boron hydrides, alkylated derivatives of boron, aluminium, and gallium, and silicon hydrides), on the one hand, and substances which can only be oxidised (phosphorus, arsenic, tellurium, and selenium hydrides), on the other, are different. In the former case, apart from the drying procedures described in the previous section, the carrier must be degassed in order to remove physically adsorbed oxygen. Furthermore, the impurities in the solid carrier can serve as oxidation catalysts. In the analysis of such products, one therefore uses as a rule solid carriers such as Celite 545 [9], Embacel [10,11], and Chromosorb W. [12,13] In the latter case, one can use gas-adsorption chromatography. Thus the adsorption of silicon, arsenic, germanium, and phosphorus hydrides on BAU activated charcoal has been investigated [118,119] in the temperature range from 0° to 100°C, and it was shown that the substances do not decompose in this temperature range and undergo physical adsorption. This justified the employment of BAU charcoal as the adsorbent in the analysis of the above hydrides.

A necessary condition for the employment of gas-adsorption chromatography is careful elimination of adsorbed oxygen from the adsorbent by evacuation at high temperatures, and careful removal of oxygen from the carrier gas in order to prevent the adsorption of oxygen on the solid carrier. In one investigation [79], graphitised carbon black was subjected to a preliminary treatment with hydrogen at 1000°C. This process should have limited the number of active centres formed by the surface oxygen complexes which are always present on the surface of adsorbents. In this case, the carbon black behaves as an inert carrier.

Readily oxidisable substances are separated on polymeric sorbents. Polysorb-1 has been used to determine arsine and phosphine in the effluent gases from phosphorus furnaces and as impurities in acetylene [120,121]. The requirements which must be met by the stationary phase are analogous to those mentioned previously and, in addition, the stationary phase must not dissolve oxygen. The method of preparation involves vacuum heat treatment followed by stabilisation of the column. Mainly liquid silicones and Apiezon are recommended as the stationary phases for the analysis of readily oxidisable substances [10,12,13,53,113,122–124].

In certain cases, the oxidation of the main substance does not interfere with the analysis, for example in the determination of stable non-oxidisable impurities in a readily oxidisable compound. Thus, in the determination of hydrocarbons in arsine [125], the mixture was passed through a tube containing copper heated to 130°C, where arsine was bound and the impurities were then separated on a chromatographic column and detected with the aid of a flame-ionisation detector. In addition, one sometimes uses the method where the main reactive substance is removed before entering the detector [126], and stable impurities are detected. The impurities are also concentrated by employing two columns, where silicon, boron, or germanium hydrides are separated in the first column from the organic impurities, which are collected in a cooled trap and then separated on the second column: the hydrides are removed and subjected to thermal decomposition [127].

Table 5 presents the conditions necessary for the chromatographic analysis of oxidisable substances.

V. ANALYSIS OF SUBSTANCES CAPABLE OF THERMAL AND CATALYTIC DEGRADATION AND ISOMERISATION

Chromatographic analysis of substances showing a tendency towards thermal and catalytic degradation is possible when a number of conditions preventing the occurrence of such reactions are maintained. These include the employment of reduced evaporator, column, and detector temperatures, the use of inert and catalytically inactive solid carriers and stationary phases, careful

selection of the material for the metering device and column, and purity of the carrier gas. The requirements which must be met by the carrier gas are similar to those described above. In contrast to the hydrolytic and oxidation reactions, which are as a rule instantaneous, the catalytic and thermal degradation and isomerisation reactions take place over a period of time. In the analysis of such substances it is therefore important to bear in mind the duration of the analysis.

The gas-chromatographic method has been used in the analysis of thermally unstable substances. Dichloroborane and monochlorodiborane are known to decompose at room temperature [128]. In the separation of a mixture of dichloroborane, monochlorodiborane, hydrogen chloride, boron trichloride, and hydrogen, a temperature of 0°C, and a column 10 mm long and 6 mm in diameter filled with Chromosorb W containing a silicone oil as the stationary phase were therefore used. It has been suggested [107] that diborane and dichloroborane be determined in hydrogen, nitrogen, and boron trichloride below 0°C. The hydrogen–diborane or hydrogen–dichloroborane–boron trichloride sample is directed to a column 25 cm long, filled with quartz sand, and cooled to −173°C, where diborane (or boron trichloride–dichloroborane) condenses, while hydrogen does not and passes subsequently through the hydrolysis column (molecular sieves treated with ethanol) and is detected. The condensation column is then warmed and the diborane (or boron trichloride–dichloroborane) sample is directed to the hydrolysis column, where it decomposes with evolution of hydrogen, which passes to the detector. This permitted the determination of diborane and dichloroborane with a high sensitivity.

The metal carbonyls $Fe(CO)_5$, $Ni(CO)_4$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ are readily oxidised and thermally unstable. However, at a reduced temperature and when the percentage impregnation of the stationary phase was low, it was possible to analyse them by gas–liquid chromatography. A column 2 m long and 6 mm in diameter, filled with molybdenum glass containing 0.5% of liquid polymethylethylsiloxane (VKZh-94), was used at 30°C for the analysis of iron pentacarbonyl and nickel tetracarbonyl, boiling at 102° and 42°C respectively [129]. Chromium, molybdenum, and tungsten carbonyls were separated at 76°C on a 3 m × 3 mm column filled with 10% of 1,2,3-tris-2-cyanoethoxypropane on diazolide [130].

As a rule thermally unstable substances undergo hydrolysis and oxidation at the same time. Their chromatographic analysis therefore requires a combined approach involving precautions against both hydrolysis and oxidation. Substances of this kind include alkylated derivatives of boron, aluminium, and gallium. The possibility of using gas-chromatographic analysis for the investigation of catalytic exchange reactions between boron trialkyls and for the determination of the rates of these reactions has been demonstrated [53,114]. This was achieved by employing high carrier gas flow rates. At relatively low temperatures, boron alkyls are known to split off olefins via the reaction

$$R_2BCH_2CH_2R' \rightarrow BR_2H + CH_2 = CHR' \ .$$

The selection of the temperature of the metering device and the column is therefore very important in the analysis of these substances. It is claimed [37] that the above reaction does not play a significant role in gas-chromatographic analysis. The authors of the present review [117] determined the maximum permissible evaporator temperature, which is 100°C for tripropylboron (B.p. 160°C) and 80°C for triethylboron (B.p. 96°C). The analysis of these substances is carried out under programmed conditions. Methyldiboranes have been determined at 0°C. [131]

Not only temperature parameters but also the selection of the solid carrier and its treatment are important for substances undergoing thermal and catalytic degradation and polymerisation. A gas-chromatographic method has been proposed for the analysis of dichloro-(β-cyanoethyl)-methylsilane, which boils at 210°C and is extremely reactive, being readily hydrolysed by water and polymerising at elevated temperatures and in the presence of a number of metals [35]. In order to prevent the decomposition of the substance, a glass tube was inserted into the metallic metering device of the chromatograph, which was responsible for the non-reproducibility of the chromatograms obtained, in such a way that its end entered the initial section of the chromatographic column; the temperature of the metering device did not exceed 150°C, because decomposition was observed already at 180°C. Before analysis, the column was flushed with the dry carrier gas at 200°C for 2 h and the sorbent was then additionally dried by introducing several trichlorosilane samples in succession; the column was stabilised by injecting samples of the substance to be analysed.

A direct gas-chromatographic method for the analysis of triethylaluminium and triethylgallium, which are also readily oxidised and thermally unstable, has been proposed [132]. The boiling point of triethylaluminium is 186.6°C and it begins to decompose in an inert atmosphere already at 120–125°C. The authors propose a method for the removal and injection of these substances into the chromatograph without coming into contact with air, but do not indicate the range of evaporator temperatures and do not quote quantitative data, which precludes an assessment of the reliability of this procedure. In most studies, reaction chromatography is used for the analysis of organoaluminium compounds [99–103].

The fundamental conditions in the selection of the solid carriers are its complete catalytic inertness, the employment of modifying carriers [133], and the stabilisation of the sorbent by passing through the column compounds resembling those to be analysed. Thus, in the analysis of bisethylbenzenemolybdenum, the column was first modified by passing bisarene complexes of chromium through it, 3–5 analyses were carried out, and the column was then modified [134].

An interesting procedure has been proposed for the analysis of organophosphorus compounds, which tend to isomerise [135]. An isomerisation inhibitor was added to the stationary phase, which permitted the gas-chromatographic analysis of these substances. The separation of dichloroborane and monochlorideborane [54] at 40°C on a column filled with Chromosorb containing 30% of n-hexadecane, saturated with boron trichloride, is based on the same principle. Since it was known that dichloroborane and monochlorodiborane are most stable in the presence of boron trichloride, the saturation of the stationary phase by the latter made it possible to achieve the separation [54].

A decrease of the resonance time of the unstable substance in the column should undoubtedly improve the results results of the chromatographic analysis. A study has been made [136] of the influence of the solid carrier, of the percentage content of the stationary phase and its nature, and of the residence time of the sample in the column (i.e. the carrier gas flow rate) on the separation of the isopropylphenyl hydroperoxide. It was shown that tricresyl phosphate (TCP), which has the smallest acid number, is the best stationary phase; common salt and silanised Chromosorb W were used as the solid carriers and it was

shown that the degree of decomposition diminishes with increase of the percentage of the stationary phase and with the carrier gas flow rate. Conditions were selected on the basis of the percentage decomposition for the separation of a mixture of isopropylbenzene, acetophenone, and isopropylphenyl hydroperoxide. Glass columns, high carrier gas flow rates, and low temperatures are as a rule employed in the analysis of hydroperoxides. Thus *n*-butyl hydroperoxide was isolated on a glass column (Celite with 30% of dinonyl phthalate) at 40–60°C and a helium flow rate of 120 ml min^{-1}, the sample being injected directly into the column[137]. A mixture containing isopropylphenyl hydroperoxide was analysed on Chromosorb treated with dichlorodimethylsilane (DCDMS) with 1.5% of TCP at 80°C; after preliminary flushing of the column for 8 h at 100°C and the injection of 15–16 hydroperoxide samples into the chromatograph, the decomposition of isopropylphenyl hydroperoxide was not observed[138]. Ethylphenyl hydroperoxide was analysed on Chromaton treated with DCDMS containing 5% of poly(ethylene glycol) (PEG) distearate at a nitrogen flow rate of 210 ml min^{-1}.[139]

We considered specially the procedures used in the analysis of organic peroxides which are thermally and catalytically unstable, since analogous methods are used in the analysis of organoelement compounds. For example GLC analysis of alkylmercury derivatives showed that RHgX and R_2Hg are effectively separated on glass and metallic columns when the sample size is 10^{-5} g; when the sample size is reduced to 10^{-8} g, RHgX decomposes on a steel column[140]. Similar experiments showed that stable MgHgX peaks may be obtained by increasing the mass of the chromatographed sample[141]. To prevent a long residence time of the unstable hydrides in the column, a short column (40 cm long, containing Celite with 30% of silicone 702) was used in a study of the pyrolysis of diborane[7].

VI. IDENTIFICATION OF UNSTABLE COMPOUNDS AND QUANTITATIVE INTERPRETATION OF CHROMATOGRAMS

Several methods are available for the identification of compounds. They include identification on the basis of chromatographic parameters, i.e. the determination of the dependence of the retention time on the nature of the substance and the determination of the relation between the retention volume and the number of similar groups or atoms (analogously to the relations observed in homologous series of organic compounds), preparative isolation followed by the employment of physicochemical methods of analysis, and chromato-mass-spectrometry. The use of chromatographic relations (the dependence of the retention volume on the number of atoms and on the boiling point) is difficult, because a high reliability of the analysis requires the determination of the retention volume in stationary phases of different polarities and at different temperatures. However, this is not always possible, since the number of stationary phases and the feasible temperature ranges are limited in the analysis of unstable substances. Furthermore, the extremely high reactivity of the products may distort the measured retention volumes when the sample interacts with the solid carrier and the material of the column.

However, attempts to find relations which would assist in the identification of substances of this kind have been made. For example, the behaviour of alkoxychlorosilanes $Cl_nSi(OR)_{4-n}$ (where n = 1, 2, 3, or 4 and R = Me, Et, Pr, or Bu) at 50–90°, 80–120°, 150–190°, and 160–200°C respectively has been studied by GLC on 1 m × 3 mm columns filled with different weakly polar and polar stationary phases on Resorb and Hexasorb[142,143]. When the fluorosilicone FS-16 was used as the stationary phase, a linear relation was obtained between the heats of solution and boiling points of alkoxychlorosilanes, which may be used for the identification of these compounds. The retention indices of alkyl-, aryl-, akylaryl-, and chloroaryl-chlorosilanes have been determined[144,145] and it has been shown that the indices for substances on a non-polar stationary phase are satisfactorily correlated with their boiling points. The retention volumes of decaborane and its 1- and 2-halogeno-substituted derivatives $B_{10}H_{13}X$, where X = Cl, Br, or I, have been determined at 141°, 151°, and 161°C.[146] Using these data and the specific retention volumes of pentadecane and eicosane, the retention indices were calculated. The sorbent employed was Chromosorb W with 3% of silicone oil QF-1. It was shown that Carbowax 20 M, polyesters, and unsaturated compounds react with the substances analysed.

The retention indices of boron hydrides ranging from B_2 to B_{10} have been calculated for a column with 6% OV-17 on Chromosorb. It was found that the indices vary approximately linearly with the number of boron atoms in the boron hydride molecules, which made it possible to identify hexaborane in the mixture, the result being subsequently confirmed mass-spectrometrically[12]. Linear relations have been obtained between the logarithm of the absolute retention volume ($\lg V_g^{abs}$) and the number of atoms in silicon hydrides from Si_2 to Si_6 and between the logarithm of the relative retention volume ($\lg V_g^{rel}$) and the number of germanium atoms in germanium hydrides and silicogermanes[147]. The data for metal chlorides are contradictory. Thus it has been found[148] that the variation of $\lg V_g^{abs}$ with the boiling points of Si–Ti tetrachlorides is non-linear, while other workers[149,150] obtained a linear relation between $\lg V_g^{abs}$ for metal tetrachlorides and the reciprocal of the absolute column temperature ($1/T$), the boiling point, and the molecular refraction. There are also contradictory data for organotin compounds. It was found in a study of the chromatographic properties of Me_4Sn, Et_4Sn, and Bu_4Sn on eight stationary phases that the dependence of $\lg V_g$ on $1/T$ and the number of carbon atoms in the molecule is linear[151], while another investigation[152] demonstrated a non-linear variation of $\lg V_g$ for compounds of the type R_4Sn with the total number of carbon atoms.

Since the temperature and the stationary phase cannot always be varied in the analysis of unstable compounds, which is necessary in qualitative analysis, the preparative isolation of the unknown compounds followed by their identification by infrared spectroscopy, mass-spectrometry, etc. is the most reliable procedure. Comparative chromatography combined with infrared spectroscopic analysis of the compounds isolated has been used to identify admixtures in dichlorodiphenylsilane and trichlorophenylsilane[153]. Certain compounds, obtained in the direct synthesis of chloromethylsilanes, were identified by preparative gas chromatography followed by the study of their physicochemical constants, elemental composition, and infrared spectra[154]. Chromato-mass-spectrometry has been used to identify trialkylboranes[155] and boron hydrides[156].

The specificity of the chromatographic analysis of unstable compounds is also reflected in the quantitative interpretation of the chromatograms. The method of absolute calibration, normalisation without the introduction of calibration coefficients, and, more rarely, the internal standard method are used in quantitative analysis. When an absolute calibration is carried out, it is necessary to prepare artificial mixtures. For substances with high vapour pressures and boiling points up to 100°C, a vacuum system for the preparation of the calibration mixture is used. This procedure, proposed for the preparation of a calibration mixture of nickel and iron carbonyls [129], can be modified as a function of the reactivity of the product. A similar system can be made wholly from glass and metallic taps can be replaced by glass and Teflon taps[50,51]. Provision can be made for several flasks at once, in which the calibration mixtures are prepared. For substances with a tendency towards oxidation accompanied by explosion, the mixtures are usually prepared in metallic cylinders, their composition being followed from the pressure. Naturally the material of the cylinder should not react with the mixture. Finally, the exponential dilution method proposed by Lovelock [157] is used for the calibration.

In the calibration of sulphur compounds, a method is used which combines permeability and exponential dilution. It has been shown that the application of the exponential dilution method alone with injection of the sample into the vessel from a syringe does not yield a result with an error less than 5%. [158] On the other hand, the combination of the two methods results in a relative standard deviation not exceeding 1%. When calibration mixtures of readily hydrolysable compounds are prepared, there is a risk of an error due to their hydrolysis during the preparation of the mixture. In the study of the possibility of calculating low concentrations of readily hydrolysable chloromethyl- and chlorophenyl-silanes by a normalisation method without calibration coefficients, the errors were determined and the limits of the applicability of the method were found [159]. It was shown that, in the analysis of trichloromethylsilane (TCMS) microimpurities in chlorodimethylsilane (CDMS) up to a content of 0.75%, the systematic absolute error associated with failure to take into account the coefficients does not exceed 0.10%, which implies that, in the analysis of commercial organosilicon monomers containing 98–99% of the main substance, the concentrations of the impurities may be calculated with adequate accuracy by the normalisation method without taking into account calibration coefficients. Calculations by the normalisation method from the areas without the use of calibration coefficients have been employed by various investigators in the analysis of chlorosilanes [31], dichloro(β-cyanoethyl)methylsilane [15], alkylated boron derivatives, and boron trichloride [117].

In the absolute calibration of readily hydrolysable substances, it is possible to suppress the hydrolysis of the admixture, having prepared its calibration mixture with a more readily hydrolysable substance. This is particularly important in the determination of microimpurities. Thus mixtures of $SiCl_4$ and boron trichloride containing between 0.01 and 0.08% $SiCl_4$ have been prepared and the analytical error was about 10 rel.%. The absolute calibration method has been used in the analysis of mixtures of phosphorus, PCl_3, $POCl_3$, and $PSCl_3$ [160] (the relative error of the determination varied in the range ±6%), in the analysis of alkylchlorosilanes and chloroalkyl derivatives [161], and in the analysis of chloromethylsilanes [29,162].

The internal standard method is more rarely used in the analysis of reactive substances owing to the difficulty of selecting an internal standard and of its introduction into the mixture. As examples of the application of the internal standard method, we shall only quote studies [34,163] where ether was used as the internal standard in the analysis of chloromethylsilanes (analytical error 2%) and the study where trichloro-*n*-propylsilane chlorination products were analysed using trichloro-*n*-propylsilane as the internal standard. We believe that the employment of a substance having a similar structure and properties as the internal standard is more justified.

In order to obtain accurate quantitative results, it is desirable to use a density detector, which does not require calibration, for the analysis of unstable substances with different molecular weights. Corrosive halogen gases have been analysed quantitatively by means of a Martin nickel densitometer [164].

One should also note that, using the capacity of reactive substances for interaction with some other substance or their thermal instability, in the analysis of such substances one can carry out the reaction beyond the column and before the detector in order to detect the inert substance or the inert mixture in the detector and to calibrate the apparatus with respect to the reaction products. In the experiments on the analysis of volatile inorganic hydrides of a number of Group IV–VI elements (SiH_4, GeH_4, AsH_3, PH_3, H_2S, etc.), the furnace (10 to 15 cm long and 1.5 cm in diameter) was placed beyond the chromatographic column in order to decompose the hydrides to hydrogen at 1000°C. [46] This enabled the authors to increase the sensitivity of the determination and also to avoid (under the conditions of complete conversion) the calibration of the apparatus with respect to the hydrides, using hydrogen for this purpose. The apparatus was calibrated similarly after the decomposition of chlorophenylsilanes [165,166]. Using the hydrolysis of chlorosilanes to HCl and carrying it out before the detector with subsequent conversion into CO_2 via the reaction $HCl + NaHCO_3 = NaCl + H_2O + CO_2$, it is also possible to calibrate the apparatus with respect to the stable carbon dioxide instead of the readily hydrolysable substances. A method has been proposed [37] for the analysis of F_2, ClF, ClF_3, and ClF_5 on the basis of the products of their reaction with silicon, which results in the formation of SiF_4 and Cl_2 ($Si + 2F_2 \rightarrow SiF_4$; $Si + 4ClF \rightarrow SiF_4 + 2Cl_2$, etc.).

This is of interest also from the standpoint of quantitative interpretation, since calibration with respect to one component undoubtedly gives rise to a smaller error than calibration with respect to four different components (naturally provided that one can be certain that all the reactions go to completion). Iron carbonyls have been detected [167] by a flame-ionisation detector after conversion via the mechanism $Fe(CO)_5 \xrightarrow{T} Fe + 5CO$ and the transformation of CO into methane; after the decomposition in the column, organolead compounds were passed through a tube with a nickel catalyst and the methane formed in the presence of the catalyst from the substances separated was detected [168]. In all the instances described, the calibration procedure is simplified and can be carried out with a high accuracy, but the chromatographic set up becomes much more complex, requiring the calculation (or selection) of optimum reactor parameters and careful monitoring of the reaction conditions.

VII. CHARACTERISTICS OF THE APPARATUS USED IN THE ANALYSIS OF UNSTABLE COMPOUNDS

Analysis of readily hydrolysable, corrosive, and toxic compounds imposes additional requirements on the materials of the metering devices and it is also essential to protect the injected sample from the surrounding medium.

There is no universal metering device in chromatography; there are several possibilities for the metering of various types of samples, from which the optimum procedure must be selected. The most widely used materials for the construction of sample injection systems and metering in chromatographic analysis of the compounds under consideration are Teflon, polyethylene, glass, nickel, stainless steel, and Monel metal.

Metering by means of a syringe, whereby samples ranging from several millilitres can be injected depending on the design, is simple and fairly reliable. The possibility of using a microsyringe for the metering of corrosive readily hydrolysable compounds depends on the materials used for its construction and design solutions ensuring a fully hermetic seal. Syringes produced by U.S. and East German (GDR) firms to a large extent meet these requirements, being used, in particular, in the metering of organometallic compounds [169,170].

In the analysis of extremely reactive and toxic compounds, the authors of the present review¶ used a hermetically sealed syringe having a volume up to 10 μl with a Teflon piston, isolated from the external medium and ensuring the localisation of the sample in case of accidental breakage of the glass cylinder.

A system consisting of a glass 50 ml nitrogen-flushed cuvette with two outlets has been proposed for the removal of samples which must not be allowed to come into contact with air, for example those of organic compounds of certain metals [169]. After the insertion of the needle into the cuvette through the stopper, nitrogen was passed through the syringe until the product was collected, which ensured that the sample was preserved in the syringe until its injection into the evaporator of the chromatograph. During the transfer of the syringe to the chromatograph, the needle of the former remained inserted in an elastic stopper, which prevented its contact with air. The sample was injected with simultaneous piercing of both the stopper on the needle and the rubber membrane on the chromatograph inlet unit. A similar procedure to ensure a hermetic seal on the syringe needle was used when liquid alkylated boron [53], aluminium, and gallium [132] derivatives and dichloro-(β-cyanoethyl)methylsilane [35] were injected into the chromatograph. Triethylboron and tripropylboron were sampled in an inert atmosphere or in a stream of an inert gas [117]. One of the varieties of metering device for the injection of liquid and solid samples has been described by Wong and Schwartz [171].

In the removal of gaseous samples, vacuum sample removal and sample injection systems are used in most instances. One of such systems has been used in the analysis of trichlorosilane, germanium tetrachloride, and arsenic, phosphorus, germanium, and silicon hydrides [46,50,51]; an analogous system, with slight modifications, has been employed in the analysis of fluorine and chlorine fluorides [37,38], alkylated boron derivatives [53], and metal carbonyls [129]. Various systems made of glass, incorporating multiway taps and metering reservoirs [172-174], including experiments *in vacuo* at residual pressures down to 10^{-3} mmHg, are used in the analysis of many corrosive inorganic gases, for example nitrogen oxides, HCl, and fluorine compounds (other than HF) [175-177]. Precautions are taken to eliminate a sealing grease by employing glass and Teflon taps [50]. Samples ranging from several millilitres [175] to 10^{-5} mole have been metered with the aid of such systems [177]. Samples of readily hydrolysable corrosive and toxic substances, such as, for example, organochlorosilanes, boron hydrides, and boron and silicon chlorides, are frequently introduced into the chromatograph by means of breakable glass bulbs.

A device has been proposed [178] for the injection of very small samples (0.001–10 mole) of gases of vapours by means of a sealed glass tube, the upper, breakable part of which is made in the form of a hemisphere with a drawn out portion, where it can be sealed off. The sealed tube constitutes the lower part of an outer Pyrex tube (with an internal diameter of 15 mm and a polished inner surface) which is fitted onto the cylindrical shell of the Teflon metering device into which the carrier gas is supplied via a capillary. When the capillary comes into contact with the upper part of the sealed tube, the latter is broken and the sample is blown out by the stream of carrier gas via a side arm of the metering device directly into the chromatograph. The hermetically sealed bulb metering device, in which a sealed glass bulb with the sample of the test substance was placed, has been used in the analysis of organochlorosilanes, boron trichloride, and other products [179]. The metering device is joined directly to the evaporator of the chromatograph. The bulb is broken by a rod activated at a distance by an electromagnet; the sample is then introduced into the evaporator by the stream of carrier gas. The metering device is freed from glass fragments via a special aperture after 25–30 analyses.

The metering systems in which glass is used are unsuitable for the injection of samples containing hydrogen fluoride and highly toxic substances. Furthermore, in the removal of samples from systems under an excess pressure, glass is unsuitable because of its low mechanical strength. A metallic metering tap made of a corrosion-resistant material with a Teflon seal makes it possible to inject samples of reactive and highly toxic gases from the cylinder, provision being made for the flushing of the tap and the connecting tube by a dry inert gas with the aid of a system of valves [107]. The removal of the sample directly from the technological line can be achieved similarly, provided that conditions permit it. For the cyclic injection of liquid hydrolysable substances, particularly into an industrial chromatograph, a slide-valve metering device with a pneumatic actuator was developed; in it, a stainless steel plate is made to move through a definite cycle by means of the pneumatic device [180]. The plate, moving between stationary PTFE plates, causes the injection of the sample into the column or its flushing with the carrier gas as it allows appropriate channels to be connected. A similar system was also used in the metering of metal chlorides and phosphorus compounds [181,182].

Methods for the injection of samples by special gas tube systems and blocking devices, permitting the alteration of the direction of the stream of the carrier gas and the injection of the sample directly into the chromatograph, have been described in a number of studies [48,54,183-186]. Thus, a system consisting of sections of polyethylene capillary tubes 0.38 mm in diameter and blocking devices have been used to meter mixtures of chlorine and hydrogen fluoride [185]. Tubes were connected by nickel capillaries to a T-shaped socket made of Monel metal. In order to alter the direction of the gas streams, the tubes were closed by

¶See the footnote to p. 175.

clamping them to a solid plate by means of five bronze screws. Metallic or Teflon washers between the screw and the tube protected the latter from being crushed. By opening and closing the tubes to the gas stream in different combinations, it is possible to achieve in succession the passage of the carrier gas through a by-pass into the chromatograph with simultaneous removal of the sample into the metering reservoir, its isolation, and injection into the column. The size of the dose is determined by the length of the corresponding section of the polyethylene tube (the dose is 6.5×10^{-3} mm for a tube 50 mm long).

A system acting on a similar principle has been proposed for the removal *in vacuo* of samples of corrosive halogen-containing gases from the technological stream[48]. The gas streams are controlled by glandless needle valves made of bronze with nickel-plated inner surfaces. The gas system is welded using a silver solder. Such valves remain effective for 12–18 months of continuous operation according to the authors, after which the system is completely renewed. One of the varieties of the systems described with cut-off valves, controlled by compressed air, has been used for the injection of samples of mixtures of chlorofluoroalkanes with uranium hexafluoride. The materials used for their preparation were nickel, Monel metal, and Teflon[186]. The latter systems have definite advantages over multiway taps and slide-valve metering devices from the standpoint of reliability of operation and the hermetic seal, although their control requires a large number of operations.

In many instances, particularly in the industrial control of a technological process, the sample removed must be transported over a certain distance for its chromatographic analysis. It is then necessary to employ samplers which ensure that the sample is representative, is preserved, and can be injected into the chromatograph. A version of a 10 ml sampler, made of Teflon, for sulphur-containing gases (H_2S, SO_2, etc.) has been described[187]. A transportable sampler has been proposed† for corrosive, toxic, and readily hydrolysable gaseous media in which the volume of the working chamber is 250 cm^3 (Fig. 2). The device makes it possible to remove a sample from gaseous systems under an excess pressure or under the conditions of rarefaction. The Teflon shell of the sampler is clamped together with an elastic membrane between Textolite flanges. The membrane is connected to a plunger with a rigid centre and is moved by a guide screw with a handle, located in a guide bracket. The sampler tube is connected to the shut-off valve by a polyethylene capillary. Samples containing compounds capable of diffusing through Teflon are removed by a modified sampler with a stainless steel bellows replacing the membrane unit.

The choice of column materials is as a rule preceded by a careful analysis of their behaviour under various conditions[188]. For example, Teflon is completely inert and can be used in the separation of any substances, including HCl, HF, etc., but the temperature must not exceed 200°C. Like Teflon, glass and quartz are not catalytically active, while metallic columns can exhibit catalytic effects, particularly at high temperatures, and the sorption phenomena on their surfaces are manifested to a greater extent than for glass and Teflon. The disadvantages of metallic columns are compensated by their high resistance to heat, optimum thermal conductivity, and the technological ease of their manufacture. Thus the choice of column material depends on the nature of the substance analysed, the conditions of the analysis, and the technology of the column manufacture. Despite its disadvantages, glass is in many cases the only material suitable for the preparation of columns used in the analysis of chemically unstable compounds. For example, studies carried out with copper, stainless steel, Teflon, and glass on the chromatographic analysis of mixtures of nitrogen dioxide and air showed that materials other than glass cannot be used because of sorption on the column surface[189]. Nor could glass columns be replaced in the analysis of admixtures of hydrogen chloride, chlorine[172,190], halogenohydrocarbons[173], organic derivatives of boron, beryllium, aluminium, phosphorus, zinc, and tin[169], and phosphates, amines, and triazides[191], and in the determination of organic chloro-impurities in germanium tetrachloride and hydrocarbons[50,51]. The replacement of Teflon columns by glass columns in the analysis of tetraethyl pyrophosphate decomposition products increased the sensitivity of the determination by a factor of five[192].

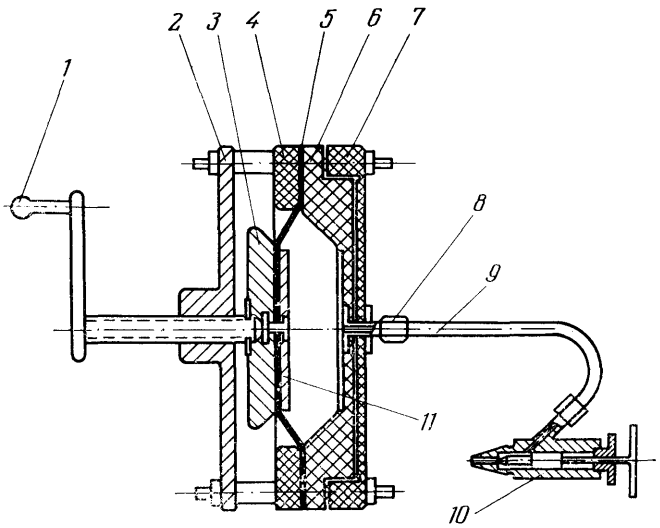


Figure 2. Gas sampler: 1) guide screw; 2) bracket; 3) plunger; 4) and 7) flanges; 5) membrane; 6) shell; 8) tube; 9) capillary; 10) valve; 11) rigid centre.

Monel metal and nickel columns are used as a rule in the chromatographic analysis of halogen and interhalogen compounds as well as metal fluorides and chlorides[40,181,184,193,194]. However, in most cases the columns are made of stainless steel in view of its ready availability and lower cost compared with nickel and Monel metal. In particular, stainless steel columns have been used in the analysis of arsenic and phosphorus hydrides, organic chloro- and bromo-compounds, and organic compounds of phosphorus, tin, and many other elements[170].

In view of the great inertness of zirconium oxides, they have been suggested as coatings for the inner walls of gas connectors and chromatographic columns to be used in the analysis of corrosive substances. For this purpose, the zirconium components are etched with oxidising solutions and kept in moist CO_2 at 450°C. The last process can be carried out directly in the chromatograph by passing

†See the NIITEKhIM Information Bulletin No. 2, Moscow, 1972.

through it moist CO_2 instead of the carrier gas [195]. The high stability and complete chemical inertness of the resulting protective film have been noted. Teflon is widely used as a material for chromatographic columns, particularly for the analysis of xenon fluoride [183], the halogens and their binary compounds [196], inorganic halogen compounds [185], hydrogen sulphides, and many sulphur compounds [187].

The problems of the detection of reactive compounds have been partly considered by Brazhnikov [197], who noted that, when the application of gas chromatography is extended from the analysis of hydrocarbons to the analysis of inorganic and organic compounds with a high reactivity, a new approach is needed for the solution of the problem of the detection of these compounds, particularly when a high sensitivity must be ensured. The detection of such compounds frequently requires both universal and selective detectors, which must be made of corrosion-resistant materials. The protection of sensor elements requires particular attention.

The thermal conductivity detector was one of the first to be used for the analysis of reactive gaseous mixtures. Many corrosive inorganic acids, certain alkylated compounds, metal chlorides, etc, have been analysed with its aid. Thus the concentration of nitrogen dioxide in air with a detection threshold of 10^{-4} vol.% [189] and MeGaCl, Me_2AlCl, H_2, and CH_4 admixtures in trimethylgallium [198] have been determined and mixtures of chlorine with chlorine, uranium, bromine, and xenon fluorides (with a lower detection limit of 0.1 vol.%), halogens and their compounds [38,40,48,183,193,196,199,200], chlorosilanes and organochlorosilanes [52,201], inorganic chlorides, and organometallic compounds [160,182,202] have been analysed using a katharometer. In order to achieve the maximum sensitivity of the katharometer, helium or hydrogen are used as the carrier gas [202], although some investigators prefer air or Freon-12. [194]

The sensor elements of the detector are mainly made of a tungsten coil with a high mechanical strength. However, tungsten is readily oxidised by traces of oxygen at high filament temperatures and is susceptible to the influence of corrosive media. To improve the stability of the sensor elements, they are gold-plated or coated with Teflon [40,181,182,200]. Although the coating of the filament with Teflon lowers the sensitivity of the detector by a factor of approximately four, its high stability in corrosive media is thereby ensured. Gold plating does not have a significant influence on the sensitivity of the detector. Platinum coils react with fluorides and are also decomposed in the presence of aluminium, gallium, and zirconium chlorides [18]. Nickel wire sensor elements have been used in the detection of chlorine and bromine chlorides, hydrogen fluoride, and fluorine, the shell of the katharometer being made of stainless steel or glass [38,183,193,196,199]. In the determination of microimpurities in Me_3Ga at concentrations of 2×10^{-3} wt.%, the detector shell was made of tantalum [198]. Thus the use of the katharometer as a rule permits the chromatographic analysis of a wide variety of reactive compounds over a wide range of concentrations, provided that materials are suitably chosen for the manufacture of its elements and special protective precautions are taken.

However, the use of extremely expensive and scarce helium and the permanent contact between the sensor element and the compounds analysed preclude the improvement of the sensitivity of the analysis when the katharometer is employed. The density detector, in which nitrogen or argon are used as the carrier gas, is free from these disadvantages. Furthermore in the analysis of substances containing components with known molecular weights, the calibration plot for the chromatograph can be calculated, which greatly facilitates work with unstable compounds. According to the literature, the density detector has been used most successfully for the analysis of organochlorosilanes [180,203-205], a sensitivity of 3.1×10^3 mV ml mg^{-1} being achieved, which is approximately two orders of magnitude higher than the sensitivity of the katharometer using nitrogen as the carrier gas and an order of magnitude lower than for the katharometer with helium as the carrier gas. This detector is recommended as the most suitable for the analysis of organosilicon monomers [205].

An industrial chromatograph with a density detector has been developed [180] and used for the analysis of admixtures in a stream of organochlorosilanes at concentrations of 0.1%, the detection threshold being 10^{-3}–10^{-4} vol.%. A densitometer with argon as the carrier gas has also been used to detect HF, H_2O, and SiF_4,[206] ClF_3, AsF_5, Cl_2, Br_2F_5, etc. and in the determination of molecular weights of a number of compounds [186,193,207]; it has been employed [193] together with the katharometer [193], and in the analysis of mixtures of aluminium, gallium, niobium, and zirconium chlorides it replaced successfully the katharometer, the platinum coils of which disintegrated in the substances analysed [18].

Organochlorine and organofluorine compounds, alkylchlorosilanes, organometallic compounds, and other extremely reactive compounds [52,208-212] have been analysed with the aid of the flame-ionisation detector (FID), this type of detector being used in many instances in conjunction with selective detectors—thermionic and flame-photometric [170,213,214] (in the analysis of organometallic compounds and arsenic and phosphorus hydrides). For example, organochlorine impurities in HCl at concentrations of $(1–1.5) \times 10^{-4}$ wt.% have been determined with the aid of the flame-ionisation detector [172]; alkylchlorosilanes have been detected with a sensitivity threshold of 10^{-3} vol.%, which is lower by a factor of 40–50 than the sensitivity threshold of the katharometer with helium as a carrier gas in relation to these compounds [52]. However, it has been noted that the operation of the flame-ionisation detector in the analysis of alkylchlorosilanes is unreliable owing to the deposition of the decomposition products (SiO_2 and rust) on the electrodes.

Analysis of inorganic halogen compounds with the aid of the flame-ionisation detector is of definite interest [185]. The detector was designed in such a way that the carrier gas was introduced directly into the hydrogen flame, which significantly enhanced ionisation. The choice of the design and the selection of the positions of the electrodes ensured the optimum stability and sensitivity of the detector under the given conditions, amounting to 40.8–77.2 ml mVμ g^{-1} for halogens, which is much superior to the sensitivity with respect to benzene (1310 ml mVμ g^{-1}) but considerably inferior to the sensitivity of the densitometer (approximately 3 ml mVμ g^{-1}). The authors preferred the flame-ionisation detector to the katharometer and the densitometer because the latter could not be used in combination with capillary columns. Experience gained in use showed the high stability of the platinum electrodes of the flame-ionisation detector with respect to corrosion, while the burner was corroded after prolonged use. The high linear dynamic detection range (10^7–10^8), the low sensitivity to variations in the carrier gas flow rate, pressure, and temperature, the possibility of detecting many classes of compounds, the degradation of highly toxic substances on

combustion, and other advantages have to a large extent favoured the wide-scale employment of the flame-ionisation detector in chromatographic analysis. However, the deposition of degradation products in the detector in the analysis of unstable compounds, which increase the detector noise, and the lack of sensitivity to certain compounds (chlorosilanes, nitrogen oxides, ammonia, and other compounds without carbon or with a low carbon content) hinder its use for the analysis of the compounds considered in the present review.

In contrast to the katharometer, the densitometer, and the flame ionisation detector, the electron capture detector (ECD) and the thermionic detector are selective. For example, the electron capture detector has proved to be the most suitable for the analysis of organometallic compounds in small amounts (3×10^{-4} mole s^{-1}), inorganic chlorides[181], and volatile fluorine compounds[184]. 1.5×10^{-6}% $SiCl_4$, 10^{-7}% PCl_3 in $POCl_3$, and 10^{-4}% of $PSCl_3$ in PCl_3 have been determined with the aid of the electron capture detector. In the analysis of admixtures in compounds which do not capture electrons, the electron capture detector is combined with the katharometer[181]. Analysis of reactive gases requires the protection of radioactive sources. The source may be exposed to an additional stream of an inert gas[181] or a special closed source may be used[184].

The thermionic detector (TID) has been known mainly as the detector most sensitive to compounds containing halogens and (particularly) phosphorus. Organochlorine impurities in germanium tetrachloride have been determined with its aid, the sensitivity being 8×10^{-6}–5×10^{-4} mole %, which exceeds by 1–2 orders of magnitude the sensitivity of the flame-ionisation detector[50], and the impurities in trichlorosilane have been determined with a sensitivity of 1×10^{-4}–5×10^{-2} mole %[43]; the possibility of the chromatographic determination of organochlorosilanes with a sensitivity threshold of 10^{-5}% has been demonstrated[215]. Studies on the sensitivity of the thermionic detector, fitted in a "Khrom-35" chromatograph, to organochlorosilanes and alkylated tin and lead compounds showed that the sensitivity is a maximum when caesium salts are used as the ion source[216]. The detector readings are then positive in relation to silicon compounds and negative in relation to tin and lead compounds. The sensitivity of the thermionic detector giving positive readings diminishes in the sequence P > Si > Br > Cl, while for negative readings it increases in the sequence Pb < S < Sn. The thermionic detector has been used also in the analysis of boron compounds[217]. It has been established that, in order to achieve the stable operation of the detector, it is necessary to increase the temperature of the flame, which led to the employment of the refractory PbCl salt, since, under the conditions used in the analysis of boron compounds, the sensitivity of the detector depends much more on the hydrogen flow rate than, for example, in the case of phosphorus compounds.

The thermionic detector has been used in many cases in combination with other types of detector. When it was combined with the flame-ionisation detector, a sensitivity of 8×10^{-7}–2×10^{-10} g s^{-1} was achieved in the analysis of phosphorus and arsenic hydrides, organochlorine and organoboron compounds, and organic derivatives of tin and phosphorus[170]. Both detectors were mounted in the same shell made of glass. In the analysis of phosphates and nitrogen-containing phosphorus compounds, the joint employment of the thermionic and thermal conductivity detectors is recommended[191].

However, together with its high selectivity, mention must be made of the comparatively short linear range of the response of the thermionic detector (up to 10^3), which limits its scope for the determination of concentrations over a wide range. The most serious disadvantage of the sodium thermionic detector is its low stability, caused largely by the quality of the alkali metal salt, which evaporates in the burner flame; for this reason, surface ionisation thermionic detectors are preferable, despite their somewhat lower sensitivity.

The flame-photometric emission detector (PPD) is also selective, and its selectivity may be varied within fairly wide limits by altering the wavelength and the width of the transmission band. The problems of the application of such a detector in the detection of a wide variety of corrosive organic and inorganic compounds have been examined[197]. Mention may be made of the use of the flame-photometric detector for the analysis of boron hydrides with a detection limit of 0.7 ng[13,156] and also the possibility of determining sulphur compounds in amounts of 10^{-7}%.[187] Like other selective detectors, the flame-photometric detector can be usefully employed in combination with, for example, the flame-ionisation detector in the analysis of organic compounds of phosphorus, tin, lead, and certain nitrogen compounds[213,214,218].

The examples considered above demonstrate the wide scope of the applications of various detectors for the chromatographic analysis of a wide range of organic and inorganic compounds with high reactivities. The wide variety of requirements which must be met by the analytical method and the sensitivity of the analysis, the operational and design features of the apparatus, the wide variety of classes of compounds analysed, and the conditions used in the analyses preclude unambiguous recommendations in the present review concerning the usefulness of a particular detector in the analysis of a specific compound. The necessary choice and combination of the optimum separation and detection systems in each individual case enable the investigator to make the correct choice of the method for the solution of the problem facing him; this is possible only after a careful preliminary study of the apparatus and of the mechanisms of the reactions occurring during separation and possible side processes.

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