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Reaction-sorption Methods for the Concentration of Impurities in Their Gas-chromatographic Determination in Air

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The role of the reaction-sorption (chemical-sorption) method in the analysis of contaminants in air is examined, the physicochemical principles of the method are briefly described, and examples of their practical use for the identification and quantitative determination of harmful impurities in the atmosphere and in the air of the workplace in factories are presented. The review is based on studies published in 1972-1985.
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I. INTRODUCTION

The successful struggle against the contaminaton of air, water, and soil by harmful chemical compounds, mainly of anthropogenic origin, often depends on the development of effective methods for the monitoring of toxic chemicals, among which gas chromatography has quite justifiably received most attention, particularly in the analysis of volatile organic compounds.[1-5] The first studies on the gas-chromatographic determination of harmful substances in the atmosphere and in the air of the workplace in factories were published about 25 years ago and at the present time ~80% of all the determinations of organic compounds in air are made by this method.[2,3,5] The develoment of gas-chromatographic methods and the expansion of their applications have continued up to the present time[6-11] and combined or hybrid methods have been acquiring increasing importance.[3,4,6] In our view, the greatest advances in the development, improvement, unification, and wide-scale employment of chromatographic methods for the monitoring of contaminants in air can be expected on these lines.[1-4,12-14]

Together with the use of physical methods,[3,4,14] the combination of chemical and chromatographic methods has been used successfully in gas chromatography for the identification of the separated substances.[6] The chemical methods in gas chromatography are based on the use of the chromatographic separation of impurities in combination with chemical reactions of the eluate.[3,6,9] The simplicity and effectiveness of the chemical methods[6] have gained for them a well established place in the analytical chemistry of the contaminants of air, particularly in the selective gas-chromatographic determination of the most important (target) components of the contamination[3,9] and for the identification of minor components in complex mixtures of harmful substances.[3,10,11] Analytical reaction gas chromatography includes three methods: the separation method (chromatography), the method used to determine the compounds analysed (physicochemical detection), and the method for the chemical transformation of the compounds analysed.[6]

This review is devoted to the use of one of the most important versions of the gas-chromatographic analysis of impurities—the reaction-sorption method (RSM), which includes the concentration, identification, and quantitative determination of harmful substances in air.

II. THE APPLICATION OF REACTION-CHROMATOGRAPHIC METHODS IN THE DETERMINATION OF CONTAMINANTS IN AIR

The most important problem in the analytical chemistry of the contaminants in air is that of the correct and reliable identification of volatile toxic substances after their chromatographic separation.[3] The determination of the qualitative chemical composition of a sample of complex and multicomponent mixtures of different nature is known to be extremely difficult and the validity of the analysis depends on many factors and in the first place on the method used to identify the mixture components.[4,10,14]

The traditional methods for identification from the chromatographic retention characteristics of the impurities[14] (the method of additives, the use of pure substances, the application of logarithmic relations between the retention volume or index and the properties of the compound analysed, etc.) make it possible to achieve reliable results only in the analysis of mixtures of known or partly known composition or mixtures of substances of one homologous series (class, type).[2-4] In more complex cases, in the analysis of compounds of several types, these methods are as a rule relatively ineffective and either chromatographic samples on columns with stationary liquid phases of different polarity, or analysis with the aid of selective detectors, or reaction-chromatographic determination (identification) of impurities are used in order to obtain reliable results.[2,3,5]

However, the identification of chromatographic spectra obtained on columns with different types of packing involves highly significant difficulties and, when selective detectors are used (for example, an electron capture or flame ionisation detector), the information obtained is not always unambiguous owing to the lack of information about the sensitivity of these detectors for compounds of different classes.[3]

In all cases of the analysis of complex mixturs of impurities in air the reaction-chromatographic methods for the identification of impurities, which make it possible to achieve significantly more reliable results than the standard chromatographic procedures, are more effective.[2,3,5,10,11] In the analysis of mixtures of inorganic compounds it is much easier to identify the impurities than to elucidate the complex chromatographic spectra of organic substances, which as

a rule correspond to many isotypical compounds with similar properties.[3,4] In the determination of inorganic substances, one therefore is more likely to be concerned with the improvement of the detection characteristics, the reduction of the limits of detection of impurities, and the increase in the selectivity of the determinations against the background of other compounds in the sample accompanying the determination or interfering with the latter.[3,9]

One of the most effective and simplest reaction-chromatographic procedures for the identification of impurities is the subtraction (absorption) method.[6] Its principle consists in the absorption of individual compounds or separate groups (classes) of chemical substances in a reactor placed in the chromatograph thermostat before or after the chromatographic column.[6,8] The combination of the methods for the subtraction of impurities with subsequent gas-chromatographic analysis of the eluate with the aid of selective detectors[6,10,11] or the combination of the reaction-chromatographic methods with the usual gas-chromatographic analytical procedures[3,5,6,9] is even more effective.

However, one extremely significant disadvantage is characteristic of all the methods listed above. When all the impurities present in air are concentrated simultaneously in the trap with the sorbent, the subsequent identification of the compounds is made very much more difficult and in addition there is an appreciable change in the composition of the sample (and the results of the analysis are therefore distorted) as a result of the chemical reactions of the test substances on contact with the adsorbent[3,11,14] or in the extraction of the sample from the trap by the thermal desorption method.[8]

The fractionating sampling method, which makes it possible to avoid the above difficulties and significantly increases the reliability of the idenfitication of impurities, is therefore much more promising.[2,5,8,11–13] One way of solving this problem involves the use in gas chromatography of the method of the reaction-sorption concentration of impurities.

III. THE REACTION-SORPTION METHOD—A NEW VERSION OF THE PROCEDURE FOR THE CONCENTRATION OF IMPURITIES IN ANALYSIS

1. Concentration of Impurities on Solid Sorbents

Analysis of the literature in recent years,[1–13] devoted to the determination of contaminants in air, has shown that in all these publications special attention has been devoted to questions of sampling and concentration of microimpurities. This is not fortuitous. Sampling is one of the most difficult stages in the analytial procedure for the determination of impurities in air. The results of exact and careful analysis lose all significance when the sample is incorrectly taken and when the sampling procedure is invalid.[3] This is particularly relevant to the analysis of contaminants in air—a complex labile system containing a multiplicity of chemical compounds with low concentrations and subjected to the action of moisture, oxidants, radiation, etc.

Analytical chemists have nowadays concentrated attention on the problem of obtaining a representative sample of the contaminants in air, whose components differ markedly from one another in their chemical and physical properties and in their concentrations (from 10^{-4} to 10^{-7} wt.%).[3,9–11] This question is extemely important because, having entered the concentrator, the compounds of the sample pass to a completely diffierent state:[3,5,7,14] (1) the concentration of impurities increases appreciably (by a factor of 100–1000 or more); (2) substances with completely different chemical properties and concentrations (differing by factors of $10–10^8$), many of which are reactive, unstable, susceptible to oxidation, and tending to hydrolyse and to undergo other reactions, accumulate simultaneously in the trap with the sorbent; (3) the increase of the concentration of the impurities in the trap tends to increase the likelihood of chemical interactions and irreversible transformations of the sample components; (4) the active centres on the large surface area of the sorbent (and sometimes also the possible impurities in the sorbent, for example, metals) have a catalytic effect, accelerating these reactions; (5) during the enrichment of the sample on the sorbent, accompanying impurities are coadsorbed (competitively sorbed), which leads to anomalies in the saturation of the sorbent surface and the initial sample composition is distorted.

As a result of these processes, the concentrations of the impurities in the trap-concentrator with the sorbent become markedly differentiated. The adsorption of impurities takes place non-uniformly, as a result of which the quantitative composition of the concentrated impurities may differ greatly from their composition in air.[3,15,16] Furthermore, the chemical reactions of the sample in the trap alter its qualitative composition and distort the analytical results.[3,13,14]

Thus amines tend to interact specifically with free vinyl groups on the surface of Chromosorb 102 and Porapak Q.[17] The presence of traces of O_2 in the carrier gas (nitrogen) during the concentration of amine impurities from air and on raising the temperature of the sorbent in thermal desorption to 100 °C leads to the depolymerisation and oxidation of the sorbent.[18] As a result, false peaks ("artefacts") of aromatic ketones and other carbonyl compounds appear on the chromatograms, distorting the results of the identification of the impurity. The same sorbents interact vigorously with NO_2, forming NO at 25 °C, and, on raising the temperature (to 125 °C), NO and H_2O are formed with simultaneous nitration of the polymeric sorbents.[19]

The sorption capacities of Tenax and Amberlite HAD-2 in relation to n-pentane, benzene, acetone, 2-propanol, and acetonitrile change significantly as a result of the nitration and sulphonation of the sorbent by the chemically active components of industrial waste (sulphur and nitrogen oxides), the maximum change in the sorbent capacity having been noted for polar sorbates.[20] All reactive gases (Cl_2, HCl, HBr, ClF_3, F_2, HF, ClO_2, O_3, SO_2, SO_3, NO_2, etc.) behave similarly, interacting with one another and with almost all known sorbents and connecting tubes of the chromatographic system.[21]

In the course of the trapping of smoke gases from air, Tenax is gradually decomposed by NO_2 and SO_2 with formation of 2,6-diphenyl-*p*-benzoquinone.[22] On sorbents such as activated charcoal, Al_2O_3, silica gel, Florisil, and Tenax, nitrosamines, which are initially absent from air, are formed when air is passed through them.[23] When impurities from air containing olefinic hydrocarbons and free halogens are concentrated on the surface of Tenax, Amberlites, and carbonaceous sorbents, chemical reactions take place (for example, the interaction of Cl_2 with but-2-ene or cyclohexene) and lead to the appearance in the mixture analysed of halogenohydrocarbons which were previously absent from it.[24]

The possibility of the appearance of false peaks during the sampling process is illustrated by the data in Table 1. By concentrating ethylbenzene, 1-hydroxyethylbenzene, acetophenone, 1-octanol, and 1-octanal from ozonised air (the O_3 content was 1.0–1.3 mg m^3) on Tenax, it was shown[25] that at room temperature these compounds are not oxidised in the column with Tenax. However, the simultaneous presence of

oxidants (O_3, NO_2, SO_2, Cl_2) and water vapour in air leads to the decomposition of Tenax and of the toluene, styrene, and cyclohexane microimpurities concentrated on it.[26] Several deuteriated oxidation, halogenation, and nitrosation products (three chlorostyrene isomers, benzaldehyde, and dimethylnitrosamine)[27] as well as acetophenone, phenol, α-hydroxyacetophenone, and epoxyethane[26] have been identified by chromato-mass-spectrometry. When analogous experiments were carried out with the preliminary passage of the air analysed through a glass filter treated with a 1% or 10% $Na_2S_2O_3$ solution, the content of the halogenation and oxidation products in the substances collected on the filter was sharply reduced.[26,27]

Table 1. The formation of 1,2-dichlorocyclohexane in the concentration of cyclohexenes and chlorine on Tenax.[24]

Inorganic contaminants*				Cyclohexene*	1,2-Dichlorocyclohexane**
O_3	NO	NO_2	Cl_2		
0	0	0	104	90	0
100	0	0	0	90	0
0	300	350	104	90	0
160	0	0	104	818	110
0	0	0	104	818	100
180	0	0	104	818	120
0	0	0	104	818	110
0	100	0	104	818	100
100	0	0	0	818	0
720	0	0	104	818	120

*The concentrations 10^7c (wt.%) are quoted.
**The amount of 1,2-dichlorocyclohexane formed (in ng) is indicated.

When styrene is concentrated by sorption in a tube with activated charcoal, there is a potential risk of a change in the initial concentration of styrene as a result of catalytic reactions.[28] During the thermal desorption of C_4–C_5 light hydrocarbons concentrated on activated charcoal, some of them isomerise at 150–250 °C, giving rise to compounds previously absent from air—*cis*-but-2-ene and *cis*-pent-2-ene.[7]

The coadsorption of impurities in the trap with the sorbent also alters the composition of the sample. The study of the quantitative characteristics of the sorption of benzene on graphitised carbon black and of their influence on the relative retention volumes of n-pentane, acetone, nitromethane, propanol, and tetrahydrofuran showed that the coadsorption of benzene can lead (depending on the degree of surface coverage of the carbon black by benzene) both to an increase (for a surface coverage of 0.3–0.5) and a decrease (for a surface coverage of less than 0.3) of the retention parameters of the impurities.[16] This is illustrated in Fig.1, which shows that the degree of sorption of acetone by Carbopack C is reduced as the free surface of the adsorbent is occupied by the benzene molecules.

Water vapour is a particularly strong competitor towards the sorption of organic impurities.[15] According to current ideas,[29] the principal cause of the strong adsorption of H_2O molecules on carbonaceous sorbents is the primary adsorption centres, which are present on the surfaces of the walls of the adsorbent pores and are capable of forming hydrogen bonds. The strong sorption of H_2O and CO_2 [15] alters the sorption of the other impurities and leads to anomalies in the process involving their concentration.[3] The polar H_2O molecules can displace the previously concentrated organic impurities from the sorbent, can dissolve them, and can alter the dynamics and kinetics of the sorption of subsequent compounds in the trap. When the weight fraction of H_2O in the activated charcoal is at the level of 0.02, the error of the determination is low,[15] but in the presence of an H_2O weight fraction of 0.15 it amounts to 45% for ethanol and increases by 6–12% for butanol and acetone.

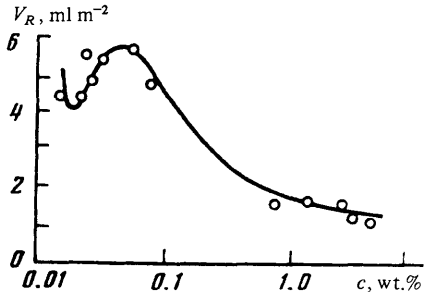


Figure 1. Dependence of the retention volume (V_R) of acetone on the benzene concentration (c) in the vapour phase on Carbopack C at 10 °C.[16]

Sulphates and nitrates can be formed in the preparation of the sample for analysis as a result of the reactions of some of the trapped substances with the sulphur- and nitrogen-containing gaseous oxides and acid vapours (SO_2, NO_2, HNO_3, etc.) present in the matrix. The above artefacts, associated with side reactions on the surfaces of sorbents, can cause an error in the determination of the impurities amounting to 8–11 mg m^{-3}.[8]

2. The Reaction-Sorption Method for the Concentration of Impurities

The reaction-sorption method (RSM) makes it possible to prevent the chemical interaction of the sample components during the concentration process and to reduce to a minimum the influence of coadsorption.[3,30,31] The essential feature of the RSM involves the preliminary removal of the intefering impurities during the sampling of air with the aid of a reactor containing sorbents or chemical reagents and placed before the concentrator. As a result of this, only the target components enter the trap with the sorbent and the method exhibits a high selectivity, which can vary within wide limits when the reactor packing is altered.[3,30] The fractionation of the compounds in the sample before their concentration not only improves the kinetics and dynamics of the sorption of the target components but also creates conditions for their more reliable identification because most of the sample components (approximately 70–80%) remain in the pre-column-reactor.

Preliminary absorption of compound interfering with analysis had already been used earlier to increase the selectivity of the determination of the toxic impurities in the air of the working zone in industrial undertakings by a linear colour [comparison?] method.[30] The analysis was carried out via a

two-step scheme: chemical separation and detection (Fig.2, Scheme *A*). The colour reactions of the impurities analysed with appropriate reagents (colorimetric and linear colour [comparison?] methods).

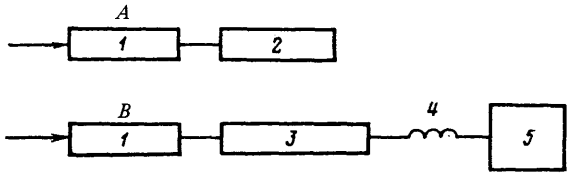


Figure 2. RSM schemes for the analysis of impurities: 1) column with sorbents and chemical reagents (pre-column-reactor); 2) column with indicator powder; 3) concentration column with sorbent; 4) chromatographic column; 5) chromatographic detector.

In the chemical-sorption versions of the concentration and gas-chromatographic determination of impurities,[30,31] it is useful to employ the following analytical scheme: chemical (or physical) separation—concentration—chromatographic separation—detection (Fig.2, Scheme *B*). In this version the selectivity of the separation of impurities (the overall selectivity of the separation in the pre-column and in the chromatographic column) is much higher than in the first version (Scheme *A* in Fig.2). The limit of the detection in analysis using Scheme *B* is usually lower by 3–4 orders of magnitude than in the linear colour method for the determination of impurities in air.[30]

On the other hand, the reaction-sorption method for the concentration of impurities differs significantly from the subtraction method employed in gas chromatography[31] and presupposes the selective absorption of the non-target components in combination with the subsequent concentration and chromatographic determination of the target components.[3,30] The reaction-sorption concentration method belongs to a new group of hybrid methods and is free from many of the disadvantages characteristic of the traditional procedures for the trapping of impurities from contaminated air.

We shall consider the possibilities of the RSM in its application to the solution of certain practical problems in the analysis of contaminated air.

3. Increase in the Reliability of the Determination (Decrease of the Probability of the Chemical Interaction of the Sample Components)

The extensive possibilities for the variation of the composition of the sorbents and chemical reagents in the packing within the fore-column-reactor make it possible to use RSM in solving a number of problems in the determination of small amounts of reactive chemical impurities in air (Table 2).

(a) Determination of corrosive gases. Apart from their interaction with the packing of the chromatographic column and their absorption by the connecting tubes in the chromatograph, reactive gases frequently react with one another (particularly when they are concentrated on sorbents), which hinders their gas-chromatographic determination or makes it impossible.[21] An example may be provided by the reactions in the Cl_2–HCl–ClO_2–O_2–NO_2 system, characterising the contamination of air in undertakings where inorganic syntheses are carried out.[38]

Table 2. Certain versions of the determination of impurities in air by the RSM method.

Compounds analysed	Sorbent in precolumn	Impurities absorbed	Target components	Refs.
SF_6, SF_4, SF_2, HF, S_2F_2, SOF_2, COF_2, SO_2F_2	NaF	F_2, HF	SF_4	[32]
Cl_2, ClO_2, HCl, O_2, NO_2	glass fibre, −78° C	ClO_2	Cl_2, NO_2	[21]
N_2O, NO, NO_2, N_2O_4	13X molecular sieve	N_2O, NO_2, N_2O_4	NO	[33, 34]
CO, CO_2, CH_4, light hydrocarbons	13X zeolite, Ascarite, activated charcoal, 0 °C	CO_2, CH_4, light hydrocarbons	CO	[35]
Olefins, NO_2, paraffins, Cl_2	$Na_2S_2O_3$	NO_2, Cl_2	hydrocarbons	[36]
Organic and inorganic acids, aldehydes, ketones	Na_2CO_3	acids	ketones, aldehydes	[36]

When the concentration process is carried out on solid sorbents (silica gas, graphitised carbon black, porous Teflon, etc.), the components of this mixture interact even at ordinary temperatures with formation of more toxic but less reactive substances.[37,38] In many cases the principal (overall) reaction is that of chlorine and nitrogen oxides:

$$ClO_2+3NO_2 \rightarrow NO_2Cl+N_2O_5. \qquad (1)$$

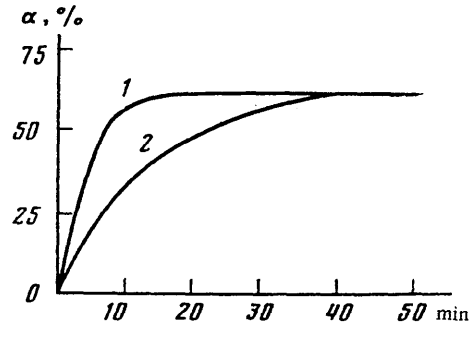


Figure 3. Dependence of the degree of conversion of NO_2 on the initial NO_2 : ClO_2 ratio; NO_2 : ClO_2 ratio: 1) 3 : 1; 2) 1 : 1.[38]

Some idea about the process kinetics can be provided by the plot of the dependence of the degree of conversion of NO_2 on the initial concentrations of the oxides (Fig.3). When air is passed through a tube with the sorbent (for example, graphitised carbon black) at 20–35 °C, the degree of reaction of ClO_2 with NO_2 is not less than 50% (Fig.3). If account is taken also of the numerous side reactions[38] and

of the decomposition of the concentrated sample in the thermal desorption process at 150 °C,[37,38] i.e.

$$2NO_2Cl \rightarrow 2NO_2 + Cl_2 + O_2 \qquad (2)$$

then it becomes evident that a mixture of corrosive gases having a composition different from that in the initial air enters the chromatographic column (Fig.4); as a result of the different reactions in the sample, the amount of NO_2 and ClO_2 diminishes and that of Cl_2 increases. A pre-column containing glass wool and cooled with dry ice traps the ClO_2 impurity from the mixture analysed before chromatography. After this, the gas-chromatographic determination becomes significantly more accurate—the standard deviations for Cl_2, NO_2, and ClO_2 decrease by a factor of 2–3.[38]

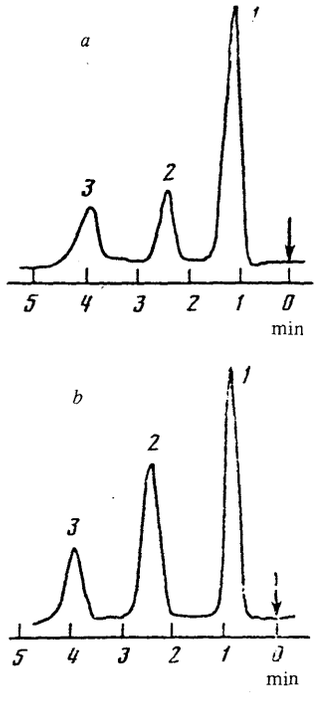


Figure 4. Chromatographic separation of the Cl_2, ClO_2, and NO_2 impurities:[38] *a*) in the usual method; *b*) in the method using a pre-column; 1) Cl_2; 2) NO_2; 3) ClO_2.

(b) Nitrogen oxides. The direct determination of NO, NO_2, N_2O_4, and N_2O is difficult as a consequence of the higher reactivity of these gases.[21] The method of reaction gas chromatography (RGC), which consists in the conversion of nitrogen oxides into organic derivatives[34] requires the preliminary oxidation of NO to NO_2 [39] with subsequent estimation of the NO content from the difference between two determinations (NO_2 and the sum of NO and NO_2). The individual determination of NO in a mixture of nitrogen oxides† which have similar properties (and are therefore difficult to distinguish) is feasible when the mixtures are concentrated by the RSM.[33,40]

The determination of NO by the RGC method in conjunction with the RSM consists in passing the air to be analysed through a pre-column (16 cm × 5 mm) containing the 13X molecular sieve (0.5–0.25 mm fraction) subjected to a preliminary heat treatment in the course of 4 h in a stream of dry nitrogen at 350 °C. This pre-chromatographic reactor absorbs 95–97% of the admixture of N_2O, NO_2, and N_2O_4, but does allow NO to go through; the loss of NO (after the preliminary conditioning of the fore-column with a mixture of nitrogen oxides, in which the concentration of NO is 10 mg m^{-3}, for 30 min) is not more than 0.5–1.2 wt.%.

When this analytical scheme is employed, the NO content in the mixture of nitrogen oxides is determined not from the difference between the two measurements but directly (after the necessary procedure involving the oxidation of NO to NO_2 by H_2O_2) in the form of a derivative (nitrobenzene) obtained by the reaction of NO_2 with benzene in the presence of concentrated sulphuric acid.[39] The limit of detection of nitrogen oxides by this method is ~10^{-6} wt.% with a relative standard deviation of 0.30. Fig.5 illustrates the chromatogram for the determination of NO (in the form of NO_2) in the exhaust gases from diesel engines, obtained using the above procedure and the RSM.[33,40]



Figure 5. Reaction-chromatographic determination of NO_2 in the exhaust gases of a diesel engine after the conversion of NO_2 into nitrobenzene[33] (glass 1.5 m × 4 mm column with 15% of Apiezon L on Chromaton N; electron capture detector; column temperature 120 °C; detector temperature 275 °C): 1) nitrobenzene; NO_2 concentration in air 8 mg m^{-3}.

(c) Sulphur fluorides. Analysis of a complex mixture of corrosive sulphur fluorides (SF_6, SF_4, S_2F_2, SO_2F_2, SOF_2, HF, and F_2) is made very difficult by the active interaction of the extremely reactive HF and F_2 with all sorbents and constructional materials of chromatographs.[21,40] This interaction results in a low reproducibility of the determination of the target component—sulphur tetrafluoride, whose toxicity is higher than that of phosgene.[32] The content of the SF_4 to be determined depends on the volume of the sample injected, the presence of moisture, the ratio of the components in the mixture of fluorides, and the amount of HF and F_2. The relative standard deviation then varies within wide limits and can be between 0.40 and 0.8.

† The separate determination of NO and NO_2 is of fundamental importance for industrial labour hygiene.

Concentration of the fluoride impurities by the RSM made it possible to eliminate the influence of the reactive F_2 and HF. The air analysed is first passed through a pre-column (4 cm × 4 mm) with sodium fluoride (0.5–0.25 mm fraction) and the fluoride impurities are then concentrated in a trap with Porapak Q.[40] The pre-column retains almost 100% of the admixture of the corrosive F_2 and HF, but does not absorb SF_4 at low concentrations (0.1–1.0 mg m^{-3}). The degree of absorption of sulphur tetrafluoride by the pre-column is less than 0.4%.[32] The chromatogram of the mixture of sulphur fluorides formed in the air of a foundry during smelting in a sulphur hexafluoride atmosphere is presented in Fig.6. Concentration of the fluoride impurities by the RSM makes it possible to determine small amounts of SF_4 (the limit of detection is 0.05 μg) with a relative stnadard deviation of 0.22.[32,40]

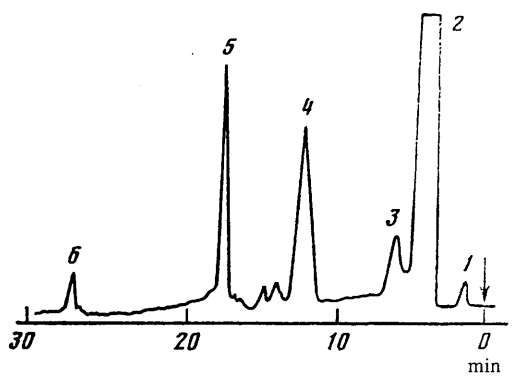


Figure 6. Chromatogram of sulphur hexafluoride and admixtures of lower sulphur fluorides on a 3 m × 4 mm stainless steel column with Porapak Q at 50 °C after the RSM removal of F_2 and HF from the mixture:[32] 1) carbon tetrafluoride; 2) sulphur hexafluoride; 3) sulphur monofluoride; 4) sulphur tetrafluoride; 5) sulphuryl fluoride; 6) thionyl fluoride.

(d) Hydrocarbons. It is much more difficult to discover the cause of the change in the composition of the impurities in air to be analysed in the determination of organic compounds (chemical interaction with the sorbent, coadsorption, polymerisation reactions, etc.) than in the determination of reactive inorganic gases, where chemical interaction usually predominates.[3,40] In the study of the processes involving the sorption (concentration) of organic impurities on solid sorbents with a high surface area, such changes are most clearly manifested in the thermal desorption of the sample from the sorbent, whereupon the concentrated impurities undergo thermal degradation and isomerisation reactions.[3,7,31] This factor becomes evident when the RSM concentration of the C_5–C_7 alkanes, isopentane, and hex-1-ene impurities in a trap with activated BAU charcoal is considered (Table 3).

Table 3 shows that the RSM concentration procedure makes it possible to obtain much more accurate isopentane contents than under the conditions of the traditional concentration of the hydrocarbon impurities on charcoal with subsequent thermal desorption. This finding can be accounted for by the isomerisation of the n-pentane, isopentane, and hex-1-ene impurities at the thermal desorption temperature (200 °C), which results in the formation of *cis*-but-2-ene and *cis*-pent-2-ene.[7]

Table 3. The reaction-sorption concentration* of isopentane in the presence of low-boiling hydrocarbons**.[36]

c_0	GC		GC-RSM	
	S	$c \pm \delta$	S	$c \pm \delta$
52	26	70±27	12	55±13
64	34	82±36	15	70±16
80	38	93±40	20	75±21
91	40	110±42	22	88±23
102	56	120±59	25	104±26

Notation: n is the number of replicate determinations ($n = 6$), c_0 the initial isopentane concentration (mg m^{-3}), c the arithmetical mean isopentane concentration for n replicate determinations found in the presence of admixtures of other hydrocarbons (mg m^{-3}), S the standard deviation (mg m^{-3}), $c \pm \delta$ the confidence interval of the concentration c (mg m^{-3}), δ the accuracy of the direct measurement of c (for a small number of measurements, $\delta = tS/n^{2/3}$, where t is the Student statistic).

*The pre-column with 5A molecular sieve absorbs hydrocarbons having the normal structure.

**The values of S and $c \pm \delta$ (fiducial probability $P = 95\%$), obtained by the traditional gas-chromatographic method (GC) and the method involving the RSM concentration procedure (GC–RSM) are quoted).

4. Reduction of the Influence of the Coadsorption of Impurities

The composition of the sample of organic impurities to be concentrated is usually distorted by the coadsorption of impurities in the trap-concentrator with the sorbent.[3,7,41] This process, which influences the validity of the analysis, takes place invariably when components of any mixtures of harmful substances are extracted from air.[3]

In order to explain the nature and mechanism of coadsorption and its influence on the parameters of the impurity sorption (concentration) process on sorbents, it is necessary to examine the behaviour of impurities in the sorption–desorption system.

(a) Sorption dynamics. In the concentrator containing the sorbent, the impurities to be analysed undergo frontal enrichment. Their concentration in the gas then usually diminishes sharply as air passes through the layer of sorbent. The end of the operation of the reactor (its becoming "spent") is assumed to be the instant of the appearance of the test substance (substances) beyond the layer of sorbent—to so-called "breakthrough".# Impurities are distributed in the sorbent layer in accordance with their adsorption isotherms.[42]

In analytical practice "breakthrough" is defined as the appearance of the impurities to be analysed beyond the sorbent layer, their concentration amounting to 5 or 10% of the initial concentration of the harmful substances in air.[5,41]

The maximum operating time of the trap with the sorbent (the time before breakthrough) τ can be determined from the Shilov equation[42,43]

$$\tau = KL - \tau_0, \quad (3)$$

where K is the coefficient of the protective action of the layer, L the length of the sorbent layer, and τ_0 the time to the end of protective action by the layer. The coefficient of protective action by the layer is defined by the expression

$$K = a_0/\omega c_0, \quad (4)$$

where a_0 is the equilibrium static activity, ω the flow rate, and c_0 the initial concentration of impurities in air.

The Shilov equation can be also presented in the following form (the Mecklenburg equation):

$$\tau = K(L - h). \quad (5)$$

It is assumed that only the adsorbent layer with the length $L-h$ is fully saturated while the layer whose length is h remains unsaturated. The graphical representation of this layer is illustrated in Fig.7. The length of the unsaturated or unused layer h is determined from the intercept on the abscissa axis obtained when the straight line B (dashed line) is produced.[43]

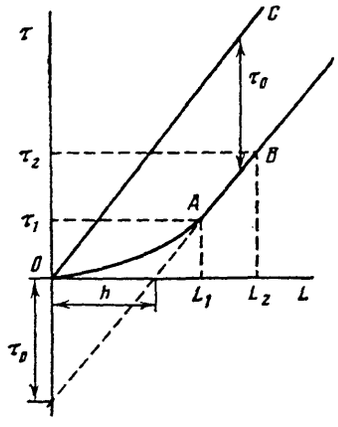


Figure 7. Dependence of the sorption time τ on the length of the sorbent bed L:[43] OC straight line—theoretical dependence of the sorption time on the length of the absorber bed for an infinitely high rate of sorption; OAB curve—actual dependence of the sorption time on the length of the absorber bed.

On comparing the Shilov and Mecklenburg equations (3) and (5), it is possible to find the relation between the loss of the time of protective action τ_0 and the length of the unused sorbent layer h:

$$\tau_0 = Kh. \quad (6)$$

During the RSM concentration process in the pre-column, all (or most of) the accompanying impurities are removed (adsorbed), which entails a change in the sorption dynamics of the target sample components on the sorbent in the trap. It follows from Eqn.(6) that Fig.7 that a decrease of h leads to a decrease of τ_0. The concentrator with the sorbent located beyond the pre-column therefore works more effectively and its sorption capacity with respect to the target components increases.

(b) Coadsorption dynamics. The impurity adsorption processes in the trap with the sorbent and the influence of the sorption of the accompanying impurities on the adsorption of the target components can be represented by several equations analogous to the equation of the Langmuir adsorption isotherm.[3,42]

In the case of the simultaneous adsorption of the target component (whose concentration in air is designated by c_1) and of the accompanying impurities (concentrations c_i), the adsorption of the target component can be represented by the following equation:[36]

$$a_1 = b_1 c_1 N \Big/ \left[1 + \sum_{i=1}^{m} \frac{b_i c_i}{K_i}\right], \quad (7)$$

where m is the number of impurities, N the maximum possible number of active centres per unit area of the adsorbent, K_i the specific degree of saturation of the active centre of the sorbent by the test substance, and b_1 the adsorption coefficient. Eqn.(7) can also be written in the following way:

$$a_1 = b_1 c_1 N \Big/ \left[1 + \frac{b_1 c_1}{K_1} + \sum_{i=2}^{m} \frac{b_i c_i}{K_i}\right]. \quad (8)$$

In this equation the term $\sum_{i=2}^{m} b_i c_i / K_i$, which determines the coadsorption of admixtures, significantly reduces the degree of adsorption of the main substance, impairing the degree of its concentration and interfering with the formation of a representative sample. This leads to systematic errors in the determination of microamounts of harmful substances in air, which it is virtually impossible to obviate in the usual version of analysis.[3,36] The employment of a pre-column enables one to increase appreciably the efficiency of the concentration of the target impurity, whose relative concentration increases in the course of the RSM concentration process to a significantly greater extent than in the usual version of the concentration procedure on sorbents. This factor creates preconditions for increasing the degree of enrichment of the sample, for reducing the detection limit for the target components (other analytical conditions being equal), and for the preparation of a representative sample of the impurities in air.[3,36,49]

(c) Decrease of the degree of coadsorption. The influence of coadsorption can be so great that the losses of the target component during the concentration of impurities can amount to 20–50%, which is 7–8 times greater than the losses due to the incomplete desorption of the impurities from the sorbent in the extraction of individual compounds from air.[3] The usual version of the concentration from air of small amounts of vinyl chloride in the presence of admixtures of chlorine-containing hydrocarbons which accompany it under real conditions (overall concentration 110 mg m^{-3}) may serve as an example. At a vinyl chloride concentration of 10 mg m^{-3}, a temperature of 20 °C, and for an air flow rate of 0.4 litre min^{-1}, breakthrough occurs after 40 min, while in the presence of impurities the time before breakthrough is reduced to 24 min. The losses of vinyl chloride in the concentration process change correspondingly from 6.2% in the concentration of vinyl chloride alone to 44% when vinyl chloride is concentrated in the presence of admixtures of chlorine-containing hydrocarbons.[49]

The coadsorption of admixtures of other organic compounds, which frequently accompany vinyl chloride in air from the workplace involved in the processing of polymers based on poly(vinyl chloride),[3,50,51] can reduce to an even greater extent the degree of adsorption of the monomer impurity by the adsorbent than halogen-containing compounds (Fig.8).

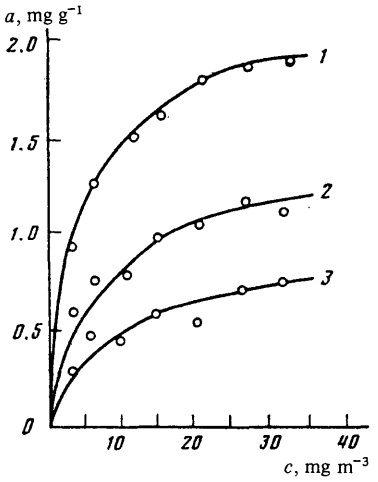


Figure 8. The influence of the coadsorption of accompanying admixtures (propene, methanol, acetone, acetaldehyde, and tetrachloroethylene) on the efficiency of the sorption of vinyl chloride by activated charcoal:[50] impurities: 1) vinyl chloride (adsorption isotherm); 2) vinyl chloride + admixtures (1 : 1); 3) vinyl chloride + admixtures (1 : 8); a = amount of vinyl chloride adsorbed by the charcoal; c = concentration of impurities.

The use of a pre-column in all the cases enumerated above gives rise to a positive result, increasing the time (volume) before the breakthrough of the target components of the sample, increasing the sorption capacity of the concentrator with the sorbent, and tending to reduce the limit of detection of the impurities. This can be illustrated by experimental data for the sorption and RSM concentration of organic impurities of different nature in a trap containing an activated charcoal (Tables 4–6).

A consequence of the increase in the volume before the breakthrough of the test substances was the corresponding increase (by a factor of 2–3) of the sorption capacity of the sorbent with respect to the target components (Table 5). The effectiveness of the sorption in the concentrator with BAU charcoal–pre-column system was compared with the analogous data calculated from the results of sorption experiments for individual compounds on the above adsorbent using literature data.[3,5,7,13,44–48] The sorption capacity was calculated from the results of the chromatography of the test mixtures, taking into account the instant of breakthrough, or was determined by a direct method involving the weighing of the tube containing the charcoal before passing the air sample through it and after breakthrough.

Tables 4 and 5 show that the removal of the accompanying admixtures by the pre-column (the sorption characteristics were calculated for each compound quoted in the Table on the assumption that all the remaining compounds are accompanying admixtures) makes it possible to avoid coadsorption and to increase the efficiency with which the target components are trapped.

Table 4. The change in quantity before breakthrough* using the RSM concentration of impurities on activated charcoal.[3,36]

Compound	c, mg m^{-3}	PDK***, mg m^{-3}	V_{br}, litre/100 mg of charcoal		
			without pre-column	with pre-column	from data in Refs. 44–48**
Benzene	100	5	30	53	42
Toluene	50	50	12	20	23.1
Hexane	100	100	14	35	33
Ethyl methyl ketone	100	200	3	8.8	8.2
Ethanol	1000	1000	4.5	11	3—25
Tetrachloroethylene	100	10	8	24	33.2
Triethylamine	100	10	4	8	6.6
Dipropyl sulphide	100	50	12	20	22

*The volume before breakthrough V_{br} was determined for individual substances in the presence of the accompanying admixtures.

**The values of V_{br} used in the table were selected from the published literature data[44–48] subject to the requirement that the experimental conditions under which all the tabulated data were obtained are similar.[36]

***Transliterated Russian abbreviation which the authors do not define. Its significance is obscure (Ed.of Translation).

Table 5. The sorption capacity of the concentration tube containing BAU activated charcoal in the trapping of organic vapours from air.[36,49,51]

Compound	Sorption capacity, mg/g of sorbent		
	without pre-column	with pre-column	according to data in Refs. 7, 13, and 45–48
Benzene	30	53	60
Toluene	80	210	280
Hexane	18	35	42
Ethyl methyl ketone	36	75	90
Ethanol	15	35	42
Tetrachloroethylene	26	78	100
Triethylamine	20	38	35.5
Dipropyl sulphide	64	170	156

The somewhat greater sorbent capacity given in the literature can be accounted for by the fact that the values quoted in the literature were calculated for pure individual substances, while a pre-column does not remove entirely the accompanying admixtures. This influences the residual sorption (coadsorption), inducing some decrease in the degree of sorption of the target components (approximately by 15–25%).

The increase in the sensitivity of the determination is a consequence of the more effective sorption of admixtures of the target components in the RSM concentration process. Table 6 shows that the reaction-sorption concentration process makes it possible to reduce the limit of detection of principal classes of organic impurities by a factor of ~2–3.

An important result of the use of the RSM, associated with the elimination of the coadsorption of admixtures, is the improvement of virtually all the metrological characteristics of the method. This can be illustrated by the data in Table 7

which presents the results of the determination of small amounts of the vinyl chloride impurity. Comparison of the results the determination of this gas by two different methods (gas chromatography and gas chromatography + RSM) shows that the latter should be preferred (Table 7).

Table 6. The sensitivity of the determination (α) of toxic impurities.[3,36,49,51]

Compound	Sensitivity of determination*, mg m^{-3}	
	α_1	α_2
Aromatic hydrocarbons	0.10	0.03
Paraffinic hydrocarbons	0.10	0.06
Halogenohydrocarbons	0.50	0.25
Oxygen-containing organic substances	0.80	0.40
Organosulphur compounds	0.60	0.40
Aromatic amines	0.20	0.10

*α_1 and α_2 are the average detection limits in the usual version of the chromatographic analysis with the aid of a flame-ionisation detector and in the RSM analysis respectively.

Table 7. The validity of the analytical results in the determination of vinyl chloride*.[52]

GC			GC-RSM		
s	s_r	$c\pm\delta$	s	s_r	$c\pm\delta$
0.28	0.40	0.70±0.20	0.17	0.18	0.98±0.12
0.16	0.36	0.44±0.12	0.56	0.14	0.56±0.10
0.05	0.45	0.11±0.04	0.03	0.30	0.10±0.02

Notation: m is the sample size (μl) and S_r the relative standard deviation; for the significance of the remaining symbols, see Table 3.
*The test was carried out by comparing the results obtained using the RSM with those obtained in the usual version of gas chromatography (for $n = 10$ and $P = 95\%$; $m = 10$ μl).

5. Improvement of the Chromatographic Separation

An important aspect of the use of the RSM in the improvement of the chromatographic separation of impurities. The absorption in the pre-column of the accompanying admixtures increases the efficiency of the separation of the target components from other compounds in the sample. Apart from the possibility of securing more reliable information about the composition of the compounds to be analysed, this procedure increases the accuracy of the determination of the target components.[3,34,36]

The direct (without the preliminary concentration of the impurities) gas-chromatographic determination of small amounts of CO, one of the principal contaminants in the air from the workplace, may serve as an example.[35] The absorption of the C_1–C_3 light hydrocarbons, O_2, N_2, CO_2, and water vapour, which interfere with the determination of CO, in a pre-column with Ascarite, 13X molecular sieve, and activated charcoal at 0 °C makes it possible to achieve a satisfactory separation of CO from CH_4 and other admixtures on an analytical column with 5A zeolite and to increase the accuracy of the determination of the concentration of CO. For CO concentrations in the range 20–50 mg m^{-3}, the use of the RSM permits the reduction of the error of the determination from 18–20% to 12%. A fore-column containing a layer of Chromosorb W impregnated with a 0.1 M solution of $SnCl_2$ (for the absorption of H_2S) and a layer of activated charcoal (210 mg) for the adsorption of oxidisable hydrocarbons is suitable for an analogous purpose.[53] In order to fractionate the mixture of reactive gases in the determination of SO_2 in air, the nitrogen oxides, which interfere with the determination, are absorbed in an absorber containing a 0.6% solution of sulphamic acid, while H_2S is removed in a pre-column with an aqueous solution of $Pb(CH_3COO)_2$.[54]

Different versions of the RSM concentration process have been used to improve the chromatographic separation of impurities comprising hydrocarbons,[49] halogenohydrocarbons, and oxygen-containing organic compounds,[36] as well as reactive inorganic gases[34] and various inorganic compounds.[40] In order to reduce the error in the determination of low concentrations of a hydrazine and asymmetric dimethylhydrazine aerosol, the admixtures of ethyl acetate, 2-furoaldehyde, and their derivatives, which interfere with the analysis, were first removed from the mixture (in the course of the extraction of the above impurities from air) by passing the mixture through a pre-column.[55]

6. The Removal of Moisture

One of the important conditions for the prevention of loss in mixtures of air contaminants to be analysed, associated with coadsorption, is the removal of moisture in the course of the extraction of the impurities from air.[3,21,34] This problem has several different solutions,[34,40] the best of which involves the application of reaction-sorption systems.[30,31] The use of the RSM concentration process, which provides for the removal of H_2O in pre-columns with zeolites, does not affect other compounds in the sample and does not distort the composition of the latter.[3]

In the automatic determination of ultramicroconcentrations of CO in the troposphere with the aid of an He-ionisation detector, an additional short column with the 5A zeolite, which is periodically regenerated, is placed before the analytical column in order to separate the interfering impurities (H_2, O_2, N_2, CO_2, and H_2O) from the bulk.[56] Another version of the RSM is based on the employment of a short column (7 cm × 4 mm) with 3A zeolite activated for several hours in a stream of dry nitrogen at 300 °C.[57] With the exception of CH_3OH, this pre-column vigorously retains H_2O, but does not sorb organic impurities. The 3A molecular sieve can therefore be regarded as the ideal drying agent for the determination of toxic microimpurities in air.[3,34,57]

IV. IDENTIFICATION OF IMPURITIES IN THE REACTION-SORPTION CONCENTRATION METHOD

The main problem in the analytical chemistry of air contaminants is that of the reliable identification of harmful impurities in complex mixtures of air contaminants.[3,30] The traditional scheme for the gas-chromatographic analysis of contaminated air presupposes the absorption of all the chemical compounds present in air on solid sorbents, the extraction of the concentrated impurity by a solvent, and the gas-chromatographic separation and identification of the sample components.[2,3] All compounds, without exception, extracted from air are detected on the chromatogram. This

factor hinders greatly the identification of impurities, since in the general case one has to deal with mixtures of impurities belonging to different classes.[4,5-7]

The difficulty of securing reliable information about the composition of complex mixtures in harmful organic substances§ is due to the insignificant differences between the retention characteristics of the impurities (for example, the Kovac indices).[3,30] The use of a kind of "chemical filter" (such as the RSM) presupposes the successive removal from the mixture to be analysed of specific classes of organic compounds, which significantly facilitates the chromatographic identification of the contaminants and makes it more reliable.[3]

1. Determination of Hydrocarbons

The simplest analytical problems which can be solved with the aid of the RSM concentration procedure is the determination of toxic hydrocarbon impurities in any complex mixtures of air contaminants.[31] This is because hydrocarbons are the most inert organic compounds and the accompanying admixtures of substances with different functional groups can be removed from the air to be analysed by means of a pre-column with a powerful reducing agent such as lithium tetrahydroaluminate without affecting the hydrocarbons themselves.[3,31,58]

A pre-column containing phosphoric acid, Versamid 900, lithium tetrahydroaluminate, and lead acetate is effective for this purpose.[59] Such a reactor absorbs satisfactorily all organic impurities with the exception of hydrcarbons. This method has been used successfully for the identification and quantitative gas-chromatographic determination of hydrocarbon impurities in the atmosphere in the workplace in factories (the gas is evolved from raw and pure rubbers, polymeric materials, solvent vapours, thermal degradation products, etc.).[3,30]

A pre-column with Chromosorb P impregnated with a solution of chromium trioxide in concentrated sulphuric acid has been used for the selective absorption of reactive organic impurities from air in a study of atmospheric photochemical reactions.[60] At a temperature of 72–77 °C, the reactive unsaturated hydrocarbons, involved in the formation of the photochemical "smog" which has a fatal effect on many plant species, are extracted from the air, analysed with the aid of such a reactor, and reliably identified.[30]

For the gas-chromatographic identification of the highly toxic styrene, air has been blown[61] through a glass pre-column (6–16 cm × 4 mm), which allows only the compound sought to pass a trap containing Tenax GC. Esters were then absorbed in a fore-column with 10% NaOH on Shimalite, while carbonyl-containing compounds were absorbed in a reactor containing a 2% solution of 2,4-dinitrophenylhydrazine deposited on glass beads. Styrene passed through these pre-columns unchanged and, after being concentrated on a porous polymeric sorbent, its content was determined on a chromatograph with a flame-ionisation detector.

A novel method for the preliminary separation of a complex mixture of the products of the oxidation of various motor fuels has been proposed.[62] Nucleophilic compounds (aldehydes, ketones, alcohols, ethers, esters, etc.) can be selectively absorbed with the aid of a pre-column containing a europium complex of *p*-di(4,4,5,5,6,6,6-heptafluoro-1,3-dioxohexyl)benzene and it is thus possible to separate such substances reliably from alkanes, alkenes, aromatic hydrocarbons, and chlorohydrocarbons before the chromatographic separation of the sample components. The chromatograms of these mixtures after separation on a capillary column 30 m long and containing silicone *SE*-54 are presented in Fig. 9. Involatile derivatives of the nucleophiles of the type of bis-(β-diketonates) are then formed in the pre-column by reacting with the polymeric lanthanide complex. So far the number of such examples is small but coordination compounds provide extensive possibilities of effective procedures in the analyses of air contaminants by the separation and preliminary concentration of toxic impurities having various chemical natures.[63]

A set of pre-column-reactors, some of which are listed in Table 8, makes possible reliable group and individual gas-chromatographic determinations of hydrocarbons in complex mixtures of air contaminants having purely hydrocarbon compositions as well as mixtures of hydrocarbons with organic and inorganic compounds having functional groups. After the separation from the hydrocarbon of admixtures which interfere with their identification, the use of the usual procedures in the qualitative chromatographic analysis (for example, the employment of retention indices) enables one to achieve a very high reliability of the results, comparable to that of the results of the chromato-mass-spectroscopic analysis.[3,30,31,68]

Table 8. Determination of hydrocarbon impurities with the aid of the RSM analysis.[30,31,64-67]

Target components	Sorbent in pre-column	Sorbed impurities
Aromatic hydrocarbons	5A molecular sieve	n-paraffins, n-olefins, and n-acetylenes
Paraffinic, naphthenic, and olefinic hydrocarbons	poly(vinyl chloride)	aromatic hydrocarbons
Paraffinic, naphthenic, olefinic, and aromatic hydrocarbons	maleic anhydride*	dienes
Paraffinic, naphthenic, and aromatic hydrocarbons	1 : 1 mixture of $Hg(ClO_4)_2$ and $HClO_4$* or mixture of 20% $HgSO_4$ and 20% H_2SO_4*	alkenes and alkynes
n-Paraffins and cycloparaffins	conc. H_2SO_4* or mixture of 4% $AgNO_3$ and 95% H_2SO_4	aromatic hydrocarbons, olefins, and acetylenes
Total hydrocarbons	10X molecular sieve	aromatic hydrocarbons

*On a diatomaceous carrier.

2. Determination of Oxygen-Containing Organic Compounds

A reactor with silver nitrate, phosphoric acid, Versamid 900, and lead acetate,[69] designed for the isolation of oxygen-containing organic compounds from a mixture of air contaminants, is not quite as reliable as a pre-column for the isolation of hydrocarbons. Together with oxygen compounds, n-paraffinic and naphthenic hydrocarbons pass through the reactor. In order to eliminate their interfering effect, the subsequent gas-chromatographic analysis of the substances concentrated in the trap is carried out on a superpolar stationary liquid phase (SLP) of the type of 1,2,3-tris(cyanoethoxy)propane, which makes it possible to separate the

§ In general there are greater differences between the properties of inorganic compounds and selective detectors, for example, are sufficient for their identification.[3]

paraffin–naphthene fraction from polar derivatives of hydrocarbons. On a column with 15 and 30% of such SLP, methanol emerges after n-decane and tridecane respectively.

This subtraction-isolation method, in which the oxygen-containing substances are separated from non-polar hydrocarbons in the first stage and the substances isolated are subjected to gas-chromatographic analysis in the second stage, is distinguished by a high selectivity, which is made up of the selectivities of the pre-column and the analytical column. This procedure has been used for the identification and reliable determination of toxic admixtures of methanol and other alcohols in the evaporation products of a petrol–methanol fuel,[70] in the determination of volatile compounds in air arising from various solvents,[30,31] and in the analysis of complex mixtures of organic compounds contaminating air in the processing of polymeric materials.[3,36,68]

In the determination of methanol in the exhaust gases from automobile engines,[3,36] where the air in the driving compartment contains aldehydes in addition to methanol, a reactor with $NaHSO_3$ on Chromaton N was used for the reliable identification of methanol with the aid of the RSM.[36] Whilst retaining low-molecular-weight aldehydes, such a pre-column lets methanol and hydrocarbons pass through to the trap with the sorbent; these substances were subsequently separated on a column with 0.2% PEG 1500 on graphitised carbon black and were unambiguously identified using the retention characteristics of the impurities.[3] The action of the pre-column is basedon the interaction of aldehydes with sodium bisulphite involving the formation of a substituted sodium sulphonate in accordance with the equation

$$RCHO+NaHSO_3 \rightarrow RCHOHSO_3Na.$$

In simpler cases, where the air analysed does not contain all possible contaminants but only compounds of specific classes (for example, only hydrocarbons, only halogenohydrocarbons, only alcohols and aldehydes, etc.), the identification of the impurities is greatly simplified (Table 9).

Table 9. The RSM concentration and identification of oxygen-containing organic impurities.[2,30,64–67]

Target components	Sorbent in pre-column	Sorbed impurities
Oxygen-containing compounds	$AgNO_3$, H_3PO_4, Versamid 900, and $Pb(CH_3COO)_2$	all organic substances other than paraffins and naphthenes
Oxygen-containing compounds	Versamid 900 and $AgNO_3$	halogenohydrocarbons
Oxygen-containing compounds	poly(vinyl chloride), $AgNO_3$, Versamid 900	halogenohydrocarbons, alkylbenzenes, olefins, and acetylenes
Aldehydes and ketones	H_3BO_3	primary and secondary alcohols
Alcohols	2,4-dinitrophenylydrazine	aldehydes and ketones
Ketones	*o*-dianisidine and 5A zeolite	aldehydes
Ethers and esters	5A molecular sieve	carboxylic acids
Lower carboxylic acids	benzidine	aldehydes and ketones
Aldehydes, ketones, ethers, and esters	KOH	carboxylic acids

The RSM concentration procedure has been used successfully also in the solution of certain simpler problems in the chemistry of air contaminants, for example, for the selective

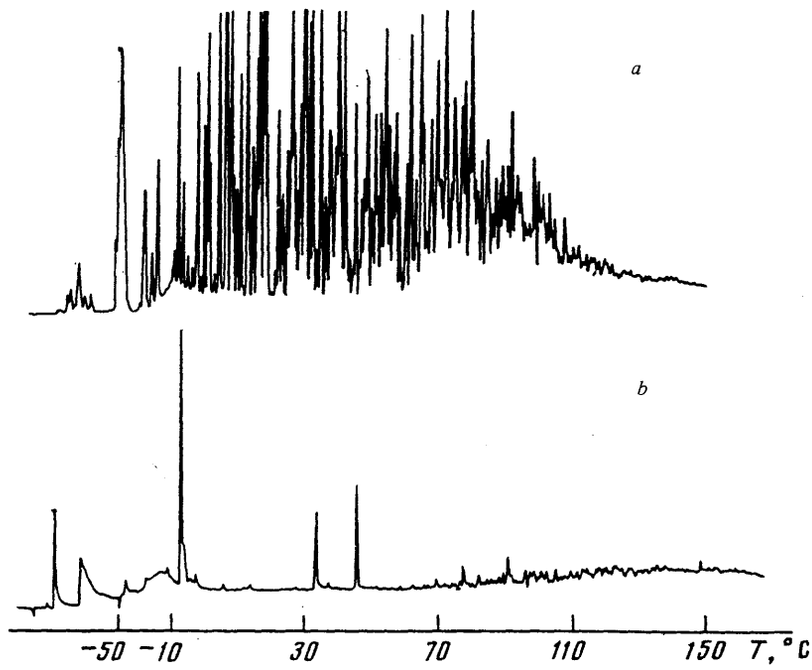


Figure 9. Chromatograms of compounds not retained (*a*) and retained (*b*) by the pre-column obtained in the analysis of the vapour of motor fuel subjected to thermo-oxidative cracking.[62]

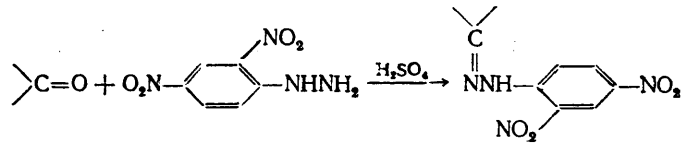
and reliable determination of admixtures of phenols or carbonyl compounds against the background of halogenohydrocarbons, hydrocarbons, or esters.[31] Organic and inorganic acids can be identified in air by a simple and effective method, for example, with the aid of a pre-column with K_2CO_3 [71] or with Chromosorb P impregnated with Na_2CO_3.[72] An analogous method of determining trace amounts of lower C_2–C_5 aliphatic acids consists in the use of a preliminary reactor with 2% NaOH on glass beads.[73] After the separation of polar acids from other compounds in the sample, they are concentrated on silica gel, desorbed with water, and then analysed on a chromatograph with a flame-ionisation detector.

A pre-column (6 cm × 5 mm) with glass beads, coated by a mixture of 0.05 g of 2,4-dinitrophenylhydrazine and 0.1 ml of H_3PO_4, has been used for the rapid determination of lower aliphatic carbonyl compounds in the waste gases from factories.[74] After the separation of the accompnaying impurities in this type of reactor, the carbonyl compounds were retained in a trap with 25% of 1,2,3-tris(cyanoethoxy)propane on Shimalite cooled with liquid argon to −186 °C. The concentrator was then heated to 120 °C, the sample was desorbed into a chromatographic column 1.5 m long with 5% of the same SLP on Carbopack B, and the toxic impurities were analysed at 70 °C using a flame-ionisation detector. For a reliable determination of phenolic and aliphatic acid microimpurities in air, the same authors[75] used a fore-column (7 cm × 4 mm) with 20% KOH on glass beads (0.6 to 0.25 mm). The presence of the sought compounds in the sample was inferred from the difference between the chromatograms obtained with and without a pre-column, in the latter case the sample being simply removed to a trap with Tenax GC. After the desorption of the enriched sample, the mixture was analysed on a glass column (1.75 m × 3 mm) with 0.1% SP-1000 on Carbopack C at 205–220 °C using a flame-ionisation detector.

Table 10. Methods for the identification of chlorohydrocarbons with the aid of the RSM.[3,64–67,79]

Target components	Sorbent in pre-column	Sorbed impurities
Chlorohydrocarbons	5A molecular sieve and conc. H_2SO_4	oxygen-containing organic compounds
Chlorohydrocarbons	ditto	hydrocarbons and oxygen-containing organic compounds
Chlorohydrocarbons	metal hydrides	oxygen-, nitrogen-, and sulphur-containing compounds
Vinyl chloride, trichloroethylene, and tetrachloroethylene	5A molecular sieve, H_2SO_4, and Versamid 900	hydrocarbons and chlorine- and oxygen-containing compounds

An interesting problem solved with the aid of the RSM [36] is that of the determination of ethanol impurities in respired air. The aldehydes (especially acetaldehyde) and ketones, which interfere with the determination, can be differentiated by an effective procedure which involves the use of several prechromatographic reactors (H_3BO_3; *o*-dianisidine; 2,4-dinitrophenylhydrazine; benzidine or hydroxylamine), which are listed in Table 11. The use of pre-columns with different combinations of the above reagents makes it possible to remove in succession ketones, aldehydes, and alcohols from the mixture analysed, in conformity with the reactions described by the equations[76]



$$RCHO + NH_2OH \cdot HCl \rightarrow RCH{=}NOH + HCl + H_2O\ ;$$

$$H_3BO_3 + C_2H_5OH \xrightarrow{H_2SO_4} (C_2H_5O)_3B + H_2O\ .$$

Table 11. The RSM identification of organosulphur impurities.[64–67]

Target components	Sorbent in pre-column	Sorbed impurities
Mercaptans	4A zeolite	C_1–C_3 hydrocarbons and C_1–C_3 alcohols
Mercaptans, sulphides, and thiophens	Versamid 900	alkyl halides and aryl halides
Mercaptans	poly(vinyl chloride)*	alkylbenzenes, primary alcohols, and amines
Sulphur dioxide	$NaHCO_3$	sulphides, mercaptans, and hydrogen sulphide

*At 55–75 °C.

These methods make it possible to identify reliably the above compounds in a complex mixture of volatile substances in the respired air.

3. Determination of Chloro-Derivatives of Hydrocarbons

The use of the RSM analysis yields satisfactory results in the gas-chromatographic determination of organochloro-compounds, many of which exhibit a pronounced carcinogenic activity, since this procedure makes it possible to detect reliably microamounts of these toxic compounds (for example, vinyl chloride) against the background of the less dangerous accompanying impurities comprising hydrocarbons, oxygen-containing compounds, etc.[30]

A pre-column with sodium bisulphite, which forms a complex with the target compound, is used to separate vinyl chloride from the acetaldehyde, which frequently accompanies vinyl chloride and interferes with its determination.[76,77] Admixtures of light hydrocarbons and oxygen-containing compounds were effectively separated on a pre-column with 5A zeolite and concentrated sulphuric acid on glass wool.[78] Vinyl chloride was analysed at the level of the maximum permissible concentration (0.1 mg m^{-3}) on a column with 0.2% of Carbowax 1500 on graphitised carbon black or Polysorb-1 at 50 °C on a chromatograph with a flame-ionisation detector. One should bear in mind that all the procedures (removal of samples onto activated charcoal, desorption of the sample by chlorobenzene, storage of the sample, etc.) must be carried out at a temperature not exceeding 0 °C to avoid losses of vinyl chloride. A chromatogram of a mixture of vinyl chloride and the admixtures interfering with its determination is presented in Fig.10.

An analogous pre-column has been used also to determine other chlorine-containing hydrocarbon impurities in air (tri- and tetra-chloroethylene, chlorobenzene, etc.). After the RSM concentration, these impurities were readily identified by standard chromatographic procedures.[79]

When it is necessary to separate halogen-containing hydrocarbons from compounds of any one class (hydrocarbons, oxygen compounds, etc.), the use of the pre-columns listed in Table 10 gives satisfactory results.

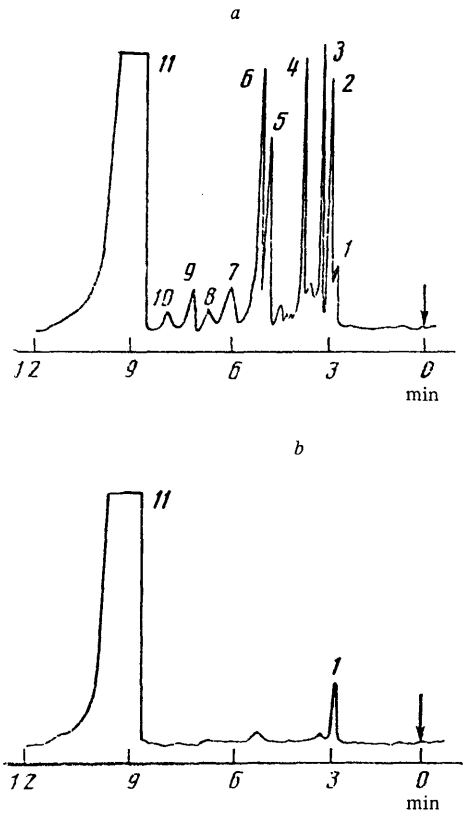


Figure 10. Identification of vinyl chloride in a complex mixture of volatile compounds evolved into air on heating artificial leather: *a*) without the use of a pre-column; *b*) beyond the pre-column containing 5A zeolite in sulphuric acid;[78] 1) vinyl chloride; chromatographic peaks *2–10* were not identified; 11) toluene (solvent).

The employment of molecular sieves can lead to the adsorption (up to 8–12%) on the outer faces of the zeolite crystals of the impurities being concentrated, i.e. can lead to additional sorption which is not taken into account.[31] This factor must be allowed for in the interpretation of the results of the identification of impurities using the 5A, 10X, and 13X zeolites as pre-column packing.[3,31,64]

4. Determination of Sulphur-Containing Organic Compounds

Sulphur-containing organic compounds, many of which are powerful odorants, are encountered in many petrochemical industries and contaminate the air in the workplace in petroleum refineries.[3]

It has been found that concentration by the RSM is a no-less effective procedure for the identification of organosulphur compounds than the use of flame-photometric and photo-ionisation detectors selective with respect to sulphur.[3,36] The former does not give rise to a significant signal with hydrocarbons but responds to many compounds with functional groups.[80] Although the latter makes it possible to determine picogram amounts of sulphur compounds,[3,40] it gives a signal with alkylbenzenes and certain other hydrocarbons of almost the same magnitude.[81]

In certain instances of practical gas-chromatographic analysis, especially when it is necessary to differentiate mercaptans and sulphides from hydrocarbons, the use of the pre-columns listed in Table 11 yields satisfactory results.

The RSM procedures for the concentration of impurities have proved effective in the identification of sulphur-containinng impurities in air contaminated by the vapour of BR-2 motor fuel[82] and white spirit,[30] in the volatile components of pure rubbers based on natural butyl-rubber,[83] and in the analysis of air from the workplace in petrochemical undertakings.[36,49] A pre-column with $NaHCO_3$ makes it possible to separate microamounts of sulphur dixoide from hydrogen sulphide, mercaptans, sulphides, and disulphides.[84]

5. Determination of Nitrogen-Containing Organic Compounds

In this case the RSM analysis is most difficult, because nitrogen compounds are very reactive. It is therefore very difficult to select chemical reagents and sorbents which would absorb the accompanying admixtures (including inert hydrocarbons) and would not react with nitrogen compounds (amines, amides, nitriles, nitro-compounds, lactams, etc.).[3,30,31] Thus a reactor with the 5A molecular sieve and Versamid 900 retains only hydrocarbons, certain oxygen-containing hydrocarbon derivatives, and a reactive halogen compound. Nevertheless, even when only 40–50% of all the admixtures interfering with the analysis are removed with the aid of this pre-column, we may hope for an appreciable increase in the reliability of the subsequent gas-chromatographic identification of the nitrogen compounds.[30,36]

Table 12. The RSM identification of nitrogen-containing organic compounds.[3,30,65]

Target components	Sorbent in pre-column	Sorbed impurities
Amines	H_3BO_3	alcohols and phenols
Amines	2,4-dinitrophenylhydrazine	aldehydes and ketones
Amines	zinc oxide	carboxylic acids, alcohols, and phenols
Amines	KOH	carboxylic acids, phenols, cresols, ethers, and esters
Nitrogen-containing compounds	Versamid 900 and silver nitrate	halogen-containing hydrocarbons

In certain cases, for example, those listed in Table 12, concentration by the RSM yields entirely satisfactory results. These procedures have been used in analytical practice for the analysis of air contaminants, for the identification and determination of amines in the gases evolved from rubber articles,[36,49] and in the elucidation of the composition of the volatile substances released into the air of the workplace in the manufacture of polymers and their processing.[3,30,36]

A pre-column with glass wool or a glass filter impegnated with [(4-nitrophenyl)methyl]propylamine has been used for the identification and quantitative determination in air of trace concentrations of aminocarbonyl derivatives of toluene.[85]

A method involving the preliminary removal of nitrites by ion exchange and denitrosation with the aid of sodium iodide or sulphanilamide is used for the determination in the air of the workplace in industrial undertakings of admixtures of *N*-nitroso-compounds (formed from anticorrosion additives to lubricating-cooling liquid compositions).[86] For the correct identification in air of microamounts of *N*-nitroso-compounds, which eliminates the interfering influence of amines (precursors of *N*-nitroso-compounds), one uses in sampling a two-section cartridge with sulphamic acid for the absorption of amines in the first section and a mixture of sulphamic acid with magnesium silicate for the trapping of *N*-nitroso-compounds in the second section. After sampling, the contents of the second section are desorbed with acetone and analysed by gas chromatography.[87]

6. Determination of Inorganic Compounds

The reaction-sorption concentration method has been used successfully also in the determination in air of trace amounts of toxic inorganic substances.[3,21,30,34,40] In order to determine nitrous oxide, air is initially freed from the H_2O and CO_2 impurities, which interfere with the analysis, by passing the sample through a pre-column containing anhydrous $CaSO_4$, $Mg(ClO_4)_2$, and Ascarite.[88] The column with 13X zeolite retains irreversibly the NO_2 and N_2O impurities, but it is possible to separate on it O_2, N_2, and NO;[33,89] this enables one to achieve the preliminary separation of the reactive nitrogen oxides, whose separate determination has always constituted a difficult problem.[21,34,40]

In order to eliminate the mutual influence of inorganic gaseous impurities, a thin-fibre polystyrene filter, containing iron chelate compounds, is employed. The concentration of the NO_2, NH_3, H_2S, and SO_2 impurities in air after it has been passed through such a filter at a rate of 0.1 litre min^{-1} diminishes by a factor of ~50 compared with the initial concentration.[90] In order to separate the highly reactive sulphur trioxide, which tends to polymerise, from one of the most important contaminants in air, namely sulphur dioxide, the air to be analysed is passed through an absorber containing 97%[91] or 100%[92] sulphuric acid, which effectively absorbs SO_3. The influence of SO_2, which interferes with the gas-chromatographic determination of H_2S microimpurities, can be eliminated by a preliminary step in which the air to be analysed is passed through a tube filled with glass beads treated with Na_2SO_3. In the subsequent chromatography of the sample on a column with Porapak Q at 100–200 °C, it was possible to determine selectively an admixture of 10^{-7}% of hydrogen sulphide in air over various regions of the Atlantic Ocean.[93]

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The hybrid reaction-sorption method, based on the simultaneous employment of chemical subtraction and sorption concentration methods, makes it possible to increase significantly the reliability and reproducibility of the identification of impurities in complex mixtures of air contaminants. The application of the RSM has greatly expanded the field in which gas chromatography can be used to determine organic and inorganic impurities in air (and in various gaseous media). The employment of the RSM concentration of impurities in their determination in various liquids (solvents, natural and waste water, brines, technological water, etc.) is undoubtedly also promising.

The reaction-sorption method is universal and can be used in combination with any analytical procedure (chromatographic, spectroscopic, electrochemical, etc.). The application of the RSM improves almost all the metrological characteristics of the methods for the determination of impurities (selectivity, detection limits, reliability, reproducibility, etc.) and expands the range of the active methods and procedures available in analytical chemistry.

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