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# Heteroatomic Components of Petroleum

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The state of the problem of the isolation, separation, and characterisation of the heteroatomic compounds of petroleum is examined and current data on the chromatographic and mass-spectrometric characteristics of organosulphur compounds in petroleum and petroleum products are surveyed. The results obtained in studies on the composition and structures of sulphides and thiophens in distillates and residual petroleum fractions are listed and the fundamental data on the oxidation of middle petroleum fraction sulphides to sulphoxides and sulphones and on the pathways followed in their further chemical transformation are compiled. Certain aspects of the utilisation of petroleum sulphides and sulphoxides in the national economy are considered. The bibliography includes 210 references.

CONTENTS

I. Introduction 701
II. Methods for the isolation of heteroatomic compounds from petroleum and petroleum products 701
III. Chromatographic and mass-spectrometric methods for characterising the sulphur compounds in petroleum and its fractions 707
IV. Petroleum sulphides and thiophens 709
V. Oxidation of petroleum sulphides 713

## I. INTRODUCTION

Modern experimental techniques have made it possible to compile information about the characteristics of the composition of complex natural formations such as petroleum and bitumens. The hydrocarbons contained in such substances have been investigated in detail. Fine instrumental analytical methods for the investigation of the compositions, structures, and properties of organic compounds and their multicomponent mixtures have been developing vigorously during the last 5–10 years. Intensive investigation of the heteroatomic components of petroleum and bitumens has been particularly characteristic of this period.

The interest in heteroatomic compounds (HAC) of petroleum is due to a number of causes: the fraction of petroleums rich in HAC has increased sharply in the world production and processing of petroleum; in the manufacture of fuel and lubricating oil, the majority of HAC constitute a harmful admixture hindering the processing of the raw material and lowering the quality of the commercial products; the HAC are responsible for the formation and stabilisation of water–petroleum emulsions on the way from the borehole to the refinery; the study of the HAC helps to approach more closely the solution of the problems of the origin of petroleum and its transformations underground and the solution of the associated problem of the distribution of petroleums of particular quality in the deposits. In other words, the knowledge of the HAC constitutes a basis for the geochemical prediction of the available raw material resources for the petrochemical processing of petroleum. Such processing has been tending to replace the production of fuel and lubricating oil at an increasing rate. The value of the petroleum HAC is also of considerable interest for fundamental science. The chemical composition and structure of the majority of the petroleum HAC were unknown. The determination of the relation between the HAC and the petroleum hydrocarbons, on the one hand, and the parent material of petroleum, on the other, is one of the most interesting problems of modern biogeochemistry.

An attempt will be made below to describe briefly certain results of studies in the past five years and, in relation to specific problems, the last ten years (from 1966 to 1976). One should note that this period has been characterised by a still unduly analytical approach to the solution of the problem of the composition of petroleum. The following factors require constant attention: the complex combination of the acid–base and oxidation–reduction properties of petroleum hydrocarbons; the characteristic donor–acceptor interactions of the HAC with condensed aromatic hydrocarbons; the problem of the colloidal, supermolecular structure of petroleum and the role of the HAC in its changes; the involvement of charge-transfer complex and clathrate compound formation in the organisation of short-range order leading to structure formation in petroleums, which has not been considered hitherto in any way at all.

## II. METHODS FOR THE ISOLATION OF HETEROATOMIC COMPOUNDS FROM PETROLEUM AND PETROLEUM PRODUCTS

Crude petroleum is characterised primarily by its elemental composition and the limits of its boiling point range corresponding to the distribution of the components with respect to their molecular weights. The elemental compositions of all petroleums are distinguished by the predominance of carbon and hydrogen, which are the main constituents not only of hydrocarbons but also of all heteroatomic compounds in petroleum. The latter are in most instances monofunctional; a more detailed study led to the discovery of the presence in petroleums of a large number of bi- and tri-functional compounds but at negligibly low concentrations. The content of carbon in petroleum is in most cases restricted to the range 80 to 87%, of hydrogen to 11–14%, of sulphur to 0.01–0.1% (up to 8% in sulphur-containing and high sulphur petroleums), and of nitrogen to 0.04–0.6% (unique petroleums with an increased nitrogen content are known). The data on the oxygen content are in most instances insufficiently accurate, since they have frequently not been obtained by direct analysis but by difference (the errors in the

determination of all the remaining elements naturally accumulate under these conditions in the calculated oxygen content); nevertheless, one can assume that the oxygen content varies in the range 0.2–7.0%, i.e. is of the same order of magnitude as the sulphur content and an order of magnitude higher than the nitrogen content. The overall content of all the remaining elements in petroleums is usually less than 1%. Most of the residue consists of vanadium derivatives.

The simplest and oldest method for the resolution of petroleums into fractions is based on their boiling points. To a first approximation, this corresponds to the distribution of the components with respect to their molecular weights in view of the validity of the expression $T \simeq aM^b$, where $T$ is the boiling point (on the Kelvin scale) and $a$ and $b$ are constants [1,2]. In most cases $b$ differs little from 2, i.e. $T \simeq a\sqrt{M}$; $a$ varies within wide limits (from 36 to 48 for hydrocarbons), being correlated with the particular homologous series to which the compound belongs (with the value of $x$ in the formula $C_nH_{2n \pm x}$ proposed by Mendeleev [3]) and with the characteristics of the heteroatoms present. When petroleum or petroleum products are distilled with the aid of relatively inefficient fractionating devices (still widely used to determine the standard characteristics of commercial products), the distribution of the components with respect to their melting points in the multicomponent fractions collected is nearly Gaussian [4].

An increase in the efficiency of fractionation entails a marked decrease of the number of compounds included in the fractions collected and in the limit leads to the isolation of individual compounds; this rules out a statistical approach to the characterisation of narrow fractions. The latter is shown particularly clearly in attempts to extend to narrow fractions the statistical methods for the analysis of composition, particularly those proposed by Waterman et al. [5] for commercial petroleum products and broad petroleum fractions. Nevertheless there is no doubt that fractionation to give comparatively broad fractions is at present useful for a preliminary resolution of petroleum and petroleum products. It is useful to set limits to the fractions collected on the basis of the structural transitions of the components, for example from alkanes to monocyclic compounds, from monocyclic to bicyclic compounds, and from the latter to polycyclic compounds.

The employment of highly efficient chromatographic devices and of mass spectrometry in the next separation stage permits the recommendation that one abandons the preliminary separation of test materials by fractionation into extremely narrow fractions, which is still used. The collossal multiplicity of the components of the middle and high petroleum fractions requires the application of the methods of group and structural-group analysis, including functional analysis, and not individual analytical techniques. In many spectroscopic, refractometric, and other physical methods for structural-group analysis, one uses the atomic or bond increments (frequencies, intensities, refractions, dispersions, etc.) obtained by averaging the data for a multiplicity of individual compounds of different structures. Naturally, the application of these increments to compounds with restricted compositions without due allowance for their characteristics may lead to an increase of error in the determination of the composition. We shall return to this problem below when modern chromatographic mass-spectrometric methods for the analysis of petroleum distillates are considered.

The distribution of the petroleum components with respect to molecular weight is different for different types of petroleum. Petroleums from gas-condensate deposits and petroleums which have undergone the greatest geochemical transformations under reducing conditions are enriched in the light components. Petroleums which have undergone least geometrical modification under reducing conditions or which have undergone oxidation transformations are enriched in the heavy components. The same group includes petroleums greatly enriched in tars and asphaltenes, which have undergone the stage of retrograde condensation accompanied by the elimination of the light fraction, which under suitable conditions might have formed gas-condensate deposits.

In conformity with all the foregoing factors, the distribution of petroleum heteroatomic compounds among its fractions varies just as strongly. Heavy petroleums are usually richest in the HAC. For a more correct understanding of this phenomenon, it is necessary to consider the differentiation of petroleums not only with respect to their boiling points but also with respect to their "component composition", which was introduced into practical technical analysis of petroleums as early as the beginning of this century by Richardson [6] and, independently, by Marcusson [7].

After the distillation of light-coloured petroleum products and dilution of the residue with benzene, asphaltogenic acids and then their anhydrides are extracted (by Marcusson's method) from the heavy component of petroleum. This is followed by the deposition of asphaltenes, carbenes, and carboids, heavy oils are eliminated from the residue, and petroleum tars ("silica gel" tars according to the method of their isolation) are obtained. This method of separation has been described in detail by Nametkin [8], who also indicates simplified versions of the method recommended by Sakhanov [9] and refined by Starostin and Boldyreva [10]. The essential feature of the simplification consists in the abandonment of the isolation of asphaltogenic acids and their anhydrides from asphaltenes. This version of the method has been widely adopted. Subsequently it was supplemented by the desorption of oils and tars from the silica gel by a series of solvents of increasing polarity, which made it possible to differentiate the oil fraction into saturated and aromatic fractions with increasing contents of heteroatomatic compounds. The development of component analysis is described in greater detail by Sergienko [11].

All the versions of the methods of component analysis considered involve the precipitation of asphaltenes by solvents of low polarity and the sorption of tars on silica gels, alumina, natural bentonite clays, or zeolites (for a description of the latter, see Benashvili [12]). It is then assumed that the majority of the heteroatoms detected in the tars and asphaltenes isolated are present as structural elements in molecules of high-molecular-weight compounds, being linked to them by $\sigma$ bonds. However, sufficiently convincing evidence for this view has not so far been adduced. Our own observations make it necessary to assume that, together with the heteroatoms entering into the composition of asphaltenes and tars with formation of classical bonds, heteroatoms in comparatively low-molecular-weight compounds, sorbed both on silica gel and on macromolecular formations generated by tars and asphaltenes, play a significant role. The stability of the supermolecular formations formed is determined under these conditions not only by the donor–acceptor interactions with participation of the heteroatom but also by the similarity of the structures of the hydrocarbon fragments of the moieties enriched in condensed aromatic and naphthenoaromatic rings. Nor can one exclude the

role of the formation of clathrate compounds by low-molecular-weight components with macromolecular components, the former being enclosed in hollow structural cells of the latter.

The characteristics of the elemental, component, and fractional compositions of the petroleums in the Soviet Union are described in a handbook[13], the majority of the data in which have been obtained by unified methods and are comparable. The same handbook quotes the structural-group characteristics of the light-coloured distillates and the compositions of the majority of petrols in terms of individual hydrocarbons.

The functional characteristics and the content of sulphur and its derivatives in petroleums from the Urals-Volga region and Siberia have been determined by Obolentsev and Baikova[14], also using unified methods. Their monograph[14] includes data concerning the presence of free, hydrogen sulphide, mercaptan, disulphide, and sulphide sulphur in fractions which begin to boil at temperatures up to 120°C, in the ranges 120–200°C, 200–250°C, and 250–300°C, and in narrow (approximately 3 K fractions) of a number of petroleums in the USSR as well as data concerning the presence of free, mercaptan, and sulphide sulphur in the initial petroleums. The monograph also contains information about the overall sulphur content, which makes it possible to deduce the presence of "residual sulphur", contained mainly in compounds belonging to the thiophen and diaryl sulphide series. Unfortunately, the authors[14] do not characterise the residues boiling above 300°C (even their yield is not quoted). The monograph lists the characteristics of a number of petroleums and fractions relating to the threshold of thermal stability, indicating the presence of thermally unstable compounds (determined using the method adopted by Coleman et al.[15]), and the analytical methods used are described.

The distribution of sulphur and nitrogen among the component fractions of the petroleums from the Urals-Volga region and Western Siberia was recently reported by Eigenson and Ivchenko[16], who established that, after the distillation of fractions boiling up to 450°C (containing about 60% of all the sulphur present in petroleum), the sulphur in the residue is present to the extent of 36–40% in oils, 42–46% in tars, and 15–20% in asphaltenes. The distribution of nitrogen is markedly different: the residue contains about 90% of the amount present in the initial raw material; the oils in the residue contain only 4–8% of the nitrogen, the tars 52–63%, and asphaltenes 37–42%. This is apparently associated with the relatively higher reactivity of the nitrogen compounds, leading to their association in the form of salts and complexes with the oxygen-containing components of petroleum—primarily acids and phenols. The overall nitrogen content is approximately an order of magnitude lower than the content of sulphur in these petroleums.

An interesting version of the component semimicro-analysis of petroleum was achieved by Pozdyshev et al.[17]: light hydrocarbons were extracted with a 1:4 methanol–acetone mixture; a 10% NaCl solution precipitates from the extract light oils with an admixture of surface-active comparatively low-molecular-weight heteroatomic compounds, which can be extracted with water. The residual tar ("Goudron") remaining after the extraction of the light oils was deposited on paper, from which heavy oils were extracted with isopropyl alcohol; after this, tars were extracted with boiling hexane and asphaltenes with boiling benzene. The method yielded data in satisfactory agreement with the results obtained in the usual way.

The petroleums from the deposits in the Western Siberian, Urals-Volga, and Western Kazakhstan regions (the Ust-Balyk, Pravdinsk, Megionsk, Uzen'sk, Romashkino, Arlansk [tentative transcription], Pokrovsk, and Mukhanovsk deposits) were investigated by this micromethod. The limits of variation of the compositions of these petroleums were found: 26–77% of light oils (with the average molecular weight $M$ = 190–241); 10–49% of heavy oils ($M$ = 311–603); 2–14% of tars ($M$ = 577–1059); 0.2–4.4% of asphaltenes ($M$ = 886–3298). The light transmission constants [presumably $\epsilon_\lambda$ values (Ed. of Translation)] of the crude petroleums and oils are similar and vary in the range 162–660; the corresponding ranges for tars and asphaltenes are 1964–3670 and 4106–15 000 respectively. The method proposed will presumably prove useful for the investigation of heteroatomic compounds in petroleum in combination with modern gas-chromatographic elemental microanalysis.

Purely chemical methods for the separation of petroleum components, based on the reactions of functional groups, are the most important for the isolation, separation, and identification of the heteroatomic components of petroleum and petroleum products. Here we shall recall the extraction from petroleum of nitrogen-containing bases by acids, the subsequent extraction of carboxylic acids with sodium carbonate, the extraction of phenols with strong alkalis, and the re-extraction of the bases liberated on hydrolysis of the salts which they have formed with petroleum acids. Since the present author and Musaev applied this method for the first time[18] in order to characterise the relation between the properties of light petroleum hydrocarbons (from deposits of different ages) and those of non-hydrocarbon components—bases, acids, tars, and asphaltenes†—it has not altered fundamentally.

It has been suggested that *o*-sulphobenzoic and sulphosalicylic acids[20] in the form of 10% aqueous solutions and in the anhydrous state be used instead of inorganic acids for the extraction of bases from fuel fractions. The extraction of bases is accompanied under these conditions by the transfer of some of the acids to the hydrocarbon phase and the elimination of acids from the extract is difficult. An important advance was the use of ion-exchange resins (anion and cation exchangers) for the selective extraction of compounds with acid and basic functions. As long as the aim of the investigations was to free the petroleum products from these components, the main task involved quantitative sorption and did not present special difficulties. Following the development of research devoted specifically to the heteroatomic components of petroleum, attention had to be concentrated on the much more difficult problem of the quantitative desorption of the test compounds in an unchanged form.

The coarsely porous sulphonic acid cation-exchange resins KU-2 and KU-23 (styrene-divinylbenzene copolymers) have been used[22–25] for the extraction of nitrogen-containing bases from crude petroleums and distillates. According to Bezinger et al.[23], the following method has been recommended for the preparation of

†This study was carried out in connection with the investigation of the role of surfactants in crude petroleums in the displacement of petroleum by water and in the formation of emulsions, carried out by Zinchenko in consultation with Rebinder and Kusakov. Evidently the suggestion[19] that the first studies on surfactants in crude petroleum were made in 1946[20] is erroneous.

nitrogen-containing concentrates from petroleum: a benzene solution of petroleum is treated with a cation exchanger and filtered, acetic anhydride and a portion of fresh cation exchanger being added to the filtrate in order to increase the sorbability of the nitrogen-containing bases on the cation-exchange resins. The rate and degree of extraction of the bases increase greatly under these conditions (one must bear in mind that the capacity of the cation exchanger with acetic anhydride is appreciably reduced). The role of acetic anhydride is in this case probably the same as in non-aqueous titration in differentiating solvents. However, one cannot rule out the possibility that acetic anhydride binds a proportion of the heteroatomic petroleum components, blocking the nitrogen of certain bases. Such ideas are supported by the finding that a similar effect can be obtained on replacing acetic anhydride by dimethylformamide.

The stepwise separation of chemisorbed bases into those extractable by benzene and ethanol, recommended by Bezinger et al.[23], is not obligatory. A series of solvents of increasing polarity can be used for selective desorption, particularly when one can postulate the presence in the mixture of compounds differing in their basicity. The complete extraction of all the bases by a highly polar solvent is also feasible. In experiments with distillates containing an appreciable amount of sulphides, it is best to convert them first into sulphoxides in order to facilitate their separation from nitrogen-containing bases on the cation-exchange resin.

The proposed version of the isolation of bases with the aid of acetic anhydride is naturally applicable only to petroleum and products which do not contain appreciable amounts of primary and secondary bases capable of chemical interaction with this reagent (acylation).

A procedure resembling the isolation of petroleum bases is the extraction of organic sulphides from petroleum distillates with sulphuric acid. There are no fundamental differences: both nitrogen and sulphur compounds of the above groups are freely converted into 'onium forms, which are readily hydrolysed with regeneration of the initial amines and sulphides:

$$R_3N + HA \rightleftarrows R_3NH^{\oplus}A^{\ominus} ,$$
$$R_2S + HA \underset{H_2O}{\rightleftarrows} R_2SH^{\oplus}A^{\ominus} .$$

The growth of interest during the last decade in the isolation of large amounts of sulphides from middle petroleum fractions stimulated vigorous research on their extraction with sulphuric acid. A version of the sulphuric acid method for the preparation of sulphide-aromatic concentrates has been proposed by Chertkov, Spirkin, and Demishev[26,27]. Subsequently, this procedure was frequently tested and refined[28,29], and has reached a stage where it can be applied on an experimental-industrial scale. The method is widely used in studies in the USSR on the sulphides of middle petroleum fractions[30].

The much lower basicity of sulphides (compared with nitrogen-containing components) and their higher concentration preclude their isolation in a pure form: sulphide-aromatic concentrates are always obtained. The same happens in sorption methods for the isolation and separation of heteroatomic petroleum compounds on silica gels, alumina, and other acid or amphoteric oxides. Certain differences between the concentrates obtained (a reduced content of light dialkylsulphides and an increased degree of extraction of thiophens into the sulphuric acid concentrate) have been examined[31].

The formation of hydrogen bonds of different types probably plays an important role in the formation of sulphide-aromatic concentrates[32]. The tendency of sulphides to form associated species with condensed aromatic compounds, recently investigated in model systems[33-35], is undoubtedly also significant[32]. It has been shown that such species are formed only by aromatic sulphides and aromatic hydrocarbons and it has been suggested that the type of association is the same as that observed in purely hydrocarbon systems. Associated species, mainly with 1:2 composition, have been observed for the latter in binary systems, while the component ratio in the associated species in sulphide-hydrocarbon systems is 1:1.

The characteristic features of the solubility of organosulphur compounds and the possibility of their isolation and separation by extraction are directly related to the characteristic features of the complex formation process. On the basis of studies of the solubilities of 30 sulphides in 24 organic solvents, Obolentsev et al.[36] divided solvents into three groups: in the first group, the solvent power depends little on the molecular weight of the sulphur compound (acetylacetone, propyl alcohol); in the second group, the solvent power varies sharply with the molecular weight; the solvents of the third group tend to dissolve selectively specific types of sulphur compounds. The study was performed by determining the consolute temperatures. In the experimental temperature ranges, the composition–temperature curves pass through a distinct maximum, with the exception of the systems formed by alkylthiophans and 2-butylthiophen with ethanol. These anomalous systems were not investigated in greater detail.

Following the development of gas-chromatographic methods for the determination of the physicochemical characteristics of organic liquids, their volatilities, activities, and extraction characteristics[37], simple and rapid methods for the estimation of the selectivities of extractants for heteroatomic compounds became possible. The relative selectivities of tens of extractants[38] have been calculated for the simplest model systems (thiophan, di-isopropyl sulphide, and hexanethiol) using literature data[39,40]. The activity coefficients (in the temperature range 60–80°C) of four alkanethiols ($C_4$–$C_8$ and six dialkyl sulphides ($C_3$–$C_{10}$), thiophan, thiophen, and 2- and 3-methylthiophens have been published[38] and the relative selectivities[41] in the separation of light sulphur compounds and hydrocarbons have been calculated. It has been shown in a report[39] covering data for 28 solvents that phenol is the best extractant for the separation of aliphatic and cyclic sulphides.

The donor–acceptor interaction of heteroaromatic compounds with metal cations and their capacity for complex formation have been known for a long time. Mercaptans and sulphides are frequently isolated from light-coloured petroleum distillates and characterised with the aid of mercury(II) salts [mercury(II) chloride and acetate]. In particular, this method has been used in Nametkin's laboratory. Nametkin always showed much interest in heteroatomic petroleum compounds, particularly in sulphur compounds. The first dissertation devoted to the sulphur compounds in petroleum from the Ishimbai deposit[42] as well as a number of reports dealing with studies on sulphur compounds in other petroleums[43-45] originated in his laboratory. Sulphur compounds were isolated and purified in these investigations via their mercury complexes. Such complexes are still being used for analytical purposes.

Systematic studies on the formation of complexes by organosulphur compounds with a number of metals were begun in 1960 in Obolentsev's laboratory. The first series

of studies devoted to complexes with mercury salts was carried out by Lyapina[46]. She established that a donor–acceptor bond is formed by sulphur in complexes of dialkyl sulphides and thiacyclanes with mercury(II) bromide and found that the energies of the bonds formed by the same sulphides with mercury(II) acetate are in the narrow range 10.5–1..5 kcal mole$^{-1}$. It has been shown that the equilibrium yield of the complexes falls with increase of the molecular weight of the sulphides and with decrease of their symmetry. The composition of stable mercury(II) acetate complexes were found to be 1 : 2 for ten sulphides and 1 : 1 for twenty sulphides. The small differences between the heats of formation of the 1 : 1 and 1 : 2 complexes led to the hypothesis that the nature of the bond formed by the second mercury(II) acetate molecule with the sulphide differs from the donor–acceptor linkage between the sulphide and a single mercury(II) acetate molecule. The majority of saturated sulphides form stable 1 : 2 complexes with mercury(II) bromide. The electron-donating capacity of aryl and diaryl sulphides is sharply reduced.

The complexes of mercury(II) halides with dialkyl sulphides are best precipitated from alcoholic solutions and those of thiacyclanes from ethereal solutions. The methods of dielectric-constant and cryoscopic titrations, developed by Gur'yanova[47], were widely used in the above investigation in relation to a wide variety of complexes of organic compounds. The formation of complexes of sulphides having different structures with tin tetrachloride[48] and with iodine[49] had been investigated previously. A decrease of the tendency by the organic sulphides towards complex formation on passing from saturated to aromatic compounds was noted.

Using the method of cryoscopic titration, Gur'yanova et al.[50] investigated the formation of complexes by the sulphides in sulphuric acid concentrates with aluminium, gallium, tin, and titanium halides and with iodine. They found that all the sulphides extracted with 86% acid from the 150–325°C fraction of Arlansk petroleum form 1 : 1 complexes with $AlCl_3$ and $GaCl_3$; about 90% of these sulphides form 1 : 2 complexes with $SnCl_4$ and $TiCl_4$, while about 10% do not react. The heats of formation of the $SnCl_4$ complexes with dialkyl sulphides are about 12.6 kcal mole$^{-1}$, while those for the formation of complexes with the sulphides in the concentrate investigated are only 7.6 kcal mole$^{-1}$. This is probably associated with the presence in the latter of aromatic sterically hindered dialkyl sulphides and $\alpha$-substituted thiacyclanes. More than 90% of the sulphides isolated from the same distillate by treatment with 91% sulphuric acid formed 1 : 1 complexes with $AlBr_3$, $GaCl_3$, and iodine and 1 : 2 complexes with $SnCl_4$. Near ultraviolet spectroscopy demonstrated the presence of aromatic compounds in these sulphides; they probably include alkyl aryl sulphides and admixtures of thiophens.

The formation of complexes by sulphides with silver nitrate[51] was investigated by Ben'kovskii and coworkers[52–55] in order to obtain pure sulphides from sulphide concentrates and for their differentiation. Complexes of 28 individual sulphides with $AgNO_3$ were investigated. Dialkyl sulphides (thia-alkanes) form 1 : 1 complexes, while thiacyclanes form both 1 : 1 and 1 : 2 complexes (mono- and di-solvates). The latter is probably due to the rigidity of the carbon–carbon bonds in thiacyclanes. The melting points of the thiacyclane complexes are much higher than those of the complexes of thia-alkanes having a similar composition. A method permitting quantitative separation of sulphides from thiophens and hydrocarbon admixtures present in sulphuric acid concentrates has been developed on model mixtures. The sulphides were regenerated from the complexes with 20% aqueous ammonia. Approximately 73% of the saturated sulphides and 24% of a mixture of thiophens and hydrocarbons were isolated from the concentrate of the 150–250°C fraction of Arlansk petroleum with the aid of silver nitrate.

The study of the solubilities of the individual complexes of sulphides with silver nitrate showed that derivatives of thia-alkanes and $\alpha$-substituted thiacyclanes dissolve in aromatic hydrocarbons and alcochols much more effectively than $\beta$-substituted thiacyclanes. The possibility, in principle, of the quantitative separation of sulphides having similar properties by formation of complexes with $AgNO_3$ and subsequent extraction of the mixture of complexes with toluene has been demonstrated for binary mixtures (6-thiaundecane–3-pentylthiophan and 2-pentylthiophan–3-pentylthiophan).[53]

Saturated sulphides have been separated from aromatic sulphides present in the higher fractions of the Dzhar-Kurgan high-sulphur petroleum by the formation of complexes with silver nitrate. This made it possible to concentrate aryl sulphides and to detect for the first time the presence in the petroleum of alkyl benzyl and alkyl naphthyl sulphides[56]. The experience gained in our laboratory also demonstrated the suitability of the method employing $AgNO_3$ for the preparation of pure saturated sulphides.

The evident unsuitability of silver nitrate as a reagent for the isolation of sulphides and their elimination from petroleum products on a large preparative scale is evident.

In the search for more readily available complex-forming agents, Nametkin and coworkers made systematic studies on reactions with iron carbonyls. They considered reactions via the mechanism[57]

$$\left.\begin{matrix}RSH\\(RS)_2\\R_2S\end{matrix}\right\} + Fe_x(CO)_y \rightarrow \begin{matrix}OC & & S & & CO\\ & \searrow & \downarrow & \swarrow & \\ OC & & Fe & & Fe\ CO\\ & \swarrow & \uparrow & \searrow & \\ OC & & S & & CO\end{matrix} + \left\{\begin{matrix}H_2\\CO\\R_2\end{matrix}\right.,$$

where $x = 1$ and $y = 5$, $x = 2$ and $y = 5$, or $x = 3$ and $y = 12$.

**Table 1.** The interaction of mercaptans, disulphides, and sulphides with iron carbonyls*.

| Iron carbonyl | Yield of complexes, wt.% (time, h) | | |
|---|---|---|---|
| | RSH | $(R'S)_2$ | $R''_2S$ |
| $Fe_3(CO)_{12}$ | 95—98 (1) | 72—76 (5) | 60—64 (18) |
| $Fe_2(CO)_9$ | 90—93 (11) | 65—67 (19) | 50—54 (24) |
| $Fe(CO)_5$ | 59—61 (22) | 54—59 (34) | 20—25 (36) |

*R = Ethyl, n-butyl, n-hexyl, n-dodecyl, phenyl, or benzene; R′ = n-butyl, n-pentyl, n-hexyl, or n-dodecyl; R″ = methyl, ethyl, n-propyl, n-butyl, n-hexyl, n-dodecyl, cyclopentyl, or phenyl.

Data for the degrees of reaction of individual compounds were obtained and are listed in Table 1, which shows that the limits of variation of the yield of each carbonyl within groups of sulphur compounds are relatively insensitive to the structure of their hydrocarbon base. This made it possible to employ a single procedure for the estimation of relative reactivities, based on the method of the

competing reactions of iron dodecacarbonyl with hexyl derivatives of sulphur, in accordance with the following scheme:

$$\left.\begin{array}{l}6\,C_6H_{13}SH\\3\,(C_6H_{13}S)_2\\6\,(C_6H_{13})_2S\end{array}\right\}2\,Fe_3(CO)_{12}\rightarrow[Fe(CO)_3SR]_2+\left\{\begin{array}{l}3\,H_2\\6\,CO\\3R_2\end{array}\right.$$

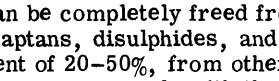
Having assumed that the value for the sulphide is unity, the authors[57] found that the relative reactivity decreases in the sequence RSH > $RS_2R$ > $R_2S$ (in proportions of 13 : 9 : 1), in agreement with the data in Table 1, from which follows the following series of the reactivities of the carbonyls in the above reactions:

$$Fe_3(CO)_{12}>Fe(CO)_9>Fe(CO)_5\ .$$

In conformity with previous studies[58,59], Nametkin et al.[57] believe that the above reactivity series for iron carbonyls is correlated with the ease of formation on thermal decomposition of the coordination-unsaturated intermediate compound $[Fe(CO)_4]^*$.

In the next communication[60], it was shown that the petrol and kerosine–gas oil petroleum distillates and the products of the thermal and thermal-catalytic processing of petroleum can be completely freed from hydrogen sulphide, mercaptans, disulphides, and free sulphur and, to the extent of 20–50%, from other organic sulphur, nitrogen and oxygen compounds with the aid of iron carbonyls, dipentadienylnickel, di(ethylphenyl)chromium, and other complexes of transition metals in their lowest valence forms. Table 2 presents data illustrating the elimination of organosulphur compounds from various petroleum products.

Table 2. The desulphurisaton of petroleum products by low-valence transition metal complexes.

| Petroleum products | Fraction, °C | Complexes | [S]·10³, % | | | |
|---|---|---|---|---|---|---|
| | | | total content | | content of mercaptan sulphur | |
| | | | initial | in purified fraction | initial | in purified fraction |
| Straight-run petrols | 50—150 | $Fe(CO)_5$ | 18 | 7 | 6.5 | 0.3 |
| | 80—140 | $(C_5H_5)_2Ni$ | 43 | 9 | 8.4 | 0.2 |
| | 50—150 | $(Et\cdot C_6H_5)_2Cr$ | 35 | 8 | 7.1 | 1.0 |
| Kerosines | 145—230 | $Fe_3(CO)_{12}$ | 170 | 8.7 | 6.0 | 0.4 |
| | 145—230 | $CO_2(CO)_8Mn(CO)_6$ | 450 | 170 | 10 | 0.5 |
| | 120—226 | $[C_5H_5W(CO)_3]_2$ | 160 | 40 | 48 | 0.05 |
| | 140—230 |  | 230 | 90 | 21 | 0.7 |
| Diesel fuels | 187—355 | $Fe_3(CO)_{12}$ | 1040 | 380 | 7.6 | 1.0 |
| | 200—380 | $[C_5H_5Co(Co)_2]_2$ | 1420 | 630 | 9.0 | 0.2 |
| | 195—370 | $C_6H_5Fe(CO)_3$ | 1200 | 270 | 10 | 0.5 |
| Kerosines* | — | $Fe_3(CO)_{12}$ | 175 | 160 | 16 | 2.4 |
| | | » | 170 | 90 | 6.6 | 0.3 |
| Straight-run mazut | — | $Fe_3(CO)_{12}$ | 560 | 200 | — | — |

*Kerosines from pilot plant.

The formation in these processes of cluster compounds of the heteroatomic components of petroleum and some of their reactions, leading to the regeneration of the mercaptans and the formation of some of their derivatives, have been reported[61]. The elimination of heteroatomic compounds by the complexes investigated is apparently accompanied by a significant entrainment of aromatic hydrocarbons[60], which is observed in all sorption and extraction processes leading to the formation of sulphide-aromatic concentrates, as stated above.

Plyusnin and coworkers[62–64] used complex formation with titanium tetrachloride for the isolation of tars, asphaltenes, and heteroatomic compounds from petroleum and petroleum fractions. Tars and asphaltenes were initially isolated from petroleum in a Soviet deposit (Tomsk region) by the method of Pozdyshev et al.[17] with the aid of methanol–acetone mixtures. This petroleum contained 2% of asphaltene, 6% of silica gel tars, 0.85% of total sulphur, and 0.19% total nitrogen (0.064% of basic nitrogen). Model solutions of tars in n-hexane and of asphaltenes in benzene were investigated: a fractional precipitation was carried out by the stepwise addition of $TiCl_4$. Eight fractions of tar complexes were obtained for the consumption of between 1 and 5 moles of $TiCl_4$ per mole of tars and three fractions of asphaltene complexes for the consumption of between 7 and 10 moles of $TiCl_4$ per mole of asphaltenes.

The degree of extraction of tars was about 95% and that of asphaltene about 99%. In view of this result, the authors[62] carried out experiments on petroleum without preliminary isolation of tars and asphaltenes. A change in the weight ratio of $TiCl_4$ to petroleum from 0.008 to 0.054 made it possible to observe the characteristics of the precipitation of the petroleum components. After the addition of 0.020 $TiCl_4$ (by weight), the asphaltenes are isolated completely, almost in proportion to the amount of added $TiCl_4$. For the complete extraction of tars, its weight fraction should be at least 0.050 of the petroleum taken. The curve describing the isolation of tars as a function of the amount of $TiCl_4$ is S-shaped with a linear section in the range 0.010–0.030 $TiCl_4$. Low-molecular-weight heteroatomic petroleum compounds, coprecipitated with asphaltenes and tars in amounts comparable to the latter, are isolated in an unusual manner. They are clearly distributed in two groups separated by a region where their isolation is not observed. This region coincides with the linear section of the tar isolation plot. It is interesting that the concentrates isolated in the presence of small amounts of added $TiCl_4$ (0.003) contain 62% of low-molecular-weight heteroatomic components, 25% of asphaltenes, and 13% of tars. Following the addition of 0.030 $TiCl_4$, a concentrate was obtained where the fractions of the same groups were 30%, 20%, and 50% respectively. The complexes of low-molecular-weight HAC with $TiCl_4$ are hydrolysed much more readily than the complexes of tars and asphaltenes, which permits their separation.

After the addition of 0.050 $TiCl_4$ to petroleum from a Soviet deposit in the Irkutsk region, more than 99% of the additive was bound in a complex. Together with tars and asphaltenes, $TiCl_4$ binds 80–95% of the nitrogen in petroleum (100% of basic nitrogen) and about 60% of sulphur. These results were used to isolate HAC concentrates of distillates. Their isolation from the 140–240°C fraction of Western Siberian petroleums, processed at the Omsk refinery, has been investigated[63]. The yield of the HAC isolated was 0.25% and their composition was as follows: 67.6%C, 14.0%H, 7.6%S, 0.9%N, and 9.9%O (by difference) ($M$ = 172). The entire nitrogen and neutral oxygen were concentrated in tar-like fractions obtained on chromatography of the HAC (after the elimination of the acid components with 10% NaOH solution) on silicic acid. Sulphur is mainly contained in higher thiacyclanes (and possibly thiophens). Neutral oxygen is present in ketones and acid oxygen in phenols. Basic nitrogen can also be

fully eliminated by $TiCl_4$ from higher-boiling fractions[64]. A considerable proportion of the sulphur and oxygen compounds are extracted at the same time, as can be seen from Table 3. The average composition of the concentrates from petroleum in the Tyumen deposit corresponds to 40–50% of sulphur compounds, 2% of carboxylic acids, 1% of ketones, and 5–9% of nitrogen compounds. Using $TiCl_4$, 98% of basic nitrogen was extracted from vacuum gas oil (340–500°C fraction) (6.8% of the concentrate containing 0.042% of basic nitrogen and 1.5% of total sulphur was obtained).

Table 3. Elemental composition of the concentrates isolated from fractions of Tyumen petroleums at the Omsk refinery (in wt. %).

| Fraction, °C | C | H | S | N | O | –COOH | >CO * |
|---|---|---|---|---|---|---|---|
| 309–325 | 81.21 | 11.18 | 5.0 | 0.3 | 2.3 | 0.35 | 0.11 |
| 325–350 | — | — | 4.2 | 0.2 | — | 0.22 | 0.05 |
| 350–375 | 81.62 | 12.07 | 4.4 | 0.4 | 1.5 | 0.34 | 0.08 |
| 375–400 | 78.39 | 11.74 | 5.5 | 0.3 | 4.0 | 0.26 | 0.12 |

*The method used to determine the carbonyl groups has been described by Maikova et al.[65]

The data considered above suggest that there are good prospects for further improvement in the methods for the differentiation of the heteroatomic components of petroleum into subgroups, particularly in relation to heavy and residual fractions, with the aid of variable-valence metal salts.

The use of complex formation and ligand exchange for the isolation and separation of the HAC is only just beginning to develop. At the present time we know much more about the extraction of metals by organosulphur compounds than about the separation of sulphur compounds by metal salts. The use of $FeCl_3$ on clay had been described previously[67].

Starting from 1973[66], groups of research workers of the American Petroleum Institute and the Bureau of Mines, investigating the composition of heavy petroleum fractions, freed the crude material from the acid and basic components with the aid of anion and cation exchangers and then extracted neutral nitrogen compounds with iron(III) chloride.

The development of ion-exchange methods (their acid–base versions were described above) led to the creation of ion-exchange resins, zeolites, and a number of amphoteric oxide sorbents in salt-forms. In these sorbents, hydrogen ions have been replaced by metals: Na, K, Mg, Ca, and, especially, the variable-valence metals Cu, Fe, Co, Ni, etc.

## III. CHROMATOGRAPHIC AND MASS SPECTROMETRIC METHODS FOR CHARACTERISING THE SULPHUR COMPOUNDS IN PETROLEUM AND ITS FRACTIONS

The commercial manufacture of satisfactory and continuously improved apparatus for different types of chromatography as well as the expansion of the range of stationary and mobile phases for chromatography have led to an appreciable increase of the efficiency of separation of multicomponent systems, particularly petroleum and petroleum products containing heteroatomic compounds of different types. The number of papers, reviews, and monographs devoted to chromatographic methods is very large and we shall describe selectively only some of them.

As already stated, most of the heteroatomic petroleum compounds have been found in higher petroleum fractions. The use of anion-exchange resins, described above, has been recommended for their isolation. Versions of liquid chromatography using ion-exchange resins have been developing in recent years. Thus the study mentioned above[66] was preceded by a methodological investigation of Haynes and coworkers[68], including chromatographic procedures for the separation of the heavy part of petroleum into acids, bases, and neutral nitrogen compounds. In 1975 Vogh and Dooley[68] suggested that the copper-form of the carboxylic acid cation-exchange resin *Bio-Rex*-70 be used. Attention has been concentrated on the shrinking of the copper-saturated cation exchanger during preparation (it amounts to 10–20% along the column length). Both in model systems and in heavy petroleum fractions containing mono-, bi-, and polyaromatic components with a mixture of polar compounds, virtually complete extraction of sulphides was achieved. Ben'kovskii and coworkers justly regard Vogh and Dooley as their predecessors[54]. However, a detailed study of the sorption of sulphur and nitrogen compounds and the static and dynamic capacities of KU-2 cation-exchange resin in metallic forms (silver, copper, mercury, lead) and AV-17-4 and AV-17-8 anion-exchange resins were not reported until later[69]. In this investigation, Ben'kovskii et al. studied the sorption of a number of mercaptans from benzene and alcoholic solutions and demonstrated the possibility of the extraction of certain individual nitrogen compounds by cation exchangers in metallic forms. Useful information concerning the separation of anion-exchange resins for the chromatography of high-boiling petroleum fractions has been published[70].

Particular attention must be concentrated on the use of liquid chromatographic methods under high and moderate pressures, whereby one can significantly reduce the diameter of the sorbent particles used, i.e. one can greatly enlarge the area of the interface and one can increase by several orders of magnitude the rate and efficiency of the separation. This method is described in greater detail by Zhukhovitskii[71] and Kirkland[72]. Bezinger succeeded in dissolving the nitrogen concentrates from petroleum in the Novo-Dmitrovsk deposit into distinct fractions in approximately 2 h using the technique developed in Chumakov's laboratory. A similar separation could not be achieved previously even after passage through a chromatographic column over a period of two months (without the application of pressure). Studies by Cook and Spangelo[73] on the separation of phenols and by Janini et al.[74] on the separation of polyaromatic hydrocarbons have shown that research on the application of liquid-crystal (nematic) phases in the gas–liquid chromatography (GLC) of heteroatomic compounds of petroleum merits attention; this has been confirmed[75]. An interesting method has been proposed by Rudenko and Ryashentseva[76] for the identification of peaks of the GLC chromatograms of multicomponent mixtures with the aid of ray diagrams; correction coefficients for a number of compounds by a procedure put forward previously were determined at the same time[77]. Postnov et al.[78] examined an internal calibration method taking into account the necessary corrections for quantitative GLC analysis. These procedures can be used

successfully in the GLC analysis of heteroatomic compounds and the petroleum fractions containing them.

A GLC analytical method without a standard, using several stationary liquid phases at different temperatures, was proposed by Golovnya and Arsen'ev [79] for the homologous series of mercaptans, sulphides, and disulphides. This investigation is a continuation of previous studies[80-82]. In order to elucidate the applicability of the approach developed by the authors to more complex systems of compounds, typical for petroleum and its derivatives, much additional research is needed.

Gusinskaya and Beiko [83] investigated the catalytic microdesulphurisation of the 140–220°C fraction of the petroleum from the Kokaity deposit in Southern Uzbekistin. Using a distribution tap, the microdesulphurisation unit was included between two chromatographs. The sulphides were separated on the first chromatograph, with a katharometer, in accordance with the chromatographic peaks and passed to a microreactor, whence the sulphide conversion products formed were transferred to the second chromatograph with a flame-ionisation detector. The best catalyst for desulphurisation proved to be the industrial AP-56 catalyst. Experiments with individual sulphides showed that hydrodesulphurisation in the presence of this catalyst yields pure hydrocarbons with the appropriate composition and structure, uncontaminated by their isomerisation or decomposition products.

Gas–liquid chromatography is at present the most rapid method for the investigation of the compositions of petrols in terms of individual compounds. For each group of organosulphur compounds (mercaptans, sulphides, and thiophenes), the number of isomers boiling in the same temperature range greatly exceeds the number of isomeric hydrocarbons having the corresponding structure. This hinders analysis for two reasons: (1) the relative concentrations of the components in the sulphur-containing fraction of petrol are much lower than the concentrations of hydrocarbons in its hydrocarbon fraction; (2) the synthesis of model sulphur compounds, which are very necessary for the labelling and interpretation of the chromatograms, is very difficult and the solution of this problem is virtually impossible for the majority of laboratories. Together with Gordadze and Gollandskikh, the author of the present review [84,85] achieved the photochemical methylenation of a number of individual thiaalkanes and thiacyclanes. It was shown that the methylene group, obtained on decomposition of diazomethane, is inserted in all the C–H bonds of sulphides. The reaction is not complicated by side processes and its course is just as rigorously statistical as with hydrocarbons [86]. The observed slight deviations towards reduced reactivities of the C–H bonds at the carbon atoms adjoining the sulphur atom play hardly any role. Individual methylenated sulphides can be fully recommended as standards for the GLC analysis of sulphide-containing fractions. For a description of the application of GLC analysis in petrochemistry, see Refs. 87–89.

Drushel [90] recommended an unusual version of the reactochromatographic analysis of the sulphide–thiophen fraction of organosulphur compounds in petroleums as a more rapid method for the determination of the group composition of such compounds. The test specimen (in a stream of nitrogen or helium) is introduced into the chromatograph via a micropyrolytic cell (at 790°C in pyrolysis and at 600°C in the presence of $Al_2O_3$; benzothiophens are dealkylated in this cell and sulphides form hydrogen sulphide and, partly, mercaptans. The mixture of products, separated in the chromatograph, is transferred to a combustion tube, where oxygen is supplied (apart from the nitrogen or helium carrier gas) ($t \simeq 850$°C). The hydrogen sulphide formed passes to a microcoulometric (iodometric) cell connected to a pen recorder, which records the integral current–time curve. We do not know how much this method is used. It makes it possible to differentiate the sulphur in heavy petroleum products into the components present in aliphatic sulphides or "non-thiophens", benzothiophens, dibenzothiophens, benzonaphthothiophens, and unknown sulphur compounds. The duration of the experiment is approximately 1 h and the accuracy is to within 2–3%. The results agree well with those obtained previously by the mass-spectrometric method [91].

A novel "centri-chromatographic" method, combined with mass-spectrometry, has been proposed by Canadian investigators [92] for the separation of small amounts of multicomponent systems. The fundamental principle of centrifugal chromatography is similar to that of liquid chromatography under pressure. The method has apparently not found applications as yet in the study of petroleums and petroleum products. Drum thin-layer chromatography, used by Sanders and Snyder [93] is of interest. The application of thin-layer chromatography to organosulphur compounds has been examined by Karaulova [94].

Gel chromatography has been recommended as a useful subsidiary method for the separation of petroleum components [95,96]. This type of chromatography has been incorporated as the final stage in the multistage schemes for the separation of petroleums, adopted by the American Petroleum Institute and the U.S. Bureau of Mines, which were described above [66,67]. These studies were preceded by the careful investigation of Coleman et al. [99] of the use of gel permeation chromatography in relation to high-boiling petroleum components.

The characteristics of the composition of the petroleum fractions obtained by different methods and the determination of the structure of their components can be achieved on the basis of the chromatographic analysis only of the most low-boiling fractions. Higher-boiling fractions require additional chemical and physical research techniques. Among the latter, mass-spectrometry has proved to be the most informative at the present time. Some of the versions of mass-spectrometry can be combined with chromatography in integral chromato-mass-spectrometric apparatus operating particularly efficiently in combination with integrating computing devices.

There is insufficient space in the present review to consider the advances in the instrumental and computing techniques associated with the development of chromatography and mass-spectrometry. Nevertheless some of the relevant investigations must be mentioned. Robinson and Cook [100] examined in detail the application of low-resolution mass-spectrometry in the study of the group composition of the aromatic fractions of petroleum and were able to identify in the latter three main groups of compounds, each of which was in turn subdivided into seven subgroups. These consisted of dibenzofurans and benzo-, dibenzo-, and benzonaphtho-thiophens. Severin et al. [101] investigated the application of 10 eV mass-spectrometry combined with field ionisation to higher petroleum fractions. Anbar and Aberth [102] recently re-examined in detail mass-spectrometry with field ionisation in relation to vacuum distillates (176–360°). They used an apparatus with multichannel recording and

automatic integration. They believe that the principal advantage of the method is a reduction of the degree of decomposition, which simplifies the spectra of the components, this being particularly important for the analysis of multicomponent systems. Problems concerning the use of mass-spectrometry with field ionisation in the study of labelled substances have been examined by many investigators; errors due to isotopic effects and fragmentation artifacts are then eliminated. The method has been recommended for the investigation of biogenic systems of complex composition. This may well prove extremely useful in the study of the heteroatomic components of the heavy part of petroleum, bitumens, and the organic material in the deposits in the existing seas and lakes.

Certain considerations favouring the use of cyclotron mass-spectrometry in the analysis of substances with ultralow vapour pressures have been described in a recent study[103]. After appropriate development, the new method will assist in the investigation of tar and asphaltene fractions of petroleum in which the majority of heteroatomic components are concentrated. Gallegos et al.[104] described in detail high-resolution chromato-mass-spectrometric analysis using as an example a study of pyrolysis products (the presence of 152 hydrocarbons, 8 cyclic and 5 acyclic dienes, and 18 unidentified compounds in such products was established).

Brodskii and coworkers[105-107] and Khmel'nitskii[108] obtained a number of new data concerning the characteristics of individual heteroatomic compounds, primarily sulphides[105-108]. Brodskii et al.[109] described the mass-spectrometric analysis of aromatic hydrocarbons and sulphur compounds present jointly in petroleum fractions; their distribution in 23 groups based on the $C_nH_{2n-x}$ and $C_nH_{2n-y}S$ homologous series with the even values $x = 6-24$ and $y = 4-22$ is described and the relative ionisation cross-sections of the compounds are given. Khmel'nitskii et al.[110] described the mass-spectrometric analysis of nitrogen-containing bases in petroleum having the composition $C_nH_{2n-z}N$ with the odd values $z = 9$, 11, and 13.

A general examination of the principles of the mass-spectrometric investigation of heterocyclic nitrogen compounds has been made in Klyuev's dissertation[111]. The mass-spectrometric analysis of nitrogen and sulphur compounds based on fragment ions has been used[112] to investigate the petroleums from the Tajik depression (Southern Uzdekistan). An analytical method based on molecular ions was developed in that investigation for sulphur compounds whose molecular weights range from 350 to 600, involving their subdivision into seven groups differing in the degree of unsaturation with respect to hydrogen. Mal'tseva's study was devoted to an examination of the mass spectra of bicyclic heterocyclic compounds[113]. Popov developed methods for the mass-spectrometric and chromato-mass-spectrometric analysis of nitrogen-containing bases in mineral fuels[114]. Such comparative studies are of undoubted interest, since latest investigations[115] have demonstrated a similarity of the composition of the products obtained from coal by mild modern procedures to the composition of the heavy components of petroleum.

Brodskii et al.[116] emphasised that, in an investigation of the composition of complex products such as petroleum distillates, data obtained by previously developed simpler methods are useful in addition to results obtained by chromatography and mass-spectrometry. Comparison of the data derived by the two groups of methods makes it possible to improve significantly the assessment of the structural-group compositions and structures of the products investigated. The development of mass-spectrometry in combination with detailed correlations for the analysis of the heteroatomic components of petroleums, coals, shales, and the products of their processing has been described by Brodskii[117].

Polyakova et al.[118] examined the possibility of using high-resolution mass-spectrometry for the investigation and quantitative determination of thiacyclane and thiophen derivatives with different numbers of rings. Petroleum fractions have been analysed in the 400–650 mass range with the aid of the spectrometry of mass defects. The authors[118] developed a novel system for the calculation of the composition of the multiplets and compiled tables of the molecular weights of ions for a series of compounds in the residual petroleum fractions.

A number of monographs, for example that of Polyakova and Khmel'nitskii[119], have been devoted to mass-spectrometry in recent years. These methods need not therefore be considered further. Interesting information about the structure and properties of the heteroatomic components of petroleums can be obtained by the application of proton magnetic resonance. Unfortunately it has not so far been adequately developed, despite the fact that Clutter et al.[120] pointed out as early as 1972 the likelihood that a method can be devised for group NMR analysis, similar to the mass-spectrometric group analytical techniques. At the same time, NMR has been used[121] to determine the content of acids and bases in organic substances. The proton magnetic resonance method has been employed[122-124] in the study of the structural-group characteristics of the nitrogen-containing bases in Sakhalin petroleums. $^1H$ NMR yielded valuable information about the admixture of oxygen compounds with a furan ring in nitrogen-containing bases (the presence of diaryl ethers is not ruled out)[122] and about the ring sequence in tricyclic systems, demonstrating that angular junctions in the latter are more probable than *peri*-junctions.

Presumably $^1H$ NMR combined with modern computing-analytical devices will take its due place in research on petroleum products in the immediate future. The information about the homology and the number of rings present yielded by mass spectrometry will then be supplemented by the characteristics of the location and mobility of hydrogen atoms, which are directly related to the reactivity of petroleum components.

## IV. PETROLEUM SULPHIDES AND THIOPHENS

In 1966 Smith[125] published a novel and elegant review of the available information concerning the qualitative and quantitative composition of crude petroleum. He recognised for the first time the quantitative equivalence of the hydrocarbon and non-hydrocarbon components of petroleum. However, the available information about the heteroatomic compounds of petroleum, particularly the high-boiling compounds, was inadequate for the determination of the correct proportions of the individual groups. A detailed survey of studies on Project 48A of the American Petroleum Institute carried out during the 20 years from 1948 to 1968 was made by a group of investigators under Thompson's supervision[126]. The group composition of the sulphur compounds in the vacuum distillates from petroleums in 17 deposits was first investigated. Determinations were made of the contents of (1) free sulphur, (2) hydrogen sulphide, (3) disulphides,

(4) mercaptans, (5) and (6) two groups of sulphides, and (7) "residual sulphur" using Ball's method[127] and it was stated that this procedure yields distorted data owing to the coprecipitation of the components when they are removed by group reagents (for further details about this, see Luk'yanitsa[128]). As a result, it was established that, for a monotonically increasing sulphur content in vacuum distillates, the qualitative compositions of sulphur compounds in the latter remain similar but the quantitative proportions of the groups vary sharply, being uncorrelated either with overall sulphur content in the petroleum or with its contents in the distillate. The distillates from the Goldsmith petroleum, where the content of free sulphur reaches 42.5% and the Deep River petroleum, where the content of mercaptans is 46%, are unique. The fraction of sulphides in the Velma petroleum is 42%. The maximum residual sulphur (80%) has been observed in the distillate from Heidelberg petroleum. The Wasson petroleum (Texas) was selected as the main object of study. The following components were identified in its fractions boiling up to 250°C as a result of the application of multi-stage separation schemes, chromatography, complex formation, mass spectrometry, etc: 47 mercaptans (including six alicyclic mercaptans and one aromatic mercaptan); 38 dialkyl sulphides; 5 alkyl cycloalkyl sulphides; 4 alkyl aryl sulphides; 21 thiacyclanes; 18 thiaindans; 2 disulphides; 22 benzothiophens; 2 dibenzothiophens; 160 compounds in all. However, alkylthiophens were not found (11 examples of this series were discovered in Wilmington petroleum). Quantitative estimates of the contents of 44 individual compounds were made. 58 papers were published on Project 48A during the period under consideration; some of these data are considered in Karaulova's monograph[129].

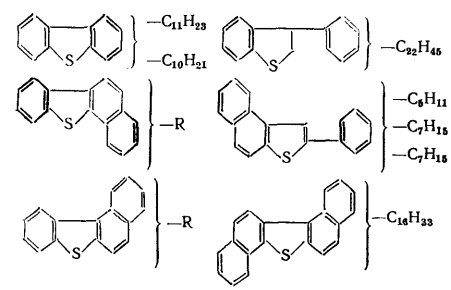
During the same period, detailed studies were made by Obolentsev and coworkers[130-133] and Vyakhirev et al.[134] on the organosulphur compounds present in the petroleums of the Urals-Volga petroleum-bearing region. The presence of mercaptans and a large number of sulphides was established in these petroleums. Among the sulphides, thia-alkanes are concentrated in the light fractions and thiacyclanes in the heavy fractions. Thiophen and methyl- and dimethyl-thiophens were identified in Romashkino petroleum[134]. These studies have been reviewed by Krivolapov[135] and Allilueva[136]. The GLC retention parameters of a number of sulphides have been calculated in the latter review.

Beiko and Gusinskaya[137] continued the investigation of the boiling points and the retention parameters of isomeric thiacyclanes. These data enabled Beiko[138] to investigate the composition of the petrol-kerosine distillates from petroleum in the Kokaity deposit. The results agree well with a series of studies devoted to the investigation of the middle fractions of petroleum from Southern Uzbekistan (the Tajik depression). A more detailed investigation of the 200–400°C fraction of combined Southern Uzbekistan petroleums (from Khaudape, Lyal'mikar, and Kokaity deposits) was made by the present author and his coworkers[139,140]‡ and in the course of this study numerous techniques were improved. The sulphides of the individual Khaudag and Kyzyl-Tumshuk petroleums were studied (simultaneously with the present author's research) at the Institute of Chemistry of the Academy of Sciences of Tajik SSR[142]. The petroleums from the Kokaity and Lyal'mikar deposits have been reinvestigated in Tashkent[143]. A mass-spectrometric investigation[112] was mentioned in the preceding Section. This was the first study to include the heavier components of the petroleums from the Tajik depression (Southern Uzbekistan). Some of the relevant data have been examined in monographs[129,144,145]. Here one must emphasise that the qualitative compositions of the petroleums from different deposits in the Tajik depression of Southern Uzbekistan are similar. This phenomenon has been known for a long time for petroleum hydrocarbons. The organosulphur compounds have been found to be similar as a result of research in recent years.

The petroleums of Southern Uzbekistan are characterised by negligible contents of light fractions and an almost complete absence of mercaptans and disulphides. The sulphides of the 200–400°C fraction consist mainly of a series of thiacyclanes[139] containing between 1 and 5 rings. Thiamonocyclanes (60%) containing between 7 and 21 carbon atoms per molecule predominate. Thiophens in this fraction also include series of compounds containing between 1 and 4 rings. The main bulk consists of benzothiophen (~33%) and condensed cycloalkyl- and dicycloalkylbenzothiophens (approximately 21% of each). The content of alkylthiophens (about 16%) is fairly high.

In terms of the order of magnitude, the values found in later studies for petroleums of Southern Uzbekistan[112,143] are close to those obtained by the present author[139]. The differences in the selection of fractions and in the details of the methods employed preclude a comparison of the quantitative data obtained in the three investigations or an estimate of the fine differences between the component compositions of the sulphur compounds in individual petroleums. The differences between the contents of thiaindans in the petroleums from different deposits in this region are significant: Kyzyl-Tumshuk—12%; Khaudag—9%; Dzhar-Kurgan—1–4%[112]; Lyal'mikar—3.3%; Kokaity—5%[143]; a mixture of Khaudag, Lyal'mikar, and Kokaity petroleums—4.5%.[139] If these data are confirmed, then the petroleum from the Kyzyl-Tumshuk deposit must be collected separately, particularly for the isolation of thiaindans, which are of special interest.

After the extraction of nitrogen compounds, it was established mass-spectrometrically in conjunction with infrared spectroscopy[112] that petroleum from the Dzhar-Kurgan deposit (150–350°C fraction) contains complex benzothiophen compounds, whose probable structure can be represented by the following formulae:




where R = $C_{19}H_{39}$, $C_{21}H_{43}$, and $C_{23}H_{47}$. Gal'pern et al.[146] investigated the structural-group composition of the sulphur-containing concentrate from the 350–370°C oil distillate of petroleum from the Romashkino deposit. The $C_{21}$–$C_{24}$ fraction with 6.00% $S_{tot}$, 2.00% $S_{R_2S}$, and $n_d^{20} = 1.4643$ was isolated by chromatography on silica gel. Oxidation with hydrogen peroxide and subsequent regeneration (by reduction with lithium tetrahydroaluminate)

‡These data have been examined in detail in a compilation published quite recently[208].

yielded, by a procedure similar to that used in another study[139], sulphides formed from sulphoxides (obtained by oxidation with hydrogen peroxide in acetic acid and acetic anhydride and residual sulphoxides). A decrease of selectivity relative to that observed in the oxidation of lower-boiling distillates in acetic acid was observed: there is a significant increase of the fraction of thiophen compounds in the oxidation products. On reoxidation in acetic anhydride, alkyl aryl sulphides and thiaindans are fully converted to oxidation products. The total sulphides obtained by two-stage oxidation exceeds the sum of the sulphides obtained in single-stage oxidation (directly in acetic anhydride). If the oxidation is restricted to the first stage only (with acetic acid), all the saturated sulphides are fully converted into sulphoxides, but the majority of thiaindans and aryl sulphides remain in the refined products. The sulphides obtained were analysed mass-spectrometrically. Altogether 14% of sulphides and 55% of thiophens were found in the fractions; their distribution among subgroups is described by Gal'pern et al.[146]

Sulphides in the petroleum from the Arlansk [tentative transcription] deposit were isolated from the 170–310°C fraction[147]. Their purification and re-extraction by sulphuric acid was completed by a mass-spectrometric study of the composition of the concentrates[148] obtained by treatment with 86% sulphuric acid, subsequent extraction with 91% acid, and chromatographic separation into narrow fractions.

A series of fundamental studies on the compositions and structures of the sulphides in the kerosene and gas oil fractions of Arlansk petroleum have been carried out by Nikitina and coworkers[52,149-151]. The average molecular weights of dialkyl sulphides and alkyl cycloalkyl sulphides are higher than those of thiamono- and thibi-cyclanes; the average molecular weight of benzothiophens is lower than the corresponding values for alkyl- and cycloalkyl-thiophens. It has been shown[55] that an increase of the concentration of sulphuric acid in the extraction of sulphide concentrates from petroleum distillates leads to an increase of the fraction of sulphides and thiaindenes extracted and to an appreciable decrease of the average molecular weights of all the components of the extracts. This phenomenon is probably associated with the enhancement of the hydrophobic properties of the sulphides with increase of their molecular weights and with decrease of the degree of dissociation of the monosolvates of the 'onium complexes of the sulphides with sulphuric acid when the concentration of the latter increases. Comparison of the compositions of the sulphides extracted from the Arlansk petroleum fractions with those of the corresponding sulphides of Romashkino and Southern Uzbekistan petroleums demonstrates their considerable similarity. The conclusion[27] that thia-alkanes and alkyl cycloalkyl sulphides are extracted in succession by dilute sulphuric acid has been disproved[55]. In the initial investigations, the mass-spectrometric technique was apparently inadequate for the determination of low concentrations of higher thia-alkanes characterised by a uniform mass distribution[208].

The experimental industrial apparatus for the preparation of sulphide concentrates from petroleum distillates has been described[153]. The Arlansk petroleum concentrates obtained[154] were investigated by the formation of complexes with $AgNO_3$ and with thiourea, this being followed by thermal diffusion fractionation and mass-spectrometric analysis. The low efficiency of the formation of adducts with thiourea by sulphides from the middle fractions of petroleums as regards their differentiation into structurally different groups was demonstrated in this investigation. Thermal diffusion makes it possible to reduce the concentration of polycyclic sulphides and to concentrate them in the last fractions. In view of the low efficiency of the method, one can hardly hope for extensive application of the thermal diffusion of sulphides. In this sense, the employment of gas–liquid chromatography under increased pressures is much more effective. It has been shown[154] that thiamonocyclanes have on average three alkyl substituents and thiabicyclanes have two substituents, only one of these with a long chain containing between 2 and 8 carbon atoms. The distribution of the sulphide subgroups with respect to mass is largely determined by the chain length. These results are fully consistent with those obtained earlier[140,208] for the corresponding sulphides from the distillate of Southern Uzbekistan petroleum.

The latest studies on the sulphides in Western Siberian petroleums (from the Western Surgut and Samotlorsk [tentative transcription] deposits[30,31,154,155]) confirm the hypothesis that the compositions of the sulphides in mercaptan-free petroleums are similar. Data for Arlansk, Western Surgut, and Samotlorsk petroleums, obtained in the same way and investigated by the same procedures, have been compared[155]. In all the 190–360°C distillates, the fraction of thiacyclanes is 85–90% of the total sulphides. The relative contents of mono-, bi-, and poly-thiacyclanes vary in the ranges 50–58%, 20–23%, and 9–14% respectively. The concentrates contain alkyl-, cycloalkyl-, benzo-, and dibenzo-thiophens and condensed naphthenobenzothiophens. Their relative concentrations for Samotlorsk petroleum (with a lower total of sulphur content) distinguish the latter from the high-sulphur petroleums, particularly from the Southern Uzbekistan and Arlansk petroleums discussed above.

A series of studies by Thompson and coworkers have been devoted to the high-boiling fractions of five individual petroleums[157-161]. A brief description of these investigations has been published[162-166] and their overall resumé can be found in the paper by Dooley et al.[167]. Acid and basic components have been extracted from distillates by liquid chromatography under pressure with the aid of Amberlyst A-29 anion-exchange resin and Amberlyst A-15 cation-exchange resin respectively, while iron(III) chloride has been used to extract neutral nitrogen compounds (after a preliminary elimination from crude petroleum of solid paraffins which were subjected to separate mass-spectrometric analysis). Distillates freed from the above compounds were analysed and subjected to preparative liquid chromatography on silica–alumina gel for separation into four fractions: saturated and mono-, di-, and poly-aromatic compounds. The fractions of saturated compounds were transferred directly to mass-spectrometric analysis and the aromatic fractions were analysed mass-spectrometrically after an additional gel-chromatographic separation. Table 4 presents data characterising the yields and compositions of the distillates, refined products, and seven fractions. Evidently the main bulk of sulphur is concentrated together with the di- and poly-aromatic compounds. Anion-exchange resins, cation-exchange resins, and iron(III) chloride extract from 370–535°C distillates about 5% of the compounds (California petroleum yielding up to 16.5% is an exception). All three sorbents extract also neutral sulphur compounds, in most cases in amounts comparable to those of the nitrogen compounds. The comparatively high concentration of sulphur in these extraction fractions does not play a

**Table 4.** The yields* of 370–535°C distillates, their chromatographic fractions, and their elemental compositions (wt.%) (based on the data of Dooley et al.[167]).

| Initial Petroleum | Yield and composition of distillate | Extracted | | | Yield and composition of refined product | Paraffin-naphthene fractions | Monoaromatic fractions | Diaromatic fractions | Polyaromatic fractions HAC |
|---|---|---|---|---|---|---|---|---|---|
| | | by anion exchanger | by cation exchanger | by $FeCl_3$ | | | | | |
| Prudhoe Bag (Alaska) | 21.630*a* | 2.840*d* | 2.460*d* | 0.900*d* | 93.800*d* | 48.310*d* | 16.98*d* | 11.910*d* | 16.600*d* |
| | 0.191*b* | 2.346*b* | 2.935*b* | 2.095*b* | 0.080*b* | 0.014*b* | 0.010*b* | 0.025*b* | 0.210*b* |
| | 0.170*c* | 0.940*c* | 2.590*c* | 2.050*c* | 1.130*c* | 0.080*c* | 0.100*c* | 2.520*c* | 3.920*c* |
| Gach Saran (Iran) | 19.670*a* | 1.710*d* | 2.120*d* | 1.170*d* | 95.000*d* | 48.490*d* | 16.830*d* | 11.700*d* | 17.980*d* |
| | 0.223*b* | 2.290*b* | 3.498*b* | 2.577*b* | 0.083*b* | 0.013*b* | 0.013*b* | 0.027*b* | 0.320*b* |
| | 1.850*c* | 1.602*c* | 2.380*c* | 3.490*c* | 1.940*c* | 0.080*c* | 1.040*c* | 3.910*c* | 5.920*c* |
| Swan Hills (Canada) | 18.350*a* | 1.770*d* | 2.190*d* | 0.460*d* | 95.580*d* | 65.940*d* | 12.550*d* | 6.270*d* | 10.820*d* |
| | 0.147*b* | 2.641*b* | 2.799*b* | 3.716*b* | 0.034*b* | 0.018*b* | 0.027*b* | 0.025*b* | 0.231*b* |
| | 0.280*c* | 0.730*c* | 1.850*c* | 3.460*c* | 0.240*c* | 0.010*c* | 0.100*c* | 0.700*c* | 1.830*c* |
| Wilmington (USA) | 24.690*a* | 5.580*d* | 6.770*d* | 4.230*d* | 88.410*d* | 36.910*d* | 16.810*d* | 12.360*d* | 17.330*d* |
| | 0.458*b* | 1.407*b* | 3.329*b* | 2.592*b* | 0.071*b* | 0.007*b* | 0.017*b* | 0.007*b* | 0.288*b* |
| | 1.580*c* | 1.400*c* | 1.230*c* | 1.740*c* | 1.600*c* | 0.090*c* | 1.020*c* | 2.810*c* | 4.600*c* |
| Recluse (USA) | 18.580*a* | 1.350*d* | 1.150*d* | 0.930*d* | 96.570*d* | 74.120*d* | 11.270*d* | 5.060*d* | 6.120*d* |
| | 0.069*b* | 1.569*b* | 2.229*b* | 2.640*b* | 0.043*b* | 0.010*b* | 0.001*b* | — | 0.100*b* |
| | 0.120*c* | 0.410*c* | 0.120*c* | 2.190*c* | 0.220*c* | 0.040*c* | 0.100*c* | 0.490*c* | 2.020*c* |

**a*—yield with respect to petroleum; *d*—yield with respect to distillates; *b*—nitrogen content; *c*—sulphur content in products *a* and *d*.

significant role in the overall sulphur balance, since their yield is low. The study of sulphur-containing components of extracts is difficult and so far is not susceptible to interpretation by mass-spectrometric methods. They probably contain a large amount of compounds, each with two and more heteroatoms per molecule (including oxygen atoms), at fairly high concentrations. This distinguishes them from the main bulk of the monofunctional organosulphur compounds transferred together with the paraffin-naphthene fractions and makes them similar to the polar polyaromatic concentrates.

The nitrogen and sulphur contents in the paraffin-naphthene fraction is low, but, despite the low concentrations of the corresponding heteroatomic compounds, one must not forget that the proportion of these saturated fractions is usually between 37 and 74% of the initial distillates. A comparatively monotonic decrease of the yields of the groups of hydrocarbons from 41 to 25% with increase of the number of rings in the latter from zero to 6 is characteristic of such distillates. In the series of petroleums considered, Wilmington petroleum is an exception, its saturated fraction containing only 13.5% of alkanes, 15.8% of monocyclanes, and 14.0% of bicyclanes; the content of tricyclanes is somewhat higher (15.8%) and there is an unusual maximum corresponding to the proportion of tetracyclanes (25.9%). The content of pentacyclanes is 9.2%, which greatly exceeds the average for remaining types of petroleum (6%). There are as yet no data concerning the nature of the sulphur compounds remaining in the saturated paraffin-naphthene part of the refined product.

The distribution of the main groups of compounds among the aromatic fractions is given in Table 5, which shows that the sulphides and thiophens in the petroleums investigated are concentrated mainly in the polyaromatic compound fractions. The contents of individual groups of organosulphur compounds are distinguished by a great variety. The differences between their overall contents are very great: from approximately 20% in Recluse petroleum to nearly 100% in Gach Saran petroleum. The aromatic fractions include the hitherto undeterminable heteroatomic oxygen and nitrogen compounds. The Gach Saran petroleum contains a relatively large amount of components with more than one sulphur atom per molecule, which reduces the accuracy of the quantitative estimate of its overall content of organosulphur compounds. The differences between the qualitative compositions of the subgroups of compounds discovered in the five distillates investigated are even greater than the differences between their overall contents.

**Table 5.** The distribution of sulphides (S), thiophens (T), and aromatic sulphur compounds with unknown structure (A) in 370–535°C distillates (in wt.%) among chromatographic fractions (according to the data of Dooley et al.[167]).

| Initial petroleum | Groups of compounds | Monoaromatic fractions | Diaromatic fractions | Polyaromatic fractions + HAC | Sums of S, T, and A |
|---|---|---|---|---|---|
| Prudhoe Bay (Alaska) | S | 0.08 | 5.06 | 21.37 | 26.91 |
| | T | 2.31 | 21.34 | 14.42 | 38.07 |
| | A | 0.58 | 0.00 | 3.27 | 3.85 |
| Gach Saran (Iran) | S | 0.76 | 9.96 | 47.73 | 58.45 |
| | T | 6.95 | 31.23 | 21.07 | 59.25 |
| | A | 3.66 | 0.00 | 1.38 | 5.04 |
| Swan Hills (Canada) | S | 0 02 | 0.00 | 6.18 | 6.20 |
| | T | 2.05 | 5.07 | 14.80 | 21.92 |
| | A | 1.00 | 1.34 | 0.19 | 2.53 |
| Wilmington (USA) | S | 0.50 | 15.36 | 36.52 | 52.40 |
| | T | 6.10 | 19.70 | 16.73 | 42.53 |
| | A | 3.23 | 0.67 | 1.86 | 5.76 |
| Recluse (USA) | S | 3.54 | 0.00 | 0.00 | 3.54 |
| | T | 1.55 | 0.96 | 7.90 | 10.41 |
| | A | 0.00 | 4.24 | 2.66 | 6.90 |

Further investigation of the heteroatomic compounds in petroleums, in particular sulphides and thiophens, requires the development of chemical methods for their differentiation into subgroups. The differentiation of these compounds on the basis of their reactivity is not only of theoretical but also of great practical interest.

Comparison of the data of Soviet and foreign investigators clearly demonstrates fairly significant differences not only in the overall contents of sulphides and thiophens in petroleums from different deposits but also in their distribution among subgroups corresponding to different structures. Naturally, these differences must be taken into account in the utilisation of sulphides and thiophens as the raw materials for the chemical processing of petroleum.

## V. OXIDATION OF PETROLEUM SULPHIDES

In the early stages of the research into the chemistry of the sulphides in the middle fractions of petroleum[168,169], the present author and his coworkers already demonstrated significant differences between the oxidation potentials of sulphides, other groups of sulphur compounds, and hydrocarbons, which made it possible to oxidise the sulphides to sulphoxides by hydrogen peroxide under mild conditions with a high degree of selectivity. The conversion of sulphides into sulphoxides alters sharply the polarity of the functional group. Sulphoxides, which are neutral under the usual conditions, behave as distinctly basic compounds in the oxidation products from petroleum distillates, which makes it possible to separate them readily from other groups of compounds both by chromatography on coarsely porous silica gels and by acid extraction[170,171]. The influence of the differentiating solvent (acetic anhydride) was investigated[172] in solutions of individual sulphides having different structures and compared with ethers in acetic acid. This established that the degree of oxidation of aromatic sulphides in acetic anhydride is three times as high as in acetic acid. The addition of perchloric acid sharply increases the rate of homogeneous oxidation of sulphides to sulphoxides in acetic anhydride.

The heterogeneous-emulsion oxidation of sulphides to sulphoxides in the presence of perchloric acid[173] made it possible to obtain sulphoxides in a single stage from distillates of sulphur-containing petroleums in which sulphoxide perchlorates are insoluble. The selectivity of the process then increases sharply owing to the acceleration of the main reaction. The process is applicable to the formation of individual sulphoxides from sulphides and to the purification, by reprecipitation, of the sulphoxides obtained by other methods. Here one should recall that the perchlorates of lower sulphoxides are explosive. The perchlorates of $C_6$ and higher sulphoxides are not quite so dangerous, but it is nevertheless recommended that they should be hydrolysed with water and aqueous solutions of alkali immediately after isolation, whereupon the resulting sulphoxides may be dried in the usual way.

The principal procedure for obtaining sulphoxides was believed to be the heterogeneous-emulsion oxidation of the sulphides present in petroleum fractions without their preliminary isolation or their isolation in the form of sulphur-containing aromatic concentrates. The method was first proposed by the present author[174] and was then elaborated in significantly greater detail and improved[175-178]. In the development of the appropriate technology, we selected foam reactors and obtained the sulphoxides under novel foam-emulsion conditions[179]. The technological development was carried out by Khitrik and coworkers[180,181] on laboratory and larger scales using a continuous-operation apparatus. The results obtained by Khitrik agreed very well with earlier data obtained by Bardina[177] on small laboratory periodic-operation devices. The Vitt bell stirrer used in these experiments created conditions close to foam-emulsion conditions. A separate experiment established that, under the conditions adopted, air always behaves as an inert gas without being involved in the reaction. The final development of the technology for obtaining sulphoxides from distillates and sulphur-containing aromatic concentrates was achieved on larger-scale continuous-operation apparatus (made of metal). The fundamental laboratory data found for the oxidation of phenolic and sulphuric acid extracts of the 275–350°C fraction of Arlansk petroleum by hydrogen peroxide under foam-emulsion conditions are presented in the report of Zagryatskaya et al.[182] The results largely agreed with those obtained previously on laboratory and large laboratory apparatus. The advantage of the sulphuric acid extracts of sulphides over the phenolic extracts was demonstrated. The selectivity of the oxidation process in the presence of catalytic amounts of acetic acid is higher than in the presence of sulphuric acid. Under foam-emulsion conditions, attention must be concentrated on the number of foaming steps, maintaining the appropriate size of the average cross-sections of the bubbles, which determine the overall areas of the liquid gas and liquid 1–liquid 2 interfaces.

Data on the kinetics of the oxidation of sulphides to sulphoxides in petroleum distillates by hydrogen peroxide under foam-emulsion conditions were published recently[183]. It was shown that the rate of the process can be expressed by the equation

$$V = 1.42 \cdot 10^{7} T^{1/2} \exp\left(-\frac{16200}{RT}\right) \cdot C_{R_2S} C_{H_2O_2} .$$

The order of the reaction with respect to the sulphide and hydrogen peroxide is unity, the overall order is two, and $\bar{E}$ = 16.2 kcal mole$^{-1}$. A significant proportion of the above studies are described in Khitrik's dissertation[184]; the studies of Masagutov et al. on pilot apparatus have also been published[209].

Experiments on the replacement of hydrogen peroxide by organic hydroperoxides in the presence of organic acids in reactions designed to obtain sulphoxides are noteworthy[185,186]. The degree of oxidation by isopropylphenyl hydroperoxide is higher by a factor of 1.5–2 than the degree of oxidation by t-pentyl and t-butyl hydroperoxides. The catalytic acceleration of the oxidation of sulphides is proportional to the strength of the carboxylic acids used.

It was natural to extend the oxidation of sulphides to sulphoxides to the next stage—the oxidation to sulphones. A test of the possibility of multistage and single-stage oxidation was of particular interest. The latter has been carried out for a long time and does not yield satisfactory results, because the sulphoxide → sulphone conversion is endothermic, in contrast to the exothermic sulphide → sulphoxide conversion. In the two-stage oxidation of petroleum distillates, one removes together with sulphoxides many impurities which char on vigorous oxidation. The refined product obtained contains hardly any sulphides or sulphoxides. On reoxidation, it gives a mixture of sulphones, among which predominate benzothienyl sulphones with an admixture of tricyclic sulphones belonging to different series (most probably dibenzothiophens, naphthothiophens, and naphtheno-, benzo-, and benzonaphtheno-thiophens).[187] The oxidation of saturated sulphoxides to sulphones is of considerable interest[188]. The authors found the optimum conditions for the oxidation of petroleum sulphoxide concentrates by hydrogen peroxide in the foam-emulsion state in the presence of catalytic amounts of sulphuric acid. The sulphoxide → sulphone conversion takes place to the extent of 95–96% in 15 min.

Petroleum sulphoxides are effective and promising extractants and floatation agents for the hydrometallurgy of non-ferrous and rare elements[189,210]. Nikitin et al.[190] reported the isolation and characterisation of 32 complexes formed by sulphoxides (obtained from the sulphuric acid concentrates of the 190–360°C sulphide fraction of Arlansk petroleum) with the nitrates and certain chlorides of magnesium, calcium, zinc, aluminium, chromium, iron,

cobalt, nickel, manganese, bismuth, uranyl, and gallium. The bathochromic shift of the characteristic wavenumber of the sulphoxide group ($\nu = 1040\ cm^{-1}$) has been used to characterise the donor–acceptor bond in these complexes. $\Delta\nu$(SO) is a maximum for iron and chromium chloride complexes ($\Delta\nu = 95\ cm^{-1}$) and for the copper chloride complexes ($\Delta\nu = 90\ cm^{-1}$); among the nitrates, the maximum corresponds to chromium nitrate ($\Delta\nu = 110\ cm^{-1}$), nickel, bismuth, and uranyl nitrates ($\Delta\nu = 95\ cm^{-1}$), and copper nitrate ($\Delta\nu = 83\ cm^{-1}$). It was shown that, regardless of the method of preparation of the complexes, anhydrous solvates are isolated preferentially, with displacement of water from the coordination spheres of the ions and its substitution by sulphoxides. It is suggested that in some complexes sulphoxides are present in the inner and outer spheres, for example in $FeCl_3$.3PSO (PSO = petroleum sulphoxide). The dependence of the extracting capacity of sulphoxides on their molecular structure has been examined[191]. It was shown that the extraction of metal salts by sulphoxides from aqueous solutions of hydrochloric, nitric, and sulphuric acids and from mixed media proceeds via hydrate-solvate and solvate mechanisms. The extraction of metals by sulphoxides from hydrochloric acid solutions has been discussed in detail[192]. It was shown for the first time in the same study that cyclic sulphoxides are extracted preferentially by uranyl nitrate from their mixtures with aliphatic sulphoxides.

Sulphoxides have been used[193] for the extraction-gravimetric determination of niobium and tantalum. It was shown that the determination is not interfered with by admixtures of magnesium, aluminium, copper, titanium, chromium, manganese, iron, cobalt, nickel, zirconium, molybdenum, tin, and lead over the entire concentration range.

Rafikov and Nikitin[194] examined the possibility of using sulphoxides and their metal salt complexes as the liquid phases in gas–liquid chromatography for the separation of saturated and unsaturated hydrocarbons. The complexes with $CuCl_2$ and $FeCl_3$ (charge-transfer complexes) were the most effective. Coloured organic glasses with improved heat resistance have been obtained on the basis of sulphoxide complexes with $MnCl_2$, $CoCl_2$, etc. added to poly(methyl methacrylates) and polystyrenes.

The extraction of organic acids by sulphoxides has been investigated and certain problems of their separation by extraction have been considered[195,196].

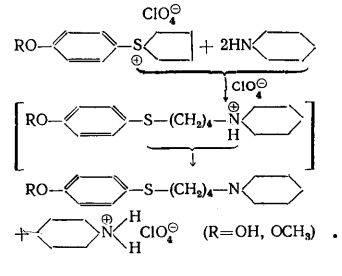
Apart from the direct utilisation of sulphides and sulphoxides in hydrometallurgy and in the chemistry of polymeric materials, it is also of interest to investigate in greater depth the chemical reactions of sulphides and sulphoxides originating from petroleum. In organic chemistry, the majority of these substances have so far been little studied or not at all. Such study required the simultaneous investigation of a number of reactions of individual compounds simulating the petroleum compounds.

The study[172] mentioned above, where sulphoxides were obtained in acetic anhydride, attracted the present author's attention to the Pummerer reaction investigated by Horner and Kaiser[197]. It has been shown[198] that the principal pathway in the reaction of $C_{10}$–$C_{12}$ dialkyl sulphoxides on heating with acetic anhydride involves the formation of $\alpha$-unsaturated sulphides (a mixture of *cis*- and *trans*-isomers). The reaction is accompanied by a side process, namely the sulphone–sulphide rearrangement of the sulphoxide. The $\alpha$-unsaturated sulphides obtained readily combine with diethyl phosphorodithioic acid, forming stable bifunctional derivatives of saturated sulphides—di-*O*-ethyl *S*-1-pentyl phosphorodithioates.

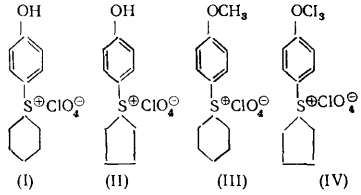
As shown above, the sulphides from the middle fractions of petroleum contain the highest concentrations of thiamonocyclanes, thiabicyclanes being next in order of abundance. When the Pummerer reaction was carried out with these sulphoxides, only the unsaturated sulphides were obtained, while the reactions with the individual substances[199] gave various results: the closest model—2-methyl-1-decalinyl sulphoxide, produced the same result—the sulphoxide was converted into the $\alpha$-unsaturated 2-methyl-1-thiaoctalin; the semiaromatic 6-methyl-1-thiachromanyl sulphoxide gave 1,2-acetoxy-1-thiachromane as the main product with an admixture of the $\alpha$-unsaturated 6-methyl-4*H*-benzothiapyran, which was readily converted into di-*O*-ethyl *S*-(6-methyl-1-thiachromanyl) phosphorodithioate. The reaction of thiophanyl sulphoxide with acetic anhydride gave mainly $\alpha$-acetoxythiophan and, in an amount smaller by an order of magnitude, the dimer of dihydrothiophen. It has been shown[200] that thiaindan is smoothly converted into thiaindene in acetic anhydride.

Karaulova[201] showed that thiacyclanyl sulphoxides react with phenol in the presence of perchloric acid and phosphoryl chloride to form *p*-hydroxyarylthiacyclanylsulphonium salts. Sulphides can be used in this process if the condensation reaction is carried out with the same reagents in the presence of hydrogen peroxide. A Japanese study[202] served as the prototype of the first method. The present author has shown[203] that the capacity for the formation of perchlorates falls sharply in the following sequence: thiophan > thiacycloheptane > methylthiacyclohexane. 2,5-Dimethylthiophen, 2,2,6,6-tetramethylthiacyclohexane, and 2-methyl-1-thiadecalin do not form arylsulphonium perchlorates (under the conditions stated above). It has been shown that 4-hydroxyarylthiacyclanylsulphonium (aryl-4-hydroxyphenyl- or 4-hydroxynaphthyl-sulphonium) perchlorates readily undergo anion-exchange reactions, forming chlorides, phosphates, and picrates. Under the influence of potassium hydroxide in methanol, 4-hydroxyphenylthiophanylsulphonium salts yield oligomeric products, for one of which a betaine-like dimeric structure has been proposed: $(C_4H_8S.C_6H_4O)_2$.

When arylthiacyclanylsulphonium salts are treated with amines[204–206], a "transonium" reaction takes place with ring opening at the C–S bond and the simultaneous addition of the base nitrogen to the $\omega$-position of the alkyl chain: the sulphonium sulphur is converted into sulphide sulphur and amino-nitrogen forms a complex ammonium salt derived from the aminoalkyl aryl sulphide. In reactions with stronger nitrogen-containing bases, the process proceeds further; the complex ammonium salt is converted into free aminoalkyl aryl sulphide with the simultaneous formation of the ammonium salt derived from the simple amine introduced into the reaction system. This can be illustrated schematically as follows:

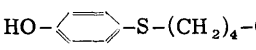


The reaction in the second stage involving fairly strong secondary bases proceeds quantitatively at a high rate, i.e. a simple single-stage method for the synthesis of ω-aminoalkyl aryl sulphides has in fact been found. The reactions of arylthiacyclanylsulphonium perchlorates with nucleophilic agents have been investigated in greater detail[207]. It was established that a number of arylsulphonium perchlorates



(I) (II) (III) (IV)

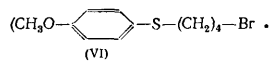
react with potassium iodide and picric acid to form arylsulphonium iodides and picrates. On reaction with potassium chloride, compound (I) is quantitatively converted into the chloride; compound (II) yields about 70% of the chloride and 16% of a product incorporating a heterocycle which has undergone ring opening, i.e.



(V) only on heating with an aqueous solution of potassium chloride. The metameric effect of the *p*-methoxy-group in compounds (III) and (IV) sharply reduces the extent of the exchange reaction with potassium chloride: only about 2% of the chloride of compound (III) was obtained, while that of compound (IV) was not formed. The reactions of compounds (I) and (II) with potassium bromide yield the corresponding sulphonium bromides and compound (III) gives the corresponding sulphonium bromide hydrate with an admixture of 6% of a compound of type (V). On heating with an aqueous solution of potassium bromide, compound (IV) gives rise to 12% of compound (V) and approximately 80% of compound (VI):

$$OH^- \geqslant Cl^- > Br^- > I^- \geqslant (NO_2)_2C_6H_2O^- .$$

Compound (VI) readily cyclises to the initial sulphonium bromide (IV); the reactions of compounds (I) and (II) with aqueous and methanol solutions of potassium hydroxide give rise to the corresponding free bases. On heating with an aqueous potassium hydroxide solution, compounds (I) and (II) form methoxyaryl derivatives of a compound of type (V), while compounds (III) and (IV) yield the corresponding methoxyaryl, methoxybutyl, or pentyl sulphides. The reactions of compounds (III) and (IV) with aqueous potassium hydroxide solutions give only complex cleavage products. The ease of dissociation of the C–S bond in the saturated heterocycle in arylthiacyclanylsulphonium salts by nucleophilic agents varies in parallel with their electronegativity§:



(VI)

The relative stabilities of the heterocycles correspond to the sequence of compounds (I) and (IV) represented above.

The compounds obtained in the reactions enumerated above are of significant interest in the study of biological activity and complex-forming properties and as starting materials for fine organic synthesis.

The involvement in these reactions of petroleum sulphides is of dual interest: (1) some of them may be suitable for the development of chemical methods for the differentiation of these sulphides into subgroups and (2) some can give rise to a mixture of substances suitable for further use without additional separation.

It is evident from all the foregoing findings that a huge advance has been made in the accumulation of data on the compositions and properties of the heteroatomic petroleum components, particularly sulphides, in the last 5–10 years. The vigorous development of research on the heteroatomic components of petroleum is only beginning. Presumably, during the coming decade, many of these components will find applications in the national economy and the elucidation of the interactions between them will open up new pathways to the rational chemical processing of petroleum and will lead to further advances in the production, transport, and utilisation of petroleum and its derivatives.

§$OH^-$ represents a methanolic solution of KOH.

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